Chemistry in the Environment

# Biological Treatment of Industrial Wastewater

Edited by Maulin P. Shah

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Biological Treatment of Industrial Wastewater

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# *Biological Treatment of Industrial Wastewater*

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ROYAL SOCIETY
OF **CHEMISTRY**

Chemistry in the Environment Series No. 5

Print ISBN: 978-1-83916-279-4
PDF ISBN: 978-1-83916-539-9
EPUB ISBN: 978-1-83916-540-5
Print ISSN: 2516-2624
Electronic ISSN: 2516-2632

A catalogue record for this book is available from the British Library

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Printed in the United Kingdom by CPI Group (UK) Ltd, Croydon, CR0 4YY, UK

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Published by the Royal Society of Chemistry, www.rsc.org

CHAPTER 1

# Industrial Wastewater and Its Toxic Effects

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## 1.1 Introduction

The escalating population is causing rapid expansion in agricultural and industrial sectors, and this results in a higher demand for water, which is essential for sustaining every life-form on this blue planet. The major sources of water for irrigation of agricultural fields, industry and human and animal consumption are rivers, groundwater and lakes. Due to climatic changes, the occurrence of floods and droughts has become frequent in many parts of the world. On top of that, increasing water pollution from the waste released from various sectors like industry, agriculture, households, municipalities, *etc.*, has greatly contributed to the decline of the quality and quantity of potable water. Therefore, the proper treatment of wastewater before disseminating it into water bodies has become indispensable to maximize the quality and quantity of potable water. Polluted water can be defined as water that contains excessive hazardous contaminants that make it unsuitable for drinking, cooking, bathing and other uses.[1] Water pollution generally results from human activity, and the pollutants released mostly come

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from industrial dumps, sewage leakages, oil spillages, heavy metals, animal wastes, chemical wastes, eroded sediments, deforestation, littering, fertilizers, herbicides, pesticides, *etc.* These sectors consume around one-third of renewable freshwater that is available and the pollutants released by them contain various synthetic and natural chemical contaminants.[2]

Wastewater released from various sectors can be categorized into different types, such as, sewage wastewater, domestic wastewater, storm run-off wastewater, agricultural wastewater and industrial wastewater. In the present study, the focus is more on water pollution due to rapid industrialization and its adverse health effects. As per the AQUASTAT database, 3928 $km^3$ of global freshwater is withdrawn every year, 22% (865 $km^3$) of which is used by industry. Industrial effluents are one of the major causes of irreversible damage to the ecosystem. Improper treatment and direct release of these hazardous effluents in the sewerage drains eventually pollutes the groundwater as well as other major water bodies, causing adverse effects on the health of animals as well as aquatic life. Under-treated effluents can also cause other potential environmental pollution like air, land surface, soil, *etc.* Casual disposal of industrial wastewater used in irrigating crops can cause serious damage to the quality of the crops produced and can also reach the food chain.[3] Water-borne diseases caused by water pollution are diarrhoea, giardiasis, typhoid, cholera, hepatitis,[4] jaundice[5] and cancer.[6] Several countries are now framing policies on water quality control. Logical bases are being set up on the amount of pollutants that can be safely assimilated in specific water bodies like rivers and lakes.[7] Some such programs deciding the carrying capacity load and discharge standards of individual pollutants are the total maximum daily load (TMDL) under the US Clean Water Act, Integrated Pollution Prevention and Control (IPPC) in Europe and the Central Pollution Control Board (CPCB) in India, which set minimum acceptable standards (MINAS) for the release of municipal and industrial wastes. Several treatment plants are also being set up which use chemical, electrochemical, biological and physical processes for releasing potable water. With both economic growth as well as the scarcity of clean water in mind, several industrial developers and manufacturers are now adopting technologies to ensure cleaner production, less water consumption and less pollution.

## 1.2 Types of Wastewater

In general, wastewater has been categorized into two broad types: sewage wastewater and non-sewage wastewater.[8] Sewage wastewater includes discharge from domestic activities. The wastewater produced from places like houses, schools, hospitals, hotels, restaurants, public toilets *etc.* containing body wastes (urine and faeces) comes under sewage wastewater. All the other types of wastewater produced from commercial activities such as that generated from factories and industrial plants are termed non-sewage wastewater. The non-sewage wastewater also includes stormwater and rainwater generated after rainfall or flood events. Day-to-day human activities

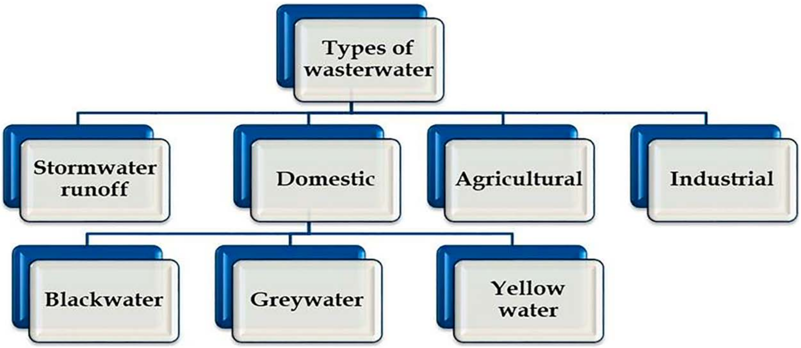

**Figure 1.1** Types of wastewater generated by various industrial and non-industrial sectors.

are majorly water dependent which makes wastewater management and treatment very important. Thus, for the effective management and targeted treatment, wastewater has been further categorized into well-defined types and sub-types depending upon the sources. The four major types of wastewater are stormwater runoff, domestic, agricultural and industrial[9] as shown in Figure 1.1. All these types and their respective sub-types are discussed in brief below.

### 1.2.1 Stormwater Runoff Wastewater

Stormwater runoff wastewater is the heavy rainfall, storm or flood water that is not soaked into the ground and flows above the street or open surfaces.[10] It is one of the leading sources of water pollution as many toxic pollutants like plastics, pesticides, herbicides, oils, chemicals, heavy metals and even various pathogens gets washed off into stormwater runoff from streets, industrial sites, construction sites and various other places. Stormwater runoff usually flows either directly or through channelled drains which eventually discharge into nearby natural waterways such as ponds, rivers, streams and lakes without any treatment. This polluted water not only hurts aquatic life, but is also a threat to the entire environment as all life forms are directly or indirectly connected to the natural waterways for their survival.

### 1.2.2 Domestic Wastewater

The wastewater produced by human household activities is known as domestic wastewater. The main source of this wastewater generally consists of two major waste streams: toilet waste, *i.e.* the liquid released from sanitary/laundry/bathing facilities, and the wastewater generated due to the other household activities such as cooking *etc.*[11] Based upon the source, domestic wastewater is categorized into three different sub-types: black, grey and yellow wastewater.[12]

#### *1.2.2.1 Blackwater*

The most contaminated form of domestic wastewater with discharge from toilets, kitchen dishwasher and sinks. The contaminants present in blackwater are urine, faecal matter, toilet paper, soaps, discarded food pieces, various chemicals and a lot of cleaning liquids.[13] It is extremely polluted wastewater with a high risk of causing diseases.

#### *1.2.2.2 Greywater*

A less contaminated form of domestic wastewater discharged from baths, washing machines and bathroom sinks.[14] To simplify, greywater or sullage is actually blackwater without faecal matter, urine and bits of food waste *i.e.* domestic/household wastewater without any contact with toilet water. Though it is not referred to as pathogenic, as it is loaded with detergents, soaps, cleaning liquids and various chemicals it should be treated well before being considered for re-use.

#### *1.2.2.3 Yellowwater*

This is specifically urine without any other contaminants of blackwater and greywater. Yellowwater does not have any faecal matter, toilet paper, chemicals or even any food particles and is pure urine water.[12] Such categorization of domestic wastewater makes the planning and execution of treatment simpler as specific treatments can be applied to the type of water based upon its characteristics.

### 1.2.3 Agricultural Wastewater

Agriculture runoff is considered as a major source of water pollution in many watersheds. Agricultural wastewater is sometimes also referred as irrigation tailwater when excess water runs off the fields during surface irrigation.[15] This excess water running through the fields become the primary cause of sediment and nutrient runoff to the nearby water sources. In addition, agrochemicals such as fertilizers, pesticides, herbicides, crop residues, animal wastes, pig, poultry and fish farm effluents and dairy farming waste are the pollutants of agricultural wastewater.[16] Many farm management techniques are used for agricultural wastewater treatment to majorly prevent surface runoff.[17,18]

### 1.2.4 Industrial Wastewater

Water with dissolved and suspended substances discharged from various industrial processes, such as the water released during manufacturing, cleaning and other commercial activities, is termed industrial wastewater.[19] The nature of the contaminants present in industrial wastewater depends on the type of the factory and the industry. Examples of industries that produce wastewater are the mining industry, steel/iron production plants, industrial laundries, power plants, oil and gas fracking plants, metal finishers and the food/beverage industry. The various contaminants commonly found in industrial water outlets are chemicals, heavy metals, oils, pesticides, silt, pharmaceuticals and other industrial by-products.[20,21] In general, it is difficult to treat industrial wastewater, as individual examination of the set-ups and specific treatment plants are required on an industry-based level. Therefore, to deal with this, on-site filter presses are installed to treat the effluent wastewater.[22]

## 1.3 Major Pollutants of Industrial Wastewater

Wastewater from various industrial sectors contains many pollutants that are toxic and have hazardous effects on human and aquatic life as well as on agriculture. Such pollutants include heavy metals like chromium (Cr), zinc (Zn), lead (Pb), copper (Cu), iron (Fe), cadmium (Cd), nickel (Ni), arsenic (As) and mercury (Hg).[4,23] Most of these heavy metal pollutants are released by paint and dye manufacturing, textile, pharmaceutical, paper and fine chemical industries. Phenol and phenolic compounds are also one of the major pollutants present in industrial wastewater.[24] They are mostly released by oil refineries, phenol–formaldehyde resin and bulk drug manufacturing industries. A number of poorly biodegradable refractory pollutants like petroleum hydrocarbons, sulfides, aniline, naphthalenic acid, organochlorines, olefins, nitrobenzene, alkanes and chloroalkanes, generated by the petrochemical industries are present in wastewater.[25] The composition of petrochemical wastes is chemically very complex and their treatment by biological methods is slow and not very effective. Even after the primary biological treatment, the organic pollutants are retained in the secondary effluents. They require chemical oxidants for the formation of inorganic end products and thus exhibit a low ratio of biological oxygen demand (BOD) to chemical oxygen demand (COD).[25] Suspended solids and highly organic materials are the major water pollutants released by the paper and pulp industry. Depending on the quality of paper produced and pulp processing, the characteristics of the effluent changes. The constituents of the effluents can be adsorbable organic halogens (AOX), phenolic compounds, biocides, colours, resin acids, non-biodegradable organic materials, tannins, sterols, lignin-derived compounds *etc.*[26,27] Urea, ammonium nitrogen ($NH_4$–N) and other nitrogenous and phosphorus wastes come from various textile printing and dyeing industries, which use water in many steps while processing. Various textile industries generate compounds ranging from heavy metals like chromium to surfactants, bleaching agents including hydrogen peroxide and chlorine, AOX, sodium silicate and alkaline bases.[28] Perfluoroalkyl acids (PFAAs) are used as surface protectors for their excellent high surface activity, stability and oil–water repellence. However, two PFAAs with potential health risks are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

**Table 1.1** Industrial sectors and their major water pollutants.

| Industry | Major water pollutants | Reference |
|---|---|---|
| Dye manufacturing | Copper, colour, salt, sulfides, formaldehydes | 23 and 28 |
| Paint manufacturing | Chromium, zinc, lead, volatile organic compounds (VOCs) | 23 and 31 |
| Textile | Iron, chromium, chlorinated compounds, urea, salts, hydrogen peroxide, high pH NaOH, surfactants | 28 |
| Pharmaceutical | Cadmium, nickel, phenolic compounds | 24 and 23 |
| Petrochemical | Petroleum hydrocarbons, phenolic compounds, nitrobenzene, alkanes, chloro alkanes, high salt, *etc.* | 24 |
| Paper and pulp | Organic and chlorophenolic compounds, suspended solids, AOX, lignin, tannins, sterols, colours, biocides, *etc.* | 26 and 27 |
| Metal working | Perfluorooctane sulfonate (PFOS), ammonium nitrogen, cyanide, phenol, oil and grease | 29 and 32 |
| Plastic | Perfluorooctanoic acid (PFOA), lead, mercury, cadmium, diethylhexyl phthalate | 29,33 and 34 |
| Agriculture | Fertilizers, pesticides, insecticides | 35 |

PFOS is released mainly by textile treatment, metal plating and semi-conductor industries, while PFOA is released by the fluoropolymer production and processing industries.[29] They are mainly circulated through the wastewater released from these industrial facilities. Besides all these pollutants, the high salinity of wastewater also has many adverse effects on life forms. Salt removal from wastewater has become as important as removal of organic matter and other pollutants in many countries. High salinity (mainly NaCl) wastewater is generated by petroleum, leather, food processing and agro-based industries.[30] Some major industrial sectors and the water pollutants released by them are summarized in Table 1.1.

## 1.4 Toxic Effects of Industrial Wastewater

Rapid industrialization during the last few decades has significantly increased the amount of pollutants in the environment. Improper treatment of some hazardous industrial wastes released into water bodies has been creating toxic effects on all type of life forms directly or indirectly. Heavy metals are one of the major water pollutants that are persistent and non-biodegradable in nature. Intake of some toxic heavy metals by aquatic fauna can cause detrimental health problems in other animals and ultimately humans *via* the food chain. They can be teratogenic, carcinogenic and can cause oxidative stress, organ damage, nervous system impairments and reduced growth and development.[36] Another most prevalent chemical pollutant released by industry are phenolic compounds. They exhibit toxicity by inhibiting normal microbial function, thus affecting biological treatment processes.[24] They can also cause reflex loss, sweating, low body temperature, cyanosis, decreased respiration and respiratory failure. The major effluent constituents of the paper and pulp industry like tannins, resins and chlorinated organic compounds can cause genotoxicity and mutagenicity.[27] The most common effluents from the paper pulp industry are lignin and its derivatives. They are poorly degradable and during biological treatment may transform into toxic compounds, which can affect the hormonal balance in aquatic animals.[37] Reproductive disruption in fish can be caused by binding of some major wood sterols like β-sitosterol and stigmasterol to oestrogen receptors of fish.[38] A collective mixture of hazardous constituents in textile effluents make them highly toxic.[6] Chromium compounds and oily scum together form a colloidal matter that acts as a barrier to prevent sunlight from entering the water body, thereby decreasing the dissolved oxygen. Many textile industries use chlorine-bound organic colourants that are carcinogenic. According to a case study reported in Tribune, on 7th April 2009, in a village near Bhatinda, Punjab, India, the farmers developed cancer as, due to the lack of canal water, they had to use toxic sludge from factories to irrigate their farms.[6] The toxicological effects of PFOA were studied in CD-1 mice that showed the toxic effects in the mother and also in the developmental stages of neonatals.[39] The mother was compromised with pregnancy loss, increased liver weight and low weight-gain during pregnancy, while the neonatals suffered reduced postnatal (approximately the first six weeks following birth) survival rates, delayed eye-opening, lower body weight, and reduced growth and development. Animal studies (on cynomolgus monkey) by using PFOS showed decreased body weight, lower triiodothyronine (T3), increased liver weight, and lower cholesterol and oestradiol levels.[40] Hypersalanity of water also greatly effects the microbial activity of non-salt-adapted micro-organisms and can also interfere with aerobic treatment processes.[30] Efficient removal strategies of these toxic pollutants before releasing them into various water bodies are therefore highly necessary for a hygienic and healthy environment.

## 1.5 Treatment of Industrial Wastewater

Various types of technologies and strategies are being developed and employed for contamination removal from wastewater released from several industries. Some of the strategies developed and used by some major wastewater producing industries for treatment of effluents are mentioned below.

### 1.5.1 Treatment of Wastewater Containing Heavy Metals

Heavy metals are considered one of the most hazardous contaminants released from chemical-intensive industries. Conventional strategies like ion-exchange methods involving synthetic ion-exchange matrices for cation and anion exchange, chemical precipitation using precipitants like lime and limestone under basic pH conditions and electrochemical deposition methods are being employed to remove heavy metals from inorganic effluents.[41] However, these methods are known to have many disadvantages when completely removing heavy metals and they also have high energy requirements.[42] Some of the cheaper and effective technologies developed for quality improvement of treated water are adsorption, membrane filtration, electrodialysis and photocatalysis.[41] Low-cost adsorbents like natural material, *e.g.* zeolites and clinoptilolite; industrial by-products such as iron slags, fly ash, hydrous titanium oxide and waste iron; biosorption using biological and agricultural wastes like inactive microbial biomass, orange peel, pecan shells, hazelnut shell, maize husk or cob, *etc.*; modified biopolymers like chitosan, starch, chitin and hydrogels are effectively used for the removal of heavy metals. The removal of heavy metals from inorganic solutions can be achieved using membrane filtration techniques like ultrafiltration employing permeable membranes of pore size (5–20 nm). Reverse osmosis capable of removing 98% copper and 99% cadmium, nanofiltration and polymer-supported ultrafiltration are some of the other techniques used to remove heavy metals.[41] The electrodialysis process involves an ion-exchange membrane through which the ionized solution is passed and membrane separation takes place under an electric potential.[43] This method is effective for the removal of heavy metal ions like Ni, Co and Cd. On the other hand, the photocatalysis method uses titanium dioxide semi-conductors capable of reduction or oxidation of species having appropriate redox potential, like $Cu^{2+}$, $Cr^{3+}$ and $Cr^{4+}$ heavy metal ions.[41]

### 1.5.2 Treatment of Wastewater Containing Phenolic Compounds

Phenol and phenolic compounds are one of the most prevalent refractory chemical pollutants present in wastewater released from industries. Phenolic wastes can be treated by a number of methods including chemical, physical, electrochemical and anaerobic biological processes. Of them, the electrochemical process has been reported to be the most effective in the removal of phenolic wastes.[24] It uses electrons as the main reagent for destruction of the pollutants by direct or indirect oxidation processes. Ti/Pt and Ti/Pt/Ir, graphite, $Ti/SnO_2–PdO_2–RuO_2$ and $TiO_2–RuO_2–IrO_2$ anodes have been reported, and are used in the electrochemical treatment of tannery wastewater,[44] landfill leachate,[45] resorcinol and cresols.[46,47] However, electrochemical treatment increases the AOX concentration in effluents and therefore, these effluents are properly treated with activated carbon before discharge into the environment.

### 1.5.3 Treatment of Wastewater Released from the Paper and Pulp Industry

The paper and pulp industry is one of most water-exhaustive and highly polluting industrial sectors. Along with water waste, it also generates a large amount of solid and gaseous waste. A number of treatment processes are used to manage these wastes. The black liquor produced is treated by a membrane filtration system by vibration separation enhanced processing (VSEP) and biological treatment, AOX are reduced by oxygen bleaching, heavy metals are treated by biological and sedimentation treatment methods, anaerobic digestion (AD) followed by pyrolysis and incineration is used for primary and secondary bio sludge treatment, *etc.*[48] AD with incineration helps in the production of beneficial by-products like biochar and biogas and also helps in lignin removal. Apart from these techniques, advanced oxidation with Fenton's reagent, ozonation, gasification and biological treatment are also employed to treat wastewater. A composite coagulant, polymeric ferric aluminium sulfate chloride (PFASC) works with polyacrylamide (PAM) as a tertiary treatment of wastewater from paper mills and reduces chroma (intensity of colour released in paper mill wastewater) by 71.2% and COD by 65.3%.[49] High content of BOD and COD in wastewater is treated by aerobic granulation,[50] which helps in the removal of tannin and lignin. The chroma produced from the paper and pulp industry can also be reduced by use of agroindustry-based residual biosorbents such as agricultural by-products and activated carbon.[51] The use of microbial fuel cells is a new approach for the treatment of wastewater generated by industries. It comes with benefits like electrical energy production and exclusion of the aeration process conventionally used for the removal of many dissolved gases.[52] The alternative eco-friendly use of enzyme bleaching, (xylanase and laccase) instead of chlorine bleaching reduces production of AOX or organic chlorinated pollutants.[53]

### 1.5.4 Treatment of Wastewater Released from the Textile Industry

The textile industry also consumes a large amount of freshwater. Water is required in many steps during processing and, as a result, it generates a large amount of wastewater. Among other wastes generated by the textile industry, dyes (azo dyes) used for colourization contribute greatly towards the wastewater. Physico-chemical-based conventional treatment processes include adsorption, membrane-based separation techniques and ion-exchange methods. Adsorbents like silicon, carbon and kaolin polymers are used for the removal of dyes.[54] Membrane separation techniques like nanofiltration and reverse osmosis are used to treat water containing reactive dyes and other chemical compounds and the ion-exchange method is used for the removal of both anionic and cationic dyes from wastewater. Apart from these, other conventional methods use Fenton's reagent, a strong oxidising agent with excess hydrogen peroxide added for decolourization.[54] Ozonation is used for toxic non-biodegradable components. Photochemical methods degrade dyes by UV treatment. Treatment with cucurbituril (a polymer of formaldehyde and glycoluril) can bring about complete degradation of basic, acidic, reactive as well as disperse dyes.[54] Besides these conventional methods, biological treatment with different micro-organisms, bacteria, fungi and algae as well as plants has shown to be very effective in the degradation of these chemically stable dyes. Bacterial treatment under anaerobic conditions with species like *Pseudomonas putida, Staphylococcus hominis* and *Citrobacter* sp. cleaves the azo linkage of the dyes with the help of reductases.[55] Under aerobic conditions, oxygen-insensitive azo-reductases produced by species like *Geobacillus stearothermophilus, Micrococcus* sp, *Staphylococcus arlettae*, having a high substrate specificity use NADH as a co-factor and cleave the azo linkages.[54] For a more advanced biodegradation of these pollutants from wastewater, a treatment system containing a mixed culture of bacteria is also employed. Fungal strains like *Phanerochaete chrysosporium* decolourizes by producing non-specific enzymes like laccase, lignin and manganese peroxides for the degradation of azo-dyes.[56] Algae help in the degradation of azo-dyes by using them as a nitrogen source and thus contribute to preventing eutrophication in water bodies.[57] Microalgae are used to treat the effluents released by the textile industry by adopting techniques like bioadsorption and biodegradation. Phytoremediation involving techniques like phytotransformation, phytostimulation, phytovolatilization, phytoaccumulation, rhizofiltration and phytostabilization are used for the treatment of textile effluents.[54]

### 1.5.5 Treatment of Hypersaline Effluents

Hypersaline effluents released by some industrial sectors are generally treated by physico-chemical methods. These methods involve thermal techniques that use multiple effect evaporators (MEE). This reduces the volume of effluent and leads to the separation of a solid salt.[30] A coagulation–flocculation method is used as a pre-treatment for removal of the colloidal COD fraction from hypersaline effluents. Some other effective techniques applied for desalination are ion-exchange methods using both anionic and cationic exchangers and membrane filtration techniques like reverse osmosis and electrodialysis.[30]

## 1.6 Conclusion

Growing industrial set-ups have increased the release of pollutants, affecting the entire ecosystem. Water pollution is one of the most devastating effects of industrialization. The potability and hygiene of drinking water have been affected by hazardous impurities that are released by industrial sectors, causing detrimental health effects to human, animal and aquatic life. Though health is of great concern, it cannot be denied that a growing economy also requires industrial growth. For overall socio-economic growth and welfare, research is encouraged into the development of such techniques that can reduce the use of freshwater by industrial sectors as well in the development of efficient and effective water treatment methods. New developments and continuous monitoring of the execution strategies of various programmes and interventions related to industrial wastewater treatment are absolutely necessary for the amelioration of any toxic effects.

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CHAPTER 2

# *Impact of Industrial Wastewater Discharge on the Environment and Human Health*

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## 2.1 Introduction

The increase in the world population has led to industrial growth and the consequent increase in pollution. Every day factories discharge wastewater that can cause serious damage to the environment. There are several reasons why this wastewater is not safely treated before discharge, including the lack of efficient treatment technologies or the high costs involved in the treatments. The focus of this chapter is to evaluate the impact of industrial wastewater discharges on the environment and human health. The chapter is structured as follows. Section 2 provides an overview of the main general environmental pollutants. The environmental pollutants are divided

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

into two categories: chemical and microbial. The main chemical pollutants highlighted are pharmaceuticals and personal care products, heavy metals, microplastics, nanoparticles and other pollutants such as volatile organic compounds, phenol and phenolic compounds, bioaerosols and aerosols. The most significant microbial pollutants found in industrial wastewaters include bacteria in general and antibiotic-resistant bacteria, parasites and viruses. This section provides an overview of the sources, main treatment possibilities and methods of detection of these pollutants. It is imperative to define these issues in order to reduce or remove these contaminants, with the aim of achieving a cleaner and safer world. In section 3, the ecological implications and health impacts of industrial wastewater discharge on the environment, including water, soil and air, are discussed. The pollution caused by industrial discharges affects living organisms, including humans. An overview of the main ecological impacts of both chemical and microbial pollutants, as well as the health impacts of these pollutants, is given. In section 4, the challenges and future perspectives related to overcoming contamination of industrial discharges are described.

## 2.2 General Environmental Pollutants

The discharge of industrial wastewater leads to the presence of various pollutants in the environment. The pollutants can be divided in two major groups: chemical and microbial. A brief summary of the types of pollutants that can be found in the environment after discharge is provided in Figure 2.1.

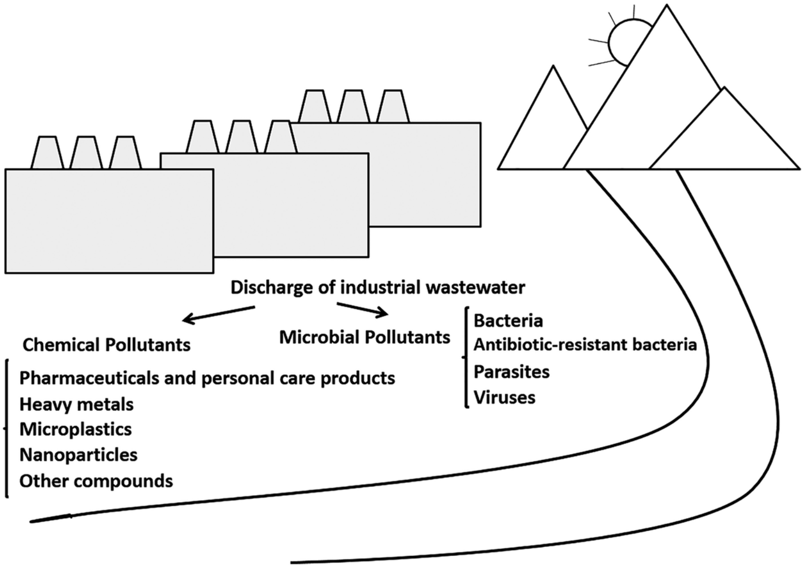

**Figure 2.1** Types of pollutants that can be found in the environment after discharge.

### 2.2.1 Chemical Pollutants

The chemical pollutants of industrial wastewater effluents that are of special concern include emerging compounds such as pharmaceuticals and personal care products, heavy metals, microplastics, nanoparticles and others.

#### *2.2.1.1 Pharmaceuticals and Personal Care Products*

In the last years the release of emerging compounds such as pharmaceutically active compounds (PhACs) and personal care products into the environment has raised great concern. In recent years much research has been dedicated to the study of the deposition of these compounds in the environment.

Ebele *et al.* analysed the presence of several pharmaceuticals and personal care products (PPCP), provided an overview of the environmental risks associated with PPCP and discussed the environmental fate and behaviour of these compounds in aquatic systems.[1] These authors reviewed the presence of non-steroidal anti-inflammatory drugs (NSAIDs) reported in surface water samples from different countries all over the world and concluded that more studies of NSAIDs are required to characterize their environmental presence in developing countries, as there are currently far fewer data for Africa, Asia and South America compared with Europe and North America. Despite this fact higher concentrations of these compounds were found in countries such as Nigeria and India. In 2014 Li *et al.* analysed emerging persistent organic pollutants in the Chinese Bohai Sea and its coastal regions and detected many widely consumed emerging pollutants in aqueous samples from the Bohai Sea.[2] This region is located near several industrial cities which makes it an ideal sink for emerging pollutants. According to the authors, Bohai sea areas, surprisingly, are not heavily contaminated by emerging contaminants, with concentrations of polybrominated diphenyl ethers ranging from 0.01 to 720 ng $g^{-1}$, perfluorinated compounds ranging from 0.1 to 304 ng $g^{-1}$, and short chain chlorinated paraffins and hexabromocyclododecanes ranging from 64.9 to 5510 ng $g^{-1}$ and 0 to 634 ng $g^{-1}$, respectively. People from this region consume seafood and the authors affirm that humans are not likely to be at serious risk from emerging pollutants exposure through consuming seafood from the Bohai Sea but suggested that more should be done to expand the knowledge about the potential risk of these compounds. Wanda *et al.* reported the occurrence of emerging micropollutants in water systems in South Africa.[3] The authors analysed carbamazepine (CBZ), galaxolide (HHCB), caffeine (CAF), tonalide (AHTN), 4-nonylphenol (NP) and bisphenol A (BPA) in water from Gauteng, Mpumalanga and North West provinces, South Africa, and found mean levels ranged from 11.2 to 18.8 ng $L^{-1}$ for CAF to 158.5–662 ng $L^{-1}$ for HHCB. BPA was the most highly represented emerging compound and was present in 62% of the aqueous samples. Globally, the results indicated that the emerging compounds found in the water of this region pose ecotoxicological risks to aquatic life as well as communities. More studies reporting the detection of PPCP in African countries, mainly

South African, can be highlighted. Agunbiade and Moodley investigated the presence of four antipyretics, three antibiotics, and one lipid regulator in wastewater, surface water and sediments from a river and found that ibuprofen (IBU) was the most abundant pharmaceutical observed ($118 \pm 0.82$ μg $L^{-1}$) in wastewater influent.[4] Archer *et al.* conducted a study on PPCP in wastewater treatment plant (WWTP) influents, effluents and river water.[5] The authors' investigation showed a total of 55 emerging contaminants (EC) in the WWTP influent, 41 EC in the effluent and 40 EC in environmental waters located upstream and downstream of the plant. It was previously reviewed[6] that pharmaceutical classes including NSAIDs, antibiotics, anti-retrovirals, anti-epileptics, steroid hormones and anti-malarial drugs have been detected in the water resources of African countries.

The occurrence of emerging contaminants in drinking, surface and ground waters and wastewaters from São Paulo State, Brazil was studied by Montagner *et al.*[7] These authors analysed 58 compounds, including hormones, pharmaceuticals and personal care products, industrial compounds, pesticides and illicit drugs, over a 10 year period, in 708 samples including raw and treated sewage, and surface, ground and drinking waters. The results show the potential risks of caffeine, paracetamol, diclofenac, 17α-ethynyloestradiol, 17β-oestradiol, oestriol, oestrone, testosterone, triclosan, 4-*n*-nonylphenol, bisphenol A, atrazine, azoxystrobin, carbendazim, fipronil, imidacloprid, malathion and tebuconazole interfering in aquatic life. The legislation on drinking water establishes the maximum admissible values for 22 of these compounds and for them no adverse effects were expected at the concentrations found, except for 17β-oestradiol. In the same country, Machado *et al.*[8] performed a preliminary nationwide survey of the presence of emerging contaminants in drinking and source waters in Brazil. The authors evaluated 100 samples from 22 Brazilian state capitals and seven water samples obtained in two of the most populous regions of the country. The study analysed emerging contaminants of different classes, including hormones, plasticizers, herbicides, triclosan and caffeine. Compounds such as caffeine, triclosan, atrazine, phenolphthalein and bisphenol A were found in at least one of the samples from the two most populous regions. Caffeine and atrazine were the most frequently detected substances in both drinking and source water with concentrations ranging from 1.8 ng $L^{-1}$ to values >2.0 μg $L^{-1}$ (drinking water) and from 40 ng $L^{-1}$ to about 19 μg $L^{-1}$ (source water) for caffeine and ranging for 2.0 to 6.0 ng $L^{-1}$ (drinking water) and up to 15 ng $L^{-1}$ in source water for atrazine. The authors highlighted that the widespread presence of caffeine in samples of treated water is an indication of the presence of domestic sewage in the source water, considering that caffeine is a compound of anthropogenic origin. These results reveal deficiencies in sanitation and water treatment employed in the water treatment processes used to remove these contaminants.

Two recent and important works[9,10] can be highlighted regarding the treatment of water and wastewater contaminated with emerging compounds. Quintelas *et al.*[9] studied a method to remove IBU and paracetamol (PARA) from wastewater. These compounds were chosen due to their high consumption. For this work a reactor was inoculated with activated sludge and a certain concentration of IBU and PARA in the range 0.4–1 mg $L^{-1}$. These authors found values of uptake from 0.192 to 0.660 mg $g^{-1}$ for IBU and from 0.104 to 0.341 mg $g^{-1}$ for PARA and removal percentages ranged from 99.1% to 99.5% for IBU and from 93.3% to 98.8% for PARA. Batch assays were also performed aiming to assess the toxicity of IBU/PARA in the activated sludge using quantitative image analysis (QIA). For IBU experiments, QIA studies showed that this compound favours the growth of aggregated biomass rather than filamentous bacteria. These authors also tested the removal of these compounds by adsorption using a commercial porous ceramic material and Pinus bark and found that the biological process using activated sludge had better performance than the adsorption materials. All these results indicate that the activated sludge biomass is efficient in the removal of these pharmaceuticals and could be a good alternative for their removal from aqueous solutions. Activated sludge proved to be very resistant to the xenobiotic effect of pharmaceuticals, which is a good indication that it could be used for the treatment of other compounds. Dhangar and Kumar analysed the removal of emerging contaminants from wastewater using hybrid treatment systems.[10] Hybrid systems are a combination of two or more processes that could include biological and/or physicochemical treatment technologies for the removal of emerging compounds. This combination is useful because frequently a single process is not efficient for the removal. These authors concluded that most of the hybrid systems apply biological treatments first and then physical or chemical treatments. As the main successful hybrid systems, the authors highlighted the combination of a membrane bioreactor (MBR) followed by membrane filtration, the combination of an activated sludge process and physical processes such as ultrafiltration (UF), reverse osmosis (RO) and gamma radiation, and the hybrid systems of MBR coupled with UV oxidation, activated carbon and ultrasound, and ozonation followed by ultrasounds, for the effective removal of several emerging compounds and trace organic pollutants.

#### *2.2.1.2 Heavy Metals*

Heavy metals are present in the environment all over the world. Anyanwu *et al.* analysed heavy metal exposure and effects in developing nations, particularly in sub-Saharan Africa.[11] The problem of the deposition of heavy metals in Africa is very serious due to increased mining activities, illegal refining, arbitrary discarding and burning of toxic waste, several discharges from different industries and inadequate environmental legislation. All these factors have resulted in high levels of contamination and pollution associated with heavy metals. The authors affirm that metals such as Cd, Hg, Pb, Cr and Ni are persistent in the sub-Saharan African environment, which is a major public health problem as they cause adverse effects on the environment and human health. Despite the fact that the problem of the deposition of heavy metals is higher in developing countries, this is a global problem that also affects other parts of the world. Tóth *et al.* analysed the presence of heavy metals in agricultural soils of the European Union with implications for food safety.[12] The authors found heavy metals such as As, Cd, Cr, Cu, Hg, Pb, Zn, Sb. Co and Ni. In specific cases, *e.g.* Hg and Cd, high concentrations of heavy metals in soil attributed to human activity can be detected at a regional level, however the majority of the agricultural land in Europe can be considered adequately safe for food production and it poses no danger to the health of the consumers. In fact, only ≈6.2% of European agricultural land needs local assessment and eventual remedial action.

The treatment of the environment, water, soil and air, contaminated with heavy metals has been studied for decades. In recent years, several important works have been published on this issue and two of them should be highlighted for their use of environmentally friendly treatments or for combining the removal of heavy metals with the elimination of other pollutants. Alalwan *et al.* studied the removal of heavy metals from wastewater using agricultural by products.[13] The authors analysed the removal of mercury (Hg), copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb), Zinc (Zn), cobalt (Co), nickel (Ni), thallium (Tl), and iron (Fe) using agricultural wastes such as rice husk and straw, Douglas fir bark, black oak bark, redwood bark, sawdust, dry redwood leaves, dyed and undyed bamboo pulp, shells of watermelons, wheat, ocra, hazelnuts, cashew nuts, palm oil fruit, the peels of pomegranates and oranges, coconut husks, tobacco, sawdust, cassava waste, loquat leaves, garden grass, poplar forest litter, azolla, barley straw, palm fruit fibre, kenaf fibre, peanut hull pellets, capsicum annum seeds and uncaria gambir, among others. The use of agricultural wastes presents economic advantages as well as high removal efficiencies attributed to different functional groups present on the surface. The main sorption mechanisms used for agricultural wastes for the removal of heavy metals include chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange. The authors' main conclusions were that coconut waste showed high adsorption results for cadmium and lead ions, wheat and banana peels efficiently removed chromium ion, while Acacia leucocephala bark and orange peel were effective in nickel ion removal and spent black tea was used in lead removal. In this context, this technology using inexpensive and efficient biosorbents obtained from agricultural waste materials has been reported as a promising replacement for existing conventional systems. Recently, Ajiboye *et al.* analysed the simultaneous removal of organics and heavy metals from industrial wastewater.[14] This simultaneous removal is very important due to the fact that heavy metals and organics co-exist in industrial effluents. Both classes of pollutants have dissimilar compositions and properties which makes their complete removal very difficult. Different technologies have been pointed out as successful for the simultaneous removal of organics and heavy metal pollutants from water, for example photocatalytic degradation using various catalysts, biological treatment, electrochemical treatment and the use of extracting agents such as weak acids, chelants, co-solvents and surfactants.

### 2.2.1.3 Microplastics

Several studies have been published revealing the presence of microplastics in the environment. Pastor and Agulló analysed the presence of microplastics in water and the potential impact on public health.[15] These authors concluded that there is disparity in the published results regarding the presence of microplastics in water systems, there is a lack of standard analytical methods, and that it is difficult to reach a consensus in the definition and description of microplastics that would allow an appropriate comparison of results; they suggested that more legislation and work should be done in this area. Koelmans *et al.* also performed a review of the presence of microplastics in freshwater and drinking water and found the same problem as Pastor and Agulló, since there are no standard sampling, extraction and identification methods for microplastics which makes the comparison difficult.[16] The order in globally detected microplastics in the studies analysed by Koelmans *et al.* is polyethylene = polypropylene > polystyrene > polyvinyl chloride > polyethylene terephthalate, which probably reflects the global plastic demand and a higher tendency for polyvinyl chloride and polyethylene terephthalate to settle as a result of their higher densities. The authors finished their analyses concluding that more studies are needed to better understand the occurrence, shape, polymer types and particle sizes, particularly for small plastic particles. Finally, Triebskorn *et al.* analysed the relevance of nano- and micro-plastics in freshwater ecosystems and found that the greatest risk is associated with microplastics with a diameter of just a few micrometres and nanoplastics, because the concentrations of these types of plastics are likely to be much higher than those currently considered and because smaller particles are more easily absorbed by tissues and cells.[17] However, once again, these authors suggest further studies to ascertain the effects of micro- and nano-plastics on the environment.

Recently, two relevant works were published about the latest developments in the treatment of environments contaminated with microplastics. Sol *et al.* analysed the treatment processes used for the removal of microplastics and highlighted froth flotation, sedimentation, pressurized fluid extraction, electrostatic separation, magnetic extraction and bioremediation as being the most effective.[18] Padervand *et al.* affirm that the main treatments include physical sorption and filtration, biological removal and ingestion, and chemical treatments.[19] Among the sorption methods the authors chose adsorption on green algae as the best option due to the high sorption capacity of microplastics. Membranes technologies were also tested with very good results and the combination of membrane technologies with biological processes increased the percentage removal of microplastics. Of the biological methods, the authors highlighted microplastic removal by marine organisms, *e.g. Antarctic Krill (Euphausiasuperba)*, *Agios Consortium*, *Souda consortium* and *Zalerion maritimum*, by bacteria, *e.g. Bacillus cereus* and *Bacillus gottheilii*, and microplastics ingestion by organisms as such as The Red Sea giant clam.

### 2.2.1.4 Nanoparticles

Engineered nanoparticles are the basis of innovative activities and are used in various industries for different purposes. Due to their widespread usage, the presence of nanoparticles in the environment has been growing from year to year. Bundschuh and his research team analysed the presence of nanoparticles in the environment and performed a review of the literature in terms of sources, fate of nanoparticles and effects of nanoparticles in the environment.[20] These authors concluded that more work should be performed aimed at the development of more efficient and reliable analytical techniques for the characterization and quantification of nanoparticles, as well as for their detection in complex environmental matrixes. Zhang *et al.*[21] are of the same opinion. They analysed the current status with regard to the detection of engineered nanoparticles in aquatic environments and concluded that more sophisticated and accurate techniques for nanoparticles detection are imperative to indicate the real situation in terms of nanoparticles in the environment.[21] These authors also suggested that appropriated legislation and regulation is required aimed at contriving/minimizing nanoparticles discharge.

### 2.2.1.5 Other Compounds

Other compounds such as volatile organic compounds, phenol and phenolic compounds, diethylketone, bioaerosols and aerosols can be found in the environment with very serious consequences for the environment and human health. Montero-Montoya *et al.* assessed the presence of volatile organic compounds in air in Mexico.[22] The authors found high levels of volatile organic compounds (VOC) and aromatic volatile compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) in industrial and suburban areas due to the burning of fossil fuels and waste emissions. For benzene the values found are much higher than the reference values for the emission of this pollutant. Quintelas *et al.* tested the removal of organic compounds (*o*-cresol, phenol and chlorophenol) using a biofilm supported on granular activated carbon.[23] With this removal method the authors achieved removal values ranging from 99.5% to 93.4% for phenol, 99.3–61.6% for chlorophenol and from 98.7% to 73.5% for *o*-cresol, for initial concentrations between 100 and 1700 mg $L^{-1}$. Kim *et al.* analysed for the presence of airborne bioaerosols and their impact on human health, as these products are suspected as the cause of various human diseases.[24] The authors found that is very hard to evaluate the risk of bioaerosols due to factors such as the complexity of the microorganisms or derivatives to be investigated, the purpose, techniques and locations of sampling as well as the lack of valid quantitative criteria. Despite all these setbacks, the authors concluded that bioaerosols are found in most enclosed environments owing to their ubiquitous presence in Nature and higher bioaerosol concentrations may be observed in indoors (compared to outdoors) due to various internal sources that are generally associated with human activities.

## 2.2.2 Microbial Pollutants

The major microorganisms found in wastewater effluent discharges are viruses, bacteria and antibiotic-resistant bacteria, and parasites.

### *2.2.2.1 Bacteria in General and Antibiotic-resistant Bacteria*

Several studies have reported the presence of bacteria and antibiotic-resistant bacteria. Silva-Bedoya *et al.* in Colombia, studied the bacterial community of an industrial wastewater treatment plant and found that the dominant bacterial population belonged to Veillonellaceae, γ-Proteobacteria, Bacteroidetes and Firmicutes families.[25] The authors found lipase activity in these bacteria and concluded that this characteristic makes them potentially useful for future bioremediation strategies in industrial wastewater treatment plants. Rodríguez-Molina *et al.* investigated the presence of antimicrobial-resistant bacteria and genes in samples collected at wastewater treatment plants and concluded that the presence of antibiotic-resistant bacteria may pose a risk of exposure to workers and nearby residents.[26] Osunmakinde *et al.* profiled bacterial diversity and potential pathogens in wastewater treatment plants using high-throughput sequencing analysis.[27] The samples were collected in three wastewater treatment plants across Gauteng province, in South Africa. Results showed the existence of four dominant phyla, Proteobacteria, Actinobacteria, Firmicutes and Chloroflexi, and four dominant classes, Alphaproteobacteria, Actinobacteria, Bacilli and Clostridia. But more relevant is the presence of pathogenic bacterial members such as Roseomonas, Bacillus, Pseudomonas, Clostridium, Mycobacterium, Methylobacterium and Aeromonas. This study concluded that bacterial pathogens were significantly abundant in the wastewater treatment systems, which represents a potential contamination risk. Yang *et al.* have conducted a study related to the activated sludge microbial community and found that Proteobacteria, Bacteroidetes, Acidobacteria, Chloroflexi, Saccharibacteria, Planctomycetes and Nitrospirae were the most abundant bacteria present in the samples.[28] The authors concluded that these bacteria can help in the removal of typical pollutants including carbon, nitrogen and phosphorus.

### *2.2.2.2 Parasites*

Industrial effluent discharges can contain a wide variety of excreted parasites, depending on the source of wastewater. In 2018, Zacharia *et al.* analysed the pathogenic parasites present in raw and treated wastewater in Africa.[29] In this geographic area, wastewater is often reused for irrigation in agriculture, which could result in the transmission of infectious organisms such as parasites. These authors found a total of 23 parasite species that pose a threat to the health of populations. In Morocco, Chaoua *et al.* assessed the efficiency of two sewage treatment systems for the removal of helminth eggs from the water.[30] One of the systems uses activated sludge and the other one is a natural lagoon. The authors found very good results with a removal efficiency of 100% using activated sludge and of 95% using natural lagoons. Domenech *et al.* determined the influence of wastewater treatment plants in increasing the consumer safety margin in relation to the presence of Cryptosporidium and Giardia in leafy green vegetables.[31] These authors analysed 108 samples from three urban wastewater treatment plants with different features and treatments. The samples included raw (influent) and treated wastewater (effluent) samples were collected over an 18 month period. Using the treated water for irrigation purposes is a very interesting option and the authors intend to evaluate the possibility of reducing the number of parasites in order to make the reuse of treated water for irrigation safe for human health. The results showed that the wastewater treatments allowed a reduction in the number of parasites which leads to an increase in the consumer safety margin. However, they highlighted that problems in the treatment performance can occasionally cause high levels of parasites in the treated water, and is very important to include the studied parasites in the regulations for water reuse.

### *2.2.2.3 Viruses*

Viruses are widespread in water systems and several researchers have dedicated their studies to this important class of microorganisms. Zhang *et al.* analysed the distribution of viruses in wastewater and found that the concentration of viruses can be as high as $10^6$–$10^8$ units $L^{-1}$ and the species that are most represented included enteroviruses, adenoviruses, rotavirus, noroviruses and astroviruses.[32] These viruses can cause several diseases, including meningitis, respiratory disease, rash, fever and gastroenteritis. In France, Bisseux *et al.* had similar results when they monitored the circulation of enteric viruses by analysis of wastewaters.[33] Over the course of 1 year the authors collected samples from raw and treated wastewaters and found the same classes of viruses as above and also parechovirus, hepatitis A and hepatitis E virus. Osuolale and Okoh reported the presence of viruses, rotavirus and enterovirus, in the treated effluent of five wastewater treatment plants in South Africa.[34] The authors collected samples from the wastewater treatment plants, monthly, for 1 year, in periods covering the different seasonal periods, in a total of 70 samples. The results showed that no enterovirus was detected in the wastewater treatment plants and the presence of rotavirus varied from 9% to 41.7% depending on the wastewater treatment plant. Due to the pandemic situation that is occurring at this moment in the world, several studies are being performed to ascertain the presence of coronavirus, SARS-CoV-2, in wastewater. La Rosa *et al.* reported the first detection of SARS-CoV-2 in untreated wastewaters in Italy.[35] The authors analysed 12 influent sewage samples from wastewater treatment plants from Rome and Milan and, due to the absence of standardized methods for Covid-19, molecular analysis was performed using three different protocols based on PCR technology. The results showed the presence of

SARS-CoV-2 in 50% of the wastewater samples. Street *et al.* highlighted that wastewater surveillance of SARS-CoV-2 has the potential to be a powerful public health tool where the wastewater treatment systems are inadequate, such as in African countries.[36]

## 2.3 Ecological Implications and Health Impacts of Industrial Wastewater Discharge on the Environment: Water, Soil and Air

### 2.3.1 Ecotoxicological and Health Effects of PPCP on the Environment

Release into the environment of effluents from production facilities containing PPCP has become a topic of great concern in the scientific community due to their persistence in water resources. This has been driven by their widespread detection in environmental samples, mainly due to recent improvements in analytical instrumentation and focused surveys. PPCP contain many different compounds that conventional technologies (biological processes, *e.g.* activated sludge or trickling filters) have not been specifically designed to detect, and thus PPCP have been shown to be persistent during wastewater treatment. Even at their trace level occurrence (ng $L^{-1}$ to mg $L^{-1}$ range) in the environment, it has been reported that PPCP (as well as their parent compounds, metabolites and transformation products) may present a potential high risk of adverse effects on living organisms.

Studies reporting the detection of PPCP in various countries have increased in the past few years, and have been summarized in several reports (*e.g.* ref. 5 and 6). These monitoring studies demonstrate that trace quantities of PPCP are widespread in surface water, treated wastewater, and sediments from rivers. There is a current lack of knowledge about the ecotoxicological effects of PPCP on aquatic and terrestrial organisms and wildlife, which are particularly important targets. Regulations for ecological risk assessment are still largely lacking, despite the significant amounts of PPCP released into the environment. Some of the described negative effects on human and animal exposures posed by the aquatic release of low concentrations of PPCP include ecotoxicity (acute and chronic ecotoxicity), endocrine disruption, development of antibiotic-resistant bacteria and association with recent trends of increased incidences of cancer.[5,37]

Environmental risk assessment of PPCP, mainly for pharmaceuticals, have been carried out in environmental matrices, including wastewater effluents, surface waters and sediments. The risk quotient (RQ) has been commonly calculated as the ratio between the maximum measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC). As an example, the maximum RQ values reported by Ashfaq *et al.*[37] were for paracetamol, naproxen, diclofenac, ibuprofen, ofloxacin and ciprofloxacin, which indicated a significant level of ecological risk due to the release of pharmaceutical industrial untreated wastewater in Pakistan. This risk may further lead to both food-web contamination and increase of antimicrobial multi-drug-resistant species. Accordingly, it is generally accepted that the increased exposure of microbial communities in the environment particularly to antibiotics can spread antibiotic resistance genes. Moreover, in the human body, antibiotic-resistant pathogens can be developed by the daily consumption of contaminated vegetables.

*Daphnia magna* is a small planktonic crustacean and commonly used in ecotoxicological tests due to its reproductive capabilities, sensitivity to its chemical environment and critical role in freshwater ecosystems. Accordingly, many studies have been carried out on the effects of pharmaceuticals and PPCP on freshwater organisms. The effects of ibuprofen (4 $\mu g\ L^{-1}$) and ketoprofen (0.005–50 $mg\ L^{-1}$ range) on *D. magna* were evaluated.[38,39] Chronic exposure to ibuprofen had no significant effect on the molecular markers nor on the life history parameters of *D. magna*, but caused lethal morphological deformities in embryos and juvenile daphnids. It was also found that up to 90% of females carried at least one deformed embryo.[38] Swimming speed frequency decreased after 24 and 48 h at all the ketoprofen concentrations used. Heart rate, thoracic limb activity and mandible movements showed slightly lower sensitivity to ketoprofen after 24 h of exposure. The behavioural endpoints were found to be inhibited after 48 h.[39]

The soil has an important and irreplaceable role in the biosphere and its quality and health is extremely important for several economic and cultural activities (*e.g.* agriculture). However, it is also the final receptor of large concentrations of contaminants, due to the use, for instance, of treated wastewater for crop irrigation in agriculture.[40] Within plants, PPCP may be translocated into edible plant parts and thus enter the food chain.[40] Accordingly, studies have been conducted on the uptake and translocation of PPCP in vegetables and fruits to evaluate the potentially harmful impact on human health; tomato plants have been widely used for such studies.[41] Effects of the usage of reclaimed water contaminated with several classes of PPCP (mainly pharmaceuticals) for irrigating real field-grown tomato crops were previously reported, confirming the presence of these compounds in leaves and in fruits.[41] These studies suggest that most applied pharmaceuticals from irrigation water are quickly dissipated in soils, which can result in reduced exposure risk over time. Nevertheless, there is a need for further research assessing environmental and food safety risks associated with using pharmaceutical-contaminated water for irrigation.

### 2.3.2 Ecotoxicological and Health Effects of Heavy Metals on the Environment

The contamination of metals is another major environmental problem in the aquatic environment. Some metals are potentially toxic or carcinogenic even at very low concentration and are thus immeasurable threats to human if they enter the food chain. Limits for heavy metal concentration in different media, particularly in water, have been imposed by government agencies to minimize the exposure of ecosystems to these toxic elements, but the concern for this issue is not still shared at the same level.[42] Thus, more environmental policies and regulation enforcement is still needed. Since the concentration of heavy metals is quite different in soil, watercourses and river sediments, the effects on the ecological and human health due to the persistence of heavy metals has been studied.[43] The discharge of wastewaters containing heavy metals into receiving waters (*e.g.* freshwaters) is considered a pathway to contamination of aquatic environments. It is known that fish assimilate heavy metals by ingestion and adsorption on tissue and membrane surfaces, thus accumulating, in water, large amount of metals.

Human exposure to heavy metals in food from aquatic ecosystems (*e.g.* fish) can pose both carcinogenic and non-carcinogenic risks, based on dietary intake, which has been found to be the main route of exposure to heavy metals.[44] Accordingly, the non-carcinogenic health hazards can be estimated by the hazard quotient (HQ), indicating the level of exposure below which it is unlikely to experience adverse health effects.[44] For carcinogens, target risks (TR) or cancer risk (CR) indicate the probability of an individual developing cancer over a lifetime as a result of exposure to that potential carcinogen. Both parameters can be estimated through fish consumption. As an example, the results obtained by Ahmed *et al.*[44] showed that the fish species analysed presented different degrees of heavy metal accumulation. Based on the HQ determination, the authors found that heavy metals do not present a non-carcinogenic health hazard individually, but their combined effect is potentially hazardous to human health. TR results revealed that the accumulation of Ni in all fish species suggests significant cancer risk through consumption.[44]

Soil can serve as both a sink and a source for heavy metals in the terrestrial environment. Excessive accumulation of heavy metals in agricultural soil not only leads to further pollution in the terrestrial and aquatic environment, but also increases the chance of human exposure to heavy metals. Human exposure to heavy metals in soil can pose both carcinogenic and non-carcinogenic risks through four different pathways: (1) dietary intake of crops, (2) direct ingestion of soil particles, (3) inhalation of soil particles from the air and (4) dermal contact with soil.[45] In soil, the RQ of heavy metals and the TR or CR can be also estimated. As an example, the maximum HQ values reported by Lian *et al.*[45] were with cadmium through dietary intake of planted crops in a watershed, which were indicative of its potential to cause adverse health effects to local residents. The CR of cadmium was found to be somewhat higher than the threshold level reported by the regulators. Thus, the authors concluded that the watershed is not suitable for the cultivation of agricultural products, since the intake of contaminated crops was identified as the predominant route for exposure to heavy metals, with potential risks to human health.[45]

Human health risks are mainly due to chemical contamination of food. As reported by Ahmed *et al.*[44] heavy metals can accumulate in vital organs in the human body such as the kidneys, bones, and liver, resulting in neurotoxic and carcinogenic effects. Cr and Ni are known to cause pulmonary disorders, while high intake of Cu can cause liver and kidney damage. Cd is toxic to the cardio-vascular system, kidneys and bones; excessive intake of Zn has negative effects on the immunological system and cholesterol metabolism.[44]

### 2.3.3 Ecotoxicological and Health Effects of Nanoparticles on the Environment

Quite recently, the behaviour of nanoparticles in the environment has attracted substantial interest due to the sharp increase in industrial applications and consumer use, which has resulted in growing exposure and is thus potentially harmful for the environment (water, soil and air) and living organisms. Nanoparticles have an enormous range of potential and actual spread, including for instance in textiles, packaging, personal care products, *etc.*, and thus there is a need to understand the ecotoxicological effects of these nanomaterials. The environmental and health effects of common metals and materials are well-known. However, when the metals and materials take the form of nanoparticles limited data are still available and their effects are yet to be investigated.

The use of silver nanoparticles (AgNPs) incorporated in consumer products has gained much popularity in the last years because of their antimicrobial and antibacterial, antiviral and anti-inflammatory properties. Accordingly, the wide range application of AgNPs in textiles (AgNPs-coated products), led to the steadily growing production volume of AgNPs in industrial facilities being released into sewage systems, and consequently, getting into the environment (*e.g.* receiving waters, soil).

Studies encompassing nanoparticles (mainly AgNPs), including toxicity assessments have been employed in fish (*e.g.* zebrafish – *Danio rerio*), shellfish (*e.g. Mytilus galloprovincialis*), crustaceans (*e.g. Hyalella azteca*), algae (*e.g. Raphidocelis subcapitata*) and other living organisms.[46–50]

Several reports evaluating the toxicity of AgNPs in zebrafish (*D. rerio*) have been published. According to Pecoraro *et al.*,[46] AgNPs can damage zebrafish gills and gut due to their ability to pass through the mucosal barrier thanks to their small size. As reviewed by Hedayati *et al.*,[47] AgNPs were previously proven to be neurotoxic, embryotoxic, cardiotoxic and oxidative stress promoters. It was also verified that AgNPs cause alterations in global gene expression profiles.[47] To date, most of the toxicological studies have been reported for chemically synthesized AgNPs. However, biologically synthesizing AgNPs has been described as a good alternative process due to its low cost and environmentally friendly production conditions, where a low number of studies have been conducted.

The effects on the growth and survival of a freshwater amphipod *H. azteca* were studied by Kühr *et al.*[48] using effluent from a wastewater treatment system containing AgNPs. The authors found that AgNPs lose most of their toxicity while passing through the wastewater treatment system, and that the accumulation of silver ions ($Ag^+$) was apparent in all animals collected. Gomes *et al.* studied the genotoxic impact of copper oxide (CuONP) and silver nanoparticles (AgNP) using *M. galloprovincialis* mussels.[49] Mussels were exposed to copper and silver (in the form of nanoparticles and ions) and the results obtained indicated that nanoparticles are mainly taken up by the gut and the gills take up dissolved metals. Ionic forms ($Cu^{2+}$ and $Ag^+$) presented higher genotoxicity than nanoparticles, suggesting different mechanisms of action that may be mediated through oxidative stress.[49]

Freshwater green algae *R. subcapitata*, a commonly used species in regulatory testing and a key constituent in aquatic systems, were recently exposed to three different AgNPs, as well as $AgNO_3$ (representing different sizes, shapes and stabilizing agents), where a combination of factors that appeared to be responsible for the observed toxicity was identified.[50] Nanoparticles find their way into the environment through different modes of application, with the impairment of soil microorganisms and plant systems. They can reach the soil, for instance, when wastewater treated for biosolids is applied to land or *via* the washing and aging of nanoparticle-containing products.

*Allium cepa*, commonly known as onion, has been used as an excellent bioindicator of environmental pollution since their roots grow in direct contact with any substance of interest and rapidly react in the presence of any materials. There are several recent reports on nanoparticles (*e.g.* AgNPs) toxicity in plants. Saha and Gupta[51] revealed that various chromosomal aberrations were induced in both mitotic and meiotic cells of *A. cepa* even at low concentrations of bio-AgNPs, and abnormalities in post-meiotic products were observed. Both mitotic and meiotic indexes decreased with increasing concentrations of bio-AgNPs in the treated cells. These findings implied that low-dose bio-AgNPs can induce significant genic effects in both meristematic and reproductive plant cells. Thus, it is reasonable to infer that nanoparticles accumulated in plant tissues can be transferred to consumers through the food chain, causing lethal effects in non-tolerant species.[51]

The toxicity of cadmium sulfide nanoparticles (CdSNPs) has recently been evaluated in broad bean plants (*Vicia faba* L.), where the results indicated that to alleviate the toxicity of CdSNPs exposure in soil, plants significantly reprogramme the metabolic profiles of leaves rather than of roots, which might subsequently impact both harvest and crop quality.[52] The impacts of nanoparticles [titanium dioxide ($TiO_2$NPs) and AgNPs] present in treated wastewater on soil ecosystems, a soil microecosystem containing *Arabidopsis thaliana* plants, soil microorganisms and *Eisenia fetida* earthworms were evaluated by ref. 53. They reported no negative impacts for organisms grown solely with $TiO_2$NPs. The shoot weight of plants, the weight of earthworms and the soil microbial biomass were all significantly reduced in the presence of Ag. No significant destructive impacts were found to the soil micro-ecosystem in the presence of the ensemble nanoparticles. Thus, the authors pointed out the relevance of investigating the effects of different nanoparticles in combination instead of only selecting a single nanoparticle.[53]

Regarding the risks for human health, the exposure of humans to NPs is inevitable due to the increasing scope of applications. Therefore, it seems from the above-mentioned studies, that a mechanism for significant nanoparticle ingestion is present, which could have implications for toxicological effects and transfer of nanomaterials to higher trophic levels. For instance, it has been previously reviewed[54] that a regular supply of $TiO_2$NPs in small doses can affect the intestinal mucosa, the brain, the heart and other internal organs, which can lead to an increased risk of developing many diseases, tumours, or progress of an existing cancer. However, the same authors suggest that research on the mechanism behind the nanotoxicity of NPs is still in its infancy and requires more research.[54] Another recent article reported that the increasing contamination of soil suggests the presence of CuONPs and ZnONPs, which will ultimately enter the human body *via* the food chain, reaching the gastrointestinal tract. However, direct exposure of humans to these NPs has not been reported yet. The studies that have been conducted using different human cell lines highlighted toxic effects of CuONPs and ZnONPs.[55]

### 2.3.4 Ecotoxicological and Health Effects of Microplastics on the Environment

The increasing production of plastics in recent years has led to severe plastic pollution in the environment. In addition, the current COVID-19 pandemic has resulted in a dramatic increase the use of personal protective equipment (*e.g.* gloves and masks) in which plastics and rubbers are two of the major components. Microplastics (MPs) are even more harmful than larger plastic items, and microplastic pollution has become an emerging environmental issue in the last two decades.[56]

MPs are widely present in our daily life. For instance, body and facial cleaning creams, contact lenses and toilet cleaning blocks contain MPs. MPs are also derived from a wide range of sources including synthetic fibres from clothing and polymer manufacturing and processing industries. MPs refers to plastic materials like polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polyether sulfone (PES), with a particle size of <5 mm. Large amounts of MPs end up in wastewater treatment plants, which have been identified both as receptors of MP pollution and as a major pathway for MPs entering the aquatic environment. The disposal of MPs in the soil has gained particular attention due to the potential dangers of widespread plastic contamination in the soil ecosystem. MPs are therefore considered a class of emerging pollutants that present a significant hazard to the environment.

Currently, much attention is paid to MP pollution particularly in marine systems; less in freshwaters ecosystems, but with increasing concern.[57] The potential toxicity of MPs to organisms has been evaluated, as reviewed by Du *et al.*[58] MPs have been also detected in various soils including agricultural/farmland, home gardens and others. It is already known that MPs affect the physical and chemical properties of soil, microbial and enzyme activities, and plant growth, and also cause adverse ecotoxicological effects to the soil ecosystem,[59] but the number of studies in this particular topic is still limited.

Accordingly, for the last few decades, zebrafish has been used as a successful model for environmental toxicology. As an example, the toxicity evaluation of PE microplastics (PE MPs) throughout the development of zebrafish, *D. rerio*, after their exposure to different concentrations of these pollutants was previously studied,[60] where the authors found that small PE MPs concentrations have harmful effects on *D. rerio* embryos and larvae. Since MPs are predicted to act as vectors for other contaminants and their combined effects are largely unknown, Qiao *et al.*[61] evaluated the combined effects of MPs and natural organic matter (NOM) on the accumulation and toxicity of Cu in zebrafish. The results showed that the combination of MPs and NOM increased Cu accumulation in the liver and gut, enhancing oxidative stress. The toxicity in –*D. rerio* was previously evaluated by combining MPs and chemical contaminants that can adhere to the plastic particles. The results, presented in ref. 62, indicated that the combined effect of MPs and sorbed contaminants produced relevant effects in zebrafish, significantly changing their organs' homeostasis compared with the contaminants alone.

Several studies have demonstrated that the presence of MPs in the digestive tract of dive zooplanktonic species (*e.g. D. magna*) can result in potentially adverse effects. Accordingly, Frydkjær *et al.*[63] demonstrated that the ingestion of MPs by *D. magna* mainly depends on the particle type, size and shape. A study with a long-term exposure to different concentrations of fluorescent green polyethylene microbeads (63–75 μm) has shown that the ingestion did not affect reproduction in *D. magna*, although the digestive tract was found to be filled with MPs.[64] More recently, De Felice *et al.*[65] assessed the long-term exposure of two different size polystyrene MPs (PS-MPs) to *D. magna*, where the results pointed to the presence of MPs in the digestive tracts of *D. magna* but, surprisingly, an increase in body size and swimming activity was noted. Based on the results obtained, it seems that PS-MPs contamination does not cause a serious risk for zooplanktonic species.[65]

The use of biological indicators is extremely significant for monitoring and evaluating the water environment. Accordingly, all changes in algae in the freshwater environment ultimately affects the structure and function of aquatic ecosystems since they are primary producers. Thus, recent research has been conducted, reporting inhibition of photosynthesis and growth with certain concentrations of MPs (PP and PVC) of algae (*Chlorella pyrenoidosa* and *Microcystis flos-aquae*), which provides evidence for understanding the risks of MPs.[66]

As evaluated by Jiang *et al.*,[67] the terrestrial environment holds huge amounts of plastic wastes which tend to be present for hundreds or even thousands of years. It is believed that the concentration of MPs in the terrestrial environment will probably increase over time, mainly due the poor fluidity of soil compared with the ocean waters. The general lack of information regarding the fate and effects of MPs in the terrestrial environment, particularly on higher plants, is troublesome given the potential for food-chain contamination and for an uncharacterized pathway of human exposure.

The reports available indicate significant effects of microplastics on plants, but future studies will be of great interest, exploring the properties of MPs and their effects. The study presented in Qi *et al.*[68] concluded that MPs affect both vegetative and reproductive growth of wheat (*Triticum aestivum*). The exposure of cress (*Lepidium sativum* L.) to MPs revealed that their accumulation on the root hairs hd significant impacts on germination and root growth.[69] Moreover, ecotoxicity effects of PS-MPs were recently reported on *V. faba*, showing their accumulation in *V. faba* root, growth inhibition, and genotoxic and oxidative damage.[67] However, more research is still needed to fill the knowledge gaps regarding the influence of MPs on plants.

Knowledge about the transfer of MPs to human beings and potential implications for human health is still in its infancy. According to the research presented above, the main risks for humans are for instance eating contaminated seafood, other kinds of food and drinking contaminated water, which are the main pathways to the gastrointestinal tract.[70] However, as reviewed by ref. 71, with an absence of strong data about the exposure levels of humans to MPs and the associated substances (chemicals), it is difficult to fairly evaluate the implications of MPs for human health. Moreover, there is still much work to be done to understand the mechanisms associated with the introduction and assimilation of MPs in the human body and its ecotoxicological effects.[71]

## 2.4 Ecotoxicological and Health Effects of Bacteria in General, antibiotic-resistant Bacteria, Parasites and Viruses on the Environment

The presence of potential emerging pathogens (*e.g. Arcobacter* spp.) widely distributed among foods of animal and vegetable origin (composite food) is becoming a matter of great concern.[72] Human exposure to contaminated food can result in dysfunctions or disorders of the gastrointestinal system with intestinal damage and inflammation, spread of infection, inflammatory bowel diseases (*e.g.* Crohn's disease), colorectal cancer, obesity and diabetes. *Arcobacter* spp. as well as for instance *Campylobacter* spp. and *Helicobacter* have also been detected in sewage, drinking water, surface water and groundwater sources, which can result in serious waterborne diseases in humans. Therefore, comprehensive information about the microbial diversity that comes from faecal contamination of different sources, especially drinking water, is required to reduce the risk of gastrointestinal diseases.[73] Research focused on human exposure particularly to *Arcobacter* spp., *Campylobacter* spp. and *Helicobacter pylori* has revealed patients with gastrointestinal diseases as well as diarrhoeal and/or foodborne illness.

Sources of antibiotic-resistant bacteria (ARB) and genes are mainly antibiotic manufacturing facilities and sewage water discharged from homes and hospitals. Wastewater treatment plants are among the main sources of antibiotic release into the environment. The extensive use of antibiotics may promote the rapid spread of antibiotic resistance in the aquatic environment, which in turn, allows the development of ARB and genes, reducing the therapeutic potential of antibiotics against human and animal pathogens, and causing high health risks to humans. Accordingly, ARB have been reported in water, soil, and the atmosphere related to antibiotic contaminated hotspots, with high microbial density, nutrient content and antibiotic concentration.[74] As an example, the evaluation of ARB at a municipal wastewater treatment plant in China was conducted by ref. 75. The authors found that Enterobacteriaceae isolated from the effluent presented resistance to chloramphenicol (69%), penicillin (63%), cephalothin (55%), ampicillin (47%), rifampicin (11%) and tetracycline (2.6%). *Escherichia coli* isolates from animal farms were found to present resistance to several antimicrobial agents (with percentages >30%), as well as to some antibiotics from a surface water (with percentages >64%).[76] The risks of transmission of antibiotic resistance from environmental sources to humans cannot be estimated based simply on the analysis of the antibiotic-resistance pool, using the current state-of-the-art screening techniques, and it is recommended that a combination of different approaches (*e.g.* culture-dependent, metagenomics and immunological) be used to assess the risks associated with ARB in the environment.

The consumption of unwashed, raw or unhygienically prepared fruits and vegetables acts as potential source for the spread of various parasitic diseases. Moreover, the level of contamination and species of contaminant parasites varies from place to place because of variations in environmental and human factors. Some pathogenic parasitic contaminants are commonly reported as agents of diarrhoea, chronic disorders or severe debilitating illnesses in humans, particularly in children and patients with acquired immune deficiency syndrome (HIV/AIDS).[77] Foodborne or waterborne transmission is the common mode of transmission for the spread of the parasite. Recently, the human pathogens *Enterocytozoon bieneusi*, *Cyclospora cayetanensis* and *Cryptosporidium parvum* were found on the surfaces of raw vegetables and fruits, indicating a risk of future disease occurring from the consumption of contaminated undercooked or uncooked vegetables and unwashed fruits.[78] Regarding waterborne transmission, great concern about serious problems in drinking water, especially in developing countries, was previously reported in ref. 79. The author indicated that drinking contaminated water can lead to scabies, a skin disease accompanied by severe itching; and that parasitic infection can cause weight loss, which is the case with tapeworms where weight loss is often accompanied by anorexia.[79]

It was recently found that pollutants (*e.g.* heavy metals, endocrine disrupters, *etc.*) where the main route of exposure in animals and humans is through diet, deliver many biological effects including immunological, mutagenic and reproductive alterations, in wildlife and humans. Thus, a relationship between pollutants and viral diseases was recently found, since pollutants can impair the immune system of animals and thus might increase the impacts of pathogens, such as the global pandemic SARS-CoV-2.[80] Due to the presence of a virus in the stools and urine of infected individuals, it was previously reported that sewage is an environment conducive to contagion. The release of drugs for medical disease therapy, into the sewage through the body fluids of infected patients, can potentially cause considerable change to watercourses and exposed biota, which needs additional attention in future research.[81]

## 2.5 Challenges and Future Perspectives

The pollution caused by industrial effluent discharge is an important issue that deserves the attention of the scientific community. In recent years, a huge number of reports about this subject were published focusing on the occurrence of pollutants from effluent discharges into the environment. The main pollutants that can be found in these industrial wastewater discharges include pharmaceutical/personal care products, heavy metals, microplastics and others, as well as microbial pollutants. A complete analysis of the industrial effluent discharges is problematic and presents several limitations. One of them is related to the processes of treatment in wastewater treatment plants. Several reports emphasized that the removal of pollutants, such as pharmaceuticals and personal care products, by a single process of treatment is not efficient and the implementation of coupled treatment systems is necessary to overcome the inadequacies of a single treatment technology. The search for novel treatment systems is strongly recommended, with special emphasis on the use of synergistic approaches to achieve highly effective and environmentally friendly treatment processes. Knowledge of the fate of emerging compounds during wastewater treatment and within the environment is also lacking and is important to determine the fate and impact of emerging compounds across their complete life cycle. In this context, analysis of the occurrence of these compounds in the soil and river sediments is very important to analyse the real impact of these compounds in the environment. The quantification of pharmaceuticals and other emerging compounds is also a weakness in the analysis of industrial discharges but technologies based on Fourier-transform infrared/Near-infrared (FTIR/NIR) spectroscopy have recently been developed with very promising results. Microplastics and nanoparticles also present limitations with regard to the identification and quantification of these materials and it is urgent that methods be found to solve this limitation. The main recommendation for microplastics is to minimize their presence in the environment; it is suggested that microplastic wastes be transformed, *e.g.* by conversion, into fuel, and that conventional plastics be substituted by biodegradable plastics.[18] Heavy metal pollution is a problem mostly in developing countries.[11] Several reports show clearly that heavy metal mixtures exist in the environment and it is imperative to study the effect of these mixtures on human health. In order to reduce the environmental and public health effects of chemical pollution caused by industrial effluents discharges, governments should implement more restrictive legislation and define lower limit values for pollutants in effluent discharges.

Microbial pollution also deserves special attention in the future. For the elimination of bacteria, parasites and viruses careful selection of the treatment processes is needed and the development of new technologies is recommended for better microbial elimination. Zhang *et al.*[32] suggested the use of UV-based advanced oxidation processes (AOPs), such as UV–$H_2O_2$, UV–$Cl_2$, UV–$O_3$ and UV–$TiO_2$, to eliminate microbial pollution. The authors highlighted the cleanness, low operation cost and efficiency for small-scale treatments, as the main advantages of these methods. More suitable indicators and methods of identification aimed at characterizing microbial pollution should also be developed. More stringent environmental legislation for the control of bacteria, parasites and viruses in water systems is also recommended.

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CHAPTER 3

# Detrimental Effects of Industrial Wastewater on the Environment and Health

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## 3.1 Introduction

Increased rates of urbanization along with rapid industrialization contribute greatly to the pollution in soil, air and water. Pollutants such as heavy metals, pesticides, antibiotics, microplastics, *etc.* are the main components of

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

wastewaters. Water bodies (river, lakes, ponds and drains) and empty land act as a sink for the discharge and dumping of different kinds of waste or effluent generated by industrial as well as domestic activities.[1] As has been reported, significant amounts of contaminants can be removed by industrial treatment systems, utilizing physical, chemical and biological treatment processes, however pollutants may still remain in the discharge effluent or generated sludge. At low concentrations, these pollutant may or may not possess toxicity, but after a certain limit, they inflict high toxicity on different life forms present on Earth.

The presence of these pollutants has been reported worldwide in water, seafood, vegetables, crops, *etc.* A high concentration of zinc (12 mg $L^{-1}$) along with other heavy metals (chromium, copper, lead, nickel and cadmium) was observed in the water used for irrigation in the Delhi region of India.[2] Different kinds of pesticides (endosulfan: 7.56 μg $L^{-1}$, chlorpyrifos: 0.86 μg $L^{-1}$ and methyl parathion: 0.43 μg $L^{-1}$) were observed in the river water samples (Tapi River, Gujrat, India).[3] A high concentration of pesticide (chlorpyrifos: 332 μg $kg^{-1}$) was observed in vegetable samples collected from a local market in Thailand and these vegetables are consumed by humans on a daily basis.[4] Smith *et al.* (2018)[5] reviewed the presence of microplastics in seafood and their toxic effect on human health. The presence of these pollutant in soil may change the physio-chemical properties as well as microbial community of the soil which may result in infertile soil.[2] The studies mentioned are a few examples that indicate the presence of toxic pollutants in each part of the ecosystem. These pollutant can cause a number of life-threating diseases in humans, from cancer to organ failure. The present chapter elaborates on the toxic effects caused by pollutants (heavy metal, antibiotic, pesticides and microplastic) in different parts of the ecosystem such as soil, water and human health.

## 3.2 Toxic Effect of Heavy Metals

Heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), zinc (Zn), nickel (Ni), lead (Pb) and others are naturally occurring elements. The large application of these heavy metals in multiple industries (paint, electroplating, batteries *etc.*), agriculture, and indomestic settings *etc.* has led to their dispersal into various parts of the environment such as water, soil, plants and organisms.[2] Due to multiple anthropogenic activities such as waste disposal, smelting and fertilizer usage, heavy metal presence in agricultural sol is very common. Moreover, usage of heavy metal contaminated water for irrigation provides an easy route for toxic heavy metals to accumulate in plants (vegetables, crops and fruits). Although some heavy metals such as Zn, Cr and Cu are essential elements for normal plant growth and development, if their concentration is above the prescribed or threshold value, it may cause multiple toxic effects such as retardation of growth, root browning, inactivation of enzymes involved in multiple metabolic activities such as carbon fixation, the electron transport chain, *etc.*, high production of reactive oxygen species (ROS), damage to cell membranes and DNA among others.[6]

Lee *et al.*, (1996)[7] observed that Zn toxicity in a plant can cause deficiency of phosphorous that can result in purplish red coloured leaves. In addition to this, the morphology of the root was changed abruptly (thickened and blunt). Scientists have observed that Zn toxicity can cause inhibition of photosynthetic activity and decrease overall production of ATP. Furthermore, Zn displaces Mg in the enzyme ribulose-1,5 bisphosphate-carboxylase/oxygenase and results in inhibition of carbon fixation that is normally performed by this enzyme. Tauqeer *et al.* (2016)[8] observed an increase in the level of various enzymes such as superoxide dismutase, peroxidase, catalase *etc.* in response to an elevated level of Cd in *Alternanthera bettzickiana*. Multiple toxic effect such as inhibition of photosynthesis activity, reduction in carbon dioxide fixation, change in integrity of cell membrane, chromosomal fragmentation and inhibition of calmodium (involve in cell signalling pathways) have been observed.[9] Although Cu is an important element for multiple metabolic activities in plants, such as carbon assimilation, adenosine triphosphate (ATP) synthesis, *etc.*, high concentrations of Cu in plants can damage the cell membrane as well as DNA.[10] Other symptoms that are associated with elevated levels of Cu includes chlorosis, retardation in plant growth, low germination rate, *etc.*11 Toxicity of mercury can cause inhibition of the electron transport chain by altering the activity of mitochondria and chloroplasts. Malar *et al.* (2015)[12] concluded that Hg toxicity may cause blockage of normal growth and development along with disruption of various cellular functions. On the other hand, Cr toxicity can cause wilting of roots, retardation in growth, chlorosis, inhibition of photosynthetic and carbon fixation activity and production of multiple metabolites such as glutathione and ascorbic acid that can negatively affect plant physiology.

The human body is exposed to toxic heavy metals in many ways, *e.g.* through consumption of heavy metal contaminated ground water, agricultural products and seafood, exposure to heavy metal contaminated atmospheric air *etc.* Cd is present in various industrial products such as batteries, soft drink vending machines, cigarettes *etc.* The human body is exposed to such items in the routines of daily life. Cd is carcinogenic as well as mutagenic in nature. Prolonged exposure to Cd can cause partial or permanent damage to kidney, bone or prostate gland. Persistent exposure to Cd metal can have adverse effects on the kidney by hindering the activity of many enzymes responsible for re-absorption of proteins or amino acids and hence may result in dysfunction of the kidney and proteinuria.[6]

Cr is another toxic heavy metal that exists in two different forms: $Cr^{VI}$ (hexavalent) and $Cr^{III}$ (trivalent). However, various studies have confirmed that the hexavalent form of Cr is more toxic as compared to the trivalent and the toxicity of Cr can cause multiple health disorders in the human body. Cr is categorized as a carcinogenic element and may cause death in some cases. Cr is widely used for various unit processes in industries such as tanning, metal refining, electroplating, drugs, inks, dyes and pigments *etc.*[1] Exposure of humans to Cr can cause physiological disorders such as skin allergy, irritation of the nasal passage, hearing loss and cancer. In was observed that in some cases Cr can cause chromosomal abnormalities or alterations in DNA replication by damaging the DNA–protein complexes responsible for the replication process.[13] Hg is widely used in biomedical devices, battery manufacturing industries, nuclear reactors, chemical processing industries *etc.* |Hg toxicity to human health has been reported by various researchers. Usually, Hg exists in mercuric, mercurous, elemental, methyl or ethyl forms. All of these forms of Hg are very toxic in nature and can cause gastro-intestinal disorders, neurological disorders, multiple organ (kidney and liver) failure *etc.* In addition to this, Hg toxicity can cause cellular damage such as inhibition of mitochondrial activity, microtubule damage, lipid peroxidation *etc.* Ni is widely used in electroplating industries and in the manufacture of alloys, batteries, paints and chemicals, jewellery, kitchen items *etc.* However, metal processing industries are the main source of Ni pollution. Ni in a trace amount helps in multiple metabolic activities performed by cells, but it can be very toxic if present at more than the maximum permissible limit. Exposure to a high concentration of Hg can cause cancer, kidney failure, allergic reaction, lung failure *etc.* Studies indicate that Ni in gaseous (nickel carbonyl) form is extremely toxic and teratogenic in nature.[6]

The literature clearly suggests that partially treated or untreated wastewater contains sufficient amount of nutrients such as nitrogen and phosphorus to help with the plant growth.[1] However such wastewater from industry may contain toxic heavy metal as a pollutant and that can cause heavy metal accumulation in the soil.[2,14] Continuous use of such wastewater for irrigation slowly builds up the concentration of heavy metals to a level that they can easily affect the normal functioning of soil in a negative way. The toxic effect of heavy metals on soil includes changes in microbial biomass, carbon mineralization, enzyme activity, nitrogen fixation, soil pH, cation exchange value *etc.*[6] Carbon mineralization or soil respiration shows the capacity of soil to support different life present in the soil such as microbes (bacteria, fungi *etc.*), insects and vegetation. In addition to this it also indicates the rate of decomposition of organic matter (cellulose and starch) present in the soil. Studies clearly indicate that accumulation of toxic heavy metals in the soil with time can decrease the rate of respiration. Further, the decomposition rate of organic matter present in soil is also inhibited due to heavy metal toxicity. Yongsheng (2008)[15] observed that the rate of soil respiration by micro-organisms in control (2.51–2.56) soil was reduced to 0.98–1.61 in the presence of heavy metals (Cu and Zn). In another study, Chen *et al.* (2014)[16] observed that heavy metal toxicity can reduce soil basal respiration by 3–45%. Vásquez-Murrieta *et al.*, (2006)[17] observed negative correlation between carbon dioxide production due to soil respiration and heavy metals present in the soil. Soil respiration is solely dependent on the microbial community and its metabolic activities. Changes in the microbial community due to the toxic effects of heavy metals might be the reason for the low rate of soil respiration.[1] Soil microbes plays an important role in maintaining the quality and structure of the soil by taking part in different nutrient cycles and controlling the decomposition of organic matter in the soil.

The toxicity of heavy metals can drastically change the dynamics of the microbial community present in the soil and hence cause a deterioration in the quality of the soil.[18]

Microbial biomass and enzyme activities due to the microbial community present in the soil acts as indicators to determine the soil health and its fertility.[1] Yu and Cheng (2014)[19] observed that the microbial biomass of the soil declined significantly in the presence of heavy metals as compared to a control. In another study, similar declines in microbial biomass along with enzyme activities of the soil were observed in the presence of heavy metals.[20] It was observed that the presence of heavy metal in the soil decreased the activity of various enzymes like dehydrogenase, alkaline phosphatase, arylsulfatase, catalase, urease *etc.*[19,21] Up to a 50% decrease in nitrogen fixation activity in soya bean plants was observed due to the presence of heavy metals in the soil.[22] In another study, heavy metal toxicity was observed to have an inhibitory effect on the activity of enzymes (glutamine synthetase and glutamate synthase) involved in nitrogen assimilation.

## 3.3 Toxic Effect of Antibiotics

Antibiotics are complex molecules with different chemical structures that are divided into many classes. These are prescribed for the treatment of infectious diseases of humans and animals. The use of antibiotics has been increased in the last decades for disease control and livestock breeding. The use of antibiotics in livestock is aimed to increase meat production by preventing disease. The use of antibiotics has increased globally (between 2000 and 2015) by 65%, and is expected to increase 200% by 2030 compared to that in 2015. The European Center for Disease Prevention and Control (ECDC) reported both increasing (Greece and Spain) and decreasing (Finland, Luxembourg, Norway and Sweden) usage of antibiotics among countries.[23] Although antibiotics have many advantages their continuous release into the environment is adversely affecting living organisms.[24] As antibiotics are not fully metabolized in the body, the majority of these drugs are released into the water and soil through municipal discharge, manure and sewage sludge.[24] The concentrations of antibiotics in wastewater may range from nanograms to micrograms per millilitre.[25] However, although wastewater treatment processes can remove antibiotics, the efficacy may vary depending upon various factors such as the nature of the influent and the type of technology.[26]

The improper use and disposal of these antibiotics aids the development of antibiotics resistance in bacteria. Such bacteria can carry one or many antibiotic resistance gene. Antibiotic contamination exists in soil, municipal or industrial wastewater, manure, sediments, surface water and groundwater. The environmental impact of antibiotics as pollutants has gained much attention in the recent past due to increased use and environmental persistence. Nowadays antibiotic resistance has become a global concern for food safety and public health. Antibiotics are widely used in the treatment of bacterial infection. There are two major concerns with regard to the effect of antibiotics: first, antibiotics in environment contributing to the development of antibiotic resistance genes in pathogens and second, the effect on human health as a consequence of antibiotics contamination in the ecosystem. Many antibiotics are reported to make their way from soil to plants.[27] In one study conducted on wastewater treatment plants (WWTPs) it has been shown that these WWTPs are becoming hotspots of antibiotic resistant pathogenic bacteria.[28] Martín *et al.* (2015)[29] reported the presence of different antibiotics (tetracycline, sulfamethoxazole, ciprofloxacin, norfloxacin, trimethoprim and ofloxacin) in the sludge of different WWTPs. Even though the sludge is usually treated before its application to land the antibiotics were found not to have been completely removed from it.[29] An investigation carried out in Korea on 24 different pharmaceuticals in 12 sewage treatment plants and 4 livestock wastewater treatment plants reported the presence of >70% of target compounds in S-sludge and L-sludge, respectively.[30] Different antibiotic resistant genes [*tet*(*X*), *tet*(*W*), *tet*(*G*), *sul*(*1*) and *intI*(*1*)] were also reported in different wastewater treatment plants.[31]

Many antibiotics such as tetracyclines, fluoroquinolones and sulfonamides are becoming a serious threat to the agroecosystem around the world.[32] There are various ways antibiotics may enter the system either by the application of manure or through human consumption of antibiotics that are released into the fields directly in faeces and urine.[33] Wastewater containing antibiotics that is used for irrigation purposes is also a major contributor.[24] Some antibiotics are highly stable and may persist in the environment for several years.[34] Antibiotics may further reach from farmland to water streams, rivers and ground water or can be ingested directly by animals. Experimental analysis of the effect of these antibiotics on plants and other organisms does not usually reflect their actual concentrations.[35] The concentration levels found for experiments done *in vitro* are much higher than those *in vivo*. The detrimental effect of antibiotics on plants, particularly on crop plant species, have been investigated by many researchers.[36] Whereas the effects of different concentrations of antibiotics in laboratory and land studies vary a lot, the effect of antibiotics on plants seems to be heavily influenced by their doses.[35]

The crops exposed to these antibiotics in the field respond in different ways depending upon the type of compounds, their sorption potential and the effect of environmental conditions.[37] The natural depletion of these antibiotics is also not very effective as it is soon recharged by ongoing antibiotics release into the system.[38] Most cultivated crop plants absorb and take up antibiotics from the soil and accumulate them in their structures.[39] Antibiotics not only affect root and shoot growth in plants but also affect their production rate, biomass and other biochemical contents.[40] Overall, the anatomy and physiology of plants are affected by antibiotics. The adverse effect on antibiotics depends upon the plant species, type of antibiotic, its concentration, *etc.* However, the effect of low concentrations of antibiotics on plants in field conditions is largely unclear. Many studies have been performed to fill this knowledge gap and to understand the effect of antibiotic concentrations that mimic the actual field concentrations on crops and non-crop plant species. Hillis *et al.* (2011)[41] studied the effect of ten antibiotics on three plant species *viz.* lettuce, alfalfa and carrot. They reported the effect of different ranges of antibiotics on germination and root and shoot elongation. The germination of seeds was found to be insensitive to the antibiotics while the shoots and roots were significantly affected. Liu *et al.* (2009)[42] also reported the impact of six antibiotics *viz.* chlortetracycline, tetracycline, tylosin, sulfamethoxazole, sulfamethazine and trimethoprim on seed germination and plant growth. The different antibiotics had different effects on plants. They reported the maximum susceptibility in rice against sulfamethoxazole ($EC_{10}$ value of 0.1 mg $L^{-1}$).

Soil microorganisms are important for soil health and quality. They mediate many important processes such as turnover of organic matter, release of nutrients, maintenance of soil fertility and its structure. Antibiotics have emerged as one of the major players in disturbing the homeostasis of soil. They affect the composition of the soil microbial community which in turn alters the properties and functionality of soil. Many methods have been developed to study the effect of different antibiotics on the microbial community as well as the effect of different antibiotics on a particular soil microorganism. Metagenomics, phospholipid fatty acids (PLFAs) and 16s RNA analysis are being used in many studies for studying the change in microbial diversity in soil.[43,44] Many important functions such as soil respiration are affected even at very low concentrations of antibiotics.[45,46] Scientists from U.S. Geological Survey documented the effect of antibiotics on soil microflora, both in the laboratory and on land. They found that the level of antibiotics affects the cell growth, denitrification and changes in the bacterial community. Inhibition of denitrification can have adverse effects on many critical ecological functions.[47] This process results in the conversion of nitrates to nitrogen gas (the main component of the atmosphere). The process also affects soil fertility and contributes to nitrate pollution. The consequences are more severe when this nitrate reaches the groundwater and causes serious health problems in infants and other persons who drinks it. Sulfadimethoxine, oxytetracycline, and sulfadiazine are reported to inhibit soil nitrification.[48] However, ciprofloxacin and norfloxacin were found to stimulate the rate of nitrification in soil.[49,50] Antibiotic contamination in soil is greater in areas used for livestock or that have been treated with manure. Some antibiotics were found in higher (oxytetracycline and chlortetracycline) and others in lower (ciprofloxacin, norfloxacin, and tetracycline) concentrations. To determine the exact concentration of antibiotics, advanced analytical methods (high-performance liquid chromatography with tandem mass spectrometry) are essential.[51] Schmitt *et al.* (2005)[52] developed a method for identifying the effect of antibiotics on soil microorganisms. The soil microorganisms were exposed to different concentrations of sulfonamide sulfachloropyridazine (SCP) and the effect on pollution-induced community tolerance (PICT) was measured. This study found increased community tolerance in soil amended with SCP.

## 3.4 Toxic Effect of Pesticides

Organochlorine pesticides such as 1,1,1-trichloro-2,2′bis(*p*-chlorophenyl) ethane (DDT), lindane, endosulfan, heptachlor *etc.* and organophosphorus pesticides such as malathion, parathion, chlorpyrifos *etc.* have been detected in significant concentrations in waterbodies in every season, indicating their widespread usage.[53] These pesticides are used for weed control in agricultural fields. They are also used to control disease-carrier pests such as ticks, mosquitoes and rodents. Farmers in developing countries use a combination of pesticides, often ignorant of their residues remaining in the soil that accumulate in the vegetables that are cultivated in such soils.[54]

The drastic impacts on human health are both short-term, causing eye and skin irritation, nausea and dizziness and long-term causing asthma and cancer. These effects depend on the nature and concentration of the pesticide and also on the duration of exposure.[55] The mechanism of the pathogenesis of diseases such Alzheimer's and Parkinson's is due to the oxidative stress caused by pesticides. This oxidative stress leads to DNA damage which results in malignancies. Furthermore, several pesticides control gene expression through the production of non-coding mRNAs, DNA methylation and histone deacetylase patterns that have a direct role in the epigenetics.[56] There is substantial evidence of the causation of chronic diseases such as respiratory problems *e.g.* asthma, cardiovascular diseases *e.g.* coronary artery disease, chronic nephropathies, chronic fatigue syndrome as well as autoimmune diseases such as rheumatoid arthritis and systemic lupus erythematous and aging. These disorders are a result of perturbances in cellular homeostasis that are induced by the main actions of pesticides, such as disturbance of enzymes, ion channels, receptors, *etc.* Such diseases are also mediated through other pathways that involve introduction of epigenetic modifications, genetic damage, mitochondrial dysfunction, endocrine disruption, endoplasmic reticulum stress, unfolded protein response (UPR), impairment of the ubiquitin proteasome system and defective autophagy.[57] Further birth defects and neurobehavioral disorders have been observed in children in farming communities due to the usage of chemical pesticides. In females, oxidative stress caused by pesticides has resulted in reproductive disorders like follicular atresia, endometriosis and spontaneous abortions.[58]

Organochlorine pesticides, previously used as vectors in controlling several diseases such as typhus and malaria, have been banned since the 1960s. Residues of the pesticides endosulfan, endrin, heptachlor and lindane that are banned in agriculture still occur in soils. The persistence of pesticides in soil are determined by characteristics such as the soil-sorption constant ($K$oc), octanol/water partition coefficient ($K$ow), water solubility and half-life in soil (DT50). Pesticides can be grouped into two categories: (1) hydrophobic pesticides that are persistent and are easily bioaccumulated and strongly chelate to the soil, *e.g.* heptachlor, endosulfan, endrin, lindane; and (2) polar pesticides that percolate into the soil thereby contaminating drinking water for human consumption, *e.g.* carbamates.

The retention of pesticides in soil depends on the soil and pesticide interaction. The amount of organic matter content in the soil directly determines the amount of pesticides chelated to the soil. Moreover, the soil tends to bind the positively charged pesticides in an exchangeable manner.[59] Further, soil pH is important in the adsorption of pesticides. Adsorption of pesticides increases with a decrease in the pH of the soil.[60] Soil microbes such as fungi and bacteria degrade organic matter and facilitate the retention of soil particles in the form of aggregates. The organic part of the soil maintains the number of fungi and bacteria that help in the retention and recycling of nutrients in the soil, which is important for overall soil fertility and consequently crop productivity.[61]

However, indiscriminate usage of pesticides impacts adversely the naturally occurring beneficial microorganisms that hold the inorganic and organic nutrients in the soil. These pesticides have serious implications for the recycling of nutrients, water and energy in soil.[62] These agrochemicals have a propensity to transfer into the environment by chelating to either the organic matter in the soil or binding to the underground/aerial parts of plants and thus enter the food chain by biomagnification in higher organisms. With the change in dynamics of soil microbes, such as a decrease in certain group of microbes, the quality of the soil is affected as an entire series of modifications takes place that leads to altering the prey–predator relationship and results in changes in soil chemistry such as soil pH, soil organic matter content and the soil aggregation. Further seepage of these agrochemicals into the soil after heavy rainfall contaminates fresh groundwater bodies.[61] The extensive usage of the herbicide glyphosate [*N*-(phosphonomethyl) glycine] has been linked to a deficiency in the micronutrients in soil by creating selection pressure in naturally occurring microbial communities.[63] Long-term use of pesticides such as DDT have effects on the non-target soil microflora such as fungi, bacteria and algae and their counts were decreased in higher concentrations of this pesticide as estimated by the microbial dehydrogenase activity.[64] In an experiment, researchers utilized integrated soil microcosms to predict interactions between soil organisms and the intricate ecosystem processes in the presence of the fungicide carbendazim.[65] The ecosystem components that were affected were the nematode and earthworm communities that directly impacted plant growth as these invertebrates are linked to nitrogen metabolism and transformation of nutrients in the soil. Hence it is imperative to remediate these hazardous pesticides so that the soils can be rendered useful for agriculture purposes.

## 3.5 Toxic Effect of Microplastics

Plastic materials such as polypropylene (PP), polyvinyl chloride (PVC), polyethylene (PE), polystyrene (PS) and polyethylene terephthalate (PET) are the major plastics developed and used worldwide. However, with lack of knowledge and improper disposal methods, these plastic materials accumulate in land and water bodies, such as lakes, rivers, seas *etc.* However, slow degradation of plastics occurs in the environment due to photo-oxidation, leading to the formation of small fragments, and particles ranging from 1 µm to 5 mm are described as microplastics.[66] These microplastics are resistant to further degradation and due to their small size they pose a greater threat to the environment than their larger forms. Researchers have highlighted the presence of tonnes of microplastics in soil, air and the marine environment; furthermore, animals, aquatic organisms and humans are regularly exposed to microplastics. Aquatic living organisms *i.e.* fishes, turtles, amphipods and other aquatic animals have been found to translocate microplastics in their tissues after ingestion, leading to the obstruction of various body tracts, malfunctioning and damage to organs. As these organisms acts as a food source, they easily enter food chain and affect birds, animals and humans. Humans are also exposed to microplastics regularly from air, water and contaminated food.

After ingestion, microplastics are absorbed in the intestine, affecting the amount and diversity of gut microbiota. Inhalation of microplastics also causes deposition in the respiratory tract and lesions in the lungs. Microplastics, due to their large surface area, causes an increase in permeability leading to chronic inflammation.[67] Small fibres of microplastics have been observed in human lung biopsies, including in cancer biopsies.[68] Studies have also shown that microplastics can lead to oxidative stress, cytotoxicity, neurodegenerative diseases and translocation to other tissues. Additionally other contaminants such as dyes, heavy metals and synthetic chemicals can attach to microplastics and be transported and accumulate in the bodies of aquatic organisms. Seafood consumers are at greater risk due to the biomagnification of a variety of contaminants along with microplastics.

These minute plastics have been shown to inhibit sunlight penetration in water bodies, directly harming the aquatic environment. A detailed assessment and more scientific evaluation is required to study the routes of microplastic intake, its transportation in organs and its mechanism of damage. Understanding the potential risk associated with plastics many countries have already formulated policies and have already banned different grades of plastics, however more strict rules should be implemented worldwide to decrease the adverse impacts of plastics on the environment.[69] Awareness among people about the harmful effects and proper disposal should be carried out to manage plastic wastes at regular intervals. Moreover, research to study the immediate and long-term effects of microplastics and their monitoring should be taken up as a prime objective by scientists.

## 3.6 Conclusion

Over the past few decades, the rise in human population and rapid industrialization has caused a tremendous increase in wastewater generation. Studies suggest that waste generated globally contains large amount of heavy metals, pesticides, antibiotics, dyes and plastics, leading to ecological disequilibrium and also affecting the different life forms on Earth. These contaminants accumulate in soil, air and water bodies, and with their slow degradation they are posing a great danger to humans, animals, plants and aquatic organisms. The presence of these contaminants have been observed in plants and aquatic animals showing blockages and tissue/organ damage. In humans, various lethal effects such as, mutations, cancers, disruption of the endocrine system, neurotoxicity, compromised immune system and disorders in reproductive systems have been observed. Therefore, proper waste disposal and banning of non-degradable waste materials, especially plastics, can save the ecosystem. Furthermore, implementing strict guideline polices and worldwide awareness of toxic pollutants can also help to reduce the unwanted load of contaminants in the earth's environment.

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CHAPTER 4

# *Treatment and Management Strategies for Industrial Wastewater*

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## 4.1 Introduction

In the 21st century, environmental issues have always been at the forefront of sustainable development, which has now become a serious matter of concern. Due to rapid industrialization, sustainability of environmental assets is seen as one of the major challenges worldwide. Industry is considered a key driver in boosting the economic growth of countries and fulfilling market demands. At the same time it is a major contributor to environmental pollution owing to the discharge of partially or untreated toxic and hazardous wastes which have severe effects on living beings.[1] Among the several kinds of environmental pollution, water pollution is one of the biggest problems faced by several countries in the current scenario. This is because water is considered as one of the precious elements of the earth and it has an extensive impact on all living and non-living creatures. Water is an essential resource for agricultural,

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

industry and other human activities. Earth consists of 1.386 billion $km^3$ of water of which 97.5% is salt water and the remaining 2.5% freshwater. In this freshwater, merely 0.3% is available in liquid form that is accessible for human consumption.[2] With the extensive growth rate of the population all over the world, the consumption of water has increased enormously through both domestic and industrial activities. Nowadays, it is noted that some parts of the world have come to the phase of "water crunch". UN reports describe that 1.8 billion people will suffer from water scarcity and two-thirds of the total world population could face water stressed conditions by 2025. The scarcity of water can be physical, in that availability of water is limited and demands cannot be fulfilled or it can economic, where water is available although there will be no means or infrastructure for the provision of water from the quality or quantity basis.[3] It has been reported that $\approx 10 \times 10^6$ $m^3$ per day of the total wastewater (sewage, agricultural and industrial) is discharged into the ecosystem, globally. In addition to that, a significant portion of wastewater is released untreated in the aquatic system, causing pollution of rivers and other surfacewater sources.[4] In India, water demand is increased immensely due to the rising population and industrialization. Nearly, 8–10% of total water demand in the country is accounted for by the industrial sector alone. However, a proper estimation of water usage by industries in India has yet to be made owing to the shortage of reliable data. As per the Ministry of Water Resources and Central Pollution Control Board, at the start of the of 21st century industry accounted for ≈6–8% of total freshwater abstraction. Nevertheless, as per the estimation given in an FICCI report,[5] in India the water demand for industry is on the rise and it will account for 8.5 and 10.1% of total freshwater abstraction in 2025 and 2050, respectively. All of these data indicate that water demand in industry is not negligible and is bound to rise further in the coming years due to lack of water availability. Groundwater and surfacewater are the major sources of water to fulfil the water demands of industries. The significant growth in some of the water intensive industries has put pressure on them to fulfil their water demands. For instance, the annual growth of the chemical and construction industry is ≈9%, whereas the growth of the textile and pulp and paper industries is ≈6 and 5%, respectively. Industries are not only responsible for huge consumption of water, but are also to a large extent responsible for causing water pollution. As per the World Development Report 2003, in developed countries nearly 70% of industrial wastewater is dumped into water bodies without any treatment, thus spoiling the usable water supply. Approximately, 1 L of wastewater simply discharged into a body of surfacewater further pollutes ≈5–8 L of water, which increases the share of industrial water usage to somewhere between 35 and 50% of the total water consumed in India, rather than the 7–8% that is currently considered a measure of industrial water usage. Table 4.1 shows an approximate estimation of water consumption and wastewater production by the various industries in India (CSE, 2004).[6]

In India, $\approx 62 \times 10^5$ $m^3$ of industrial effluent is produced per day of which only 60% of wastewater is treated for further usage.[7] According to the CPCB report (2009–2010),[8] the huge gap between the amount of wastewater produced and the treatment of wastewater indicates the immense requirement

**Table 4.1** Production of wastewater and utilization of water by various industries in India.

| Industry | Annual discharge of wastewater ($\times 10^6$ m$^3$) | Annual consumption of water ($\times 10^6$ m$^3$) | Total volume of water consumed by industry (%) |
|---|---|---|---|
| **Thermal power plants** | 27000.9 | 35157.4 | 87.87 |
| **Engineering** | 1551.3 | 2019.9 | 5.05 |
| **Pulp and paper** | 695.7 | 905.8 | 2.26 |
| **Textile** | 637.3 | 829.8 | 2.07 |
| **Steel** | 396.8 | 516.6 | 1.29 |
| **Sugar** | 149.7 | 194.9 | 0.49 |
| **Fertilizer** | 56.4 | 73.5 | 0.18 |
| **Other** | 241.3 | 314.2 | 0.78 |
| **Total** | 30729.2 | 40012.0 | 100.0 |

**Table 4.2** Main pollutants present in the wastewater of concerned industries.[9]

| Pollutants | Industries |
|---|---|
| Acid | Mining, machinery, chemical, steel, electroplating industries, non-ferrous metallurgy |
| Cyanide | Coke and coal processing, metal cleaning, synthesis, gold industry, acrylonitrile refining industry |
| Phenol | Coal gas, coking, oil refining, petrochemical, dyes, synthetic resins, chemicals, pulp and paper |
| Oil | Oil refining, machinery, food processing |
| Sulfide | Coking, leather, mining, oil refining, oil processing industry, dyeing |
| Polycyclic aromatic hydrocarbons | Coal and coke processing, petrochemical and oil refining, rubber and tyre manufacturing, asphalt industries, thermal power plants |
| Polychlorinated biphenyls | Plastics, lubricants, electricity |
| Cadmium | Metal mining, electroplating, batteries, smelting |
| Mercury | Explosives, chlor-alkali, mercury pesticides, electroplating, mercury refining industries, thermal power plants |
| Radioactive substances | Nuclear industry, hospitals, weapons production |
| Free chlorine | Papermaking, chemical industry, textile bleaching |

for management of water. There is a vast increase in the utilization of water and wastewater discharge due to unclear environmental policies. In addition, increased water demand in the future will put inevitable pressure on the availability of water resources.

Industries namely, pulp and paper, tannery, textile, dairy and distillery, pharmaceutical, oil and petroleum refining *etc.* generate complex wastewater and are largely responsible for the pollution of water bodies. Wastewater contains various industrial wastes comprised of organic and inorganic pollutants such as phenolic compounds, heavy metals, sulfates and nitrates, petroleum hydrocarbons, pesticides, dyes, radioactive pollutants *etc.* Table 4.2 demonstrates a few major pollutants that originate from different types of industries.

The effluent guidelines provided by national and international authorities use concentration as the measurement of contamination which encourages the practice among industry of diluting contaminated water until it reaches the permissible limit, rather than controlling pollution at the source itself.[10] In such cases, the untreated industrial wastewater will be used for irrigation purposes, causing lower agricultural yield. On the other hand, agricultural runoff water may contain several toxic chemicals originating from fertilizers and pesticides that are utilized for growth of crops. It can also become a reason for the contamination of surfacewater bodies. Hence, overall, it can be said that there is the utmost need for the treatment and management of industrial wastewater for environmental safety. Therefore, this chapter provides an overview and outlines the treatment of wastewater originating from various industries, with their characteristics, management strategies for the prevention of industrial waste and a review of different methods of wastewater treatment. The chapter further describes the rules and regulations governing the adequate discharge of industrial wastewater into surfacewater bodies.

## 4.2 Wastewater From Industries, Its Characterization and Impacts

The wastewater discharged by different industries varies in its pollutant composition. Each industry generates its own specific combination of contaminants in the context of the type of raw material used for the production of the particular product. The characteristics of industrial wastewater can be defined in terms of its physical, chemical and biological characteristics. Total suspended solids, dissolved solids, pH, temperature, colour and odour *etc.* are in the category of physical characteristics, whereas the chemical characteristics of industrial wastewater constituents are widely described as organic and inorganic. In general, organic constituents involve aliphatic and heterocyclic compounds, phenolic compounds, polycyclic aromatic hydrocarbons (PAHs), dyes, pesticides, herbicides, polychlorinated biphenyls (PCBs) and fats, oil and grease *etc.* Numerous inorganic compounds such as phosphates, sulfates, nitrates and heavy metals such as Cr, Ni, Fe, Pb, Cd and Zn are often present in industrial wastewater. The main wastewater parameters that have a large impact on water bodies include BOD (biological oxygen demand) and COD (chemical oxygen demand).

A detailed description of wastewaters with their sources, characteristics and impacts from a few of the concerned industries, namely pulp and paper, dye and textile, iron and steel, petrochemical, and tannery, are presented in the following section.

### 4.2.1 Pulp and Paper Industry

The pulp and paper industry stands out as one of the important industries in the world owing to its significant contribution to the economic growth of a country. The pulp and paper industry consumes massive amounts of resources such as wood and water and consequently generates huge amounts of wastewater which has a great impact on the surrounding territory, and on aquatic and human health. Nowadays, consumption of paper per person varies significantly in developed countries. On average, one-person usage of paper is ≈60 kg per year, the largest being ≈265 kg for each US citizen and only 7 kg for each African, while in heavily populated areas of Asia ≈40 kg of paper per person is used. This suggests that the consumption of paper by Asian countries will continue to rise considerably in the coming years.[11] The making of paper is a water intensive process owing to its requirement for lots of water for the production process, ranging from ≈20 000 to 60 000 gallons per ton of product, resulting in the generation of large amounts of wastewater.[12] The crucial factors to be considered for the growth of the pulp and paper industry are the minimization freshwater usage and the recycling of produced wastewater. The generation of a variety of pollutants depends upon the kind of pulping processes considered. The pulp and paper industry produces a huge quantity of wastewater that requires suitable treatment and management prior to its discharge into the aquatic environment.

- **Sources**
  The paper making and pulping process requires a large amount of water and produces a large discharge as wastewater. The most important sources of pollution during paper making are the pulping, pulp washing, wood preparation, washing, screening, bleaching and coating processes. Of these, pulping produces high-strength wastewater during the chemical pulping stage. The wastewater produced in these processes is comprised of wood debris and soluble wood materials. During the pulp bleaching process, the wastewater produced possess a low pH and high chloro-lignin content, whereas white water and black liquor are produced in the paper machining and chemical recovery stages, respectively.

- **Characteristics**
  The characteristics of wastewater produced during various stages of the pulp and paper making process largely depend on the type of wood, technology and amount of water used in the particular process. The major pollutants released in the pulping and bleaching process have high COD and BOD and include dissolved lignin, fatty acids, halogenated hydrocarbons, inorganic chlorines *etc.* The general characteristics of pulp and paper industry wastewater are given in Table 4.3.

- **Environmental impacts**
  The pollutants released from the pulp and paper industry have severe affects on many aspects of the environment such as water, the atmosphere, agricultural land, forests and human health. Due to chemical contamination and reduced levels of oxygen, the water quality deteriorates and considerably lowers the survival efficiency of aquatic fauna. These changes will cause delayed sexual maturity with a decrease in secondary sexual characteristics in species present near the discharged

**Table 4.3** General characteristics of different industrial wastewater.

Pulp and paper wastewater

| Process | pH | COD (mg $L^{-1}$) | BOD (mg $L^{-1}$) | Suspended Solids (SS) (mg $L^{-1}$) | TN (mg $L^{-1}$) | TS (mg $L^{-1}$) | Methanol (mg $L^{-1}$) | Reference |
|---|---|---|---|---|---|---|---|---|
| TMP | 4.2 | 7210 | 2800 | 383 | 12 | 72 | 25 | 26 |
| CTMP | — | 6000–9000 | 3000–4000 | 500 | — | 167 | — | |
| Kraft bleaching | 10.1 | 1124–1738 | 128–184 | 37–74 | — | — | 40–76 | |
| Kraft foul | 9.5–10.5 | 10 000–13 000 | 5500–8500 | — | — | 120–375 | 7500–8500 | |
| Sulfite condensate | 2.5 | 4000 | 2000–4000 | — | — | 800–850 | 250 | |
| Chip wash | — | 20 600 | 12 000 | 6095 | 86 | 315 | 70 | |

Textile industry wastewater

| pH | COD (mg $L^{-1}$) | BOD (mg $L^{-1}$) | SS (mg $L^{-1}$) | $NH_4^+$–N (mg $L^{-1}$) | P (mg $L^{-1}$) | Colour | Reference |
|---|---|---|---|---|---|---|---|
| 7.2–8.1 | 830–4750 | 115–730 | — | 5–18 | 103–118 | $Colour_{436}$ = 20.5–138 $m^{-1}$ | 27 |
| 10.8–11.2 | 800–1000 | — | 200–300 | — | — | 1000–2500 PtCo unit | 28 |
| 9.91 | 1029 ± 67.4 | 170 ± 14.14 | 180 ± 16 | 22.51 ± 2.05 | 2.39 ± 0.09 | $Colour_{669}$ = 0.21 $m^{-1}$ | 29 |
| 2–10 | 50–5000 | 200–300 | 50–500 | 18–39 | 0.3–15 | >300 mg $L^{-1}$ | 30 |
| 10 | 1150 | 170 | 150 | — | — | $Colour_{436}$ = 1.24 $m^{-1}$ | 31 |
| 9.0 | 1000 | 300 | 880 | 57 | — | — | 32 |

| Petrochemical wastewater | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Type of wastewater | pH | COD (mg $L^{-1}$) | BOD (mg $L^{-1}$) | SS (mg $L^{-1}$) | $NH_4^+$–N (mg $L^{-1}$) | TP (mg $L^{-1}$) | Oil/phenol (mg $L^{-1}$) | Reference |
| Acidic petrochemical waste water (WW) | 2.5–2.7 | 55 000–60 000 | 30 000–32 000 | 20–300 | — | 102–227 | 360 (Phenol) | 33 |
| Oil refinery WW | 7.8–8.79 | 250–613 | — | 108–159 | 56–125 | <0.5 | 35–55 (Oil) | 34 |
| Engine processing WW | — | 4345–6864 | 919–1360 | 253–889 | — | — | — | 35 |
| Heavy oil WW | 6.5–6.8 | 500–1000 | — | 90–300 | — | — | 400–1000 (Oil) | 36 |
| Oil refinery WW | — | 72.1–296.1 | 90–188 | 245–950 | — | — | 20–87 (Oil) | 37 |

| Iron and steel industry wastewater | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Section | pH | Alkalinity (mg $L^{-1}$) | TDS (mg $L^{-1}$) | TSS (mg $L^{-1}$) | VSS (mg $L^{-1}$) | Anions (mg $L^{-1}$) | Phenol (%) | Reference |
| Blast furnace | 7–9 | — | — | 330–350 | ≤200 | $MnO_4^-$ = 4 0–15<br>$CN^-$ = 0.6–1.3<br>$CNS^-$ = 0–17 | 0.5–1.2 | 38–40 |
| Slag crushing | — | 3–4 | 450–550 | 500–600 | 30–50 | $MnO_4^-$ = 100–500<br>$SO_4^{2-}$ = 100–150<br>$CNS^-$ = 3–4 | 1.0–2.5 | |
| Rolling mills | — | 3–4 | 400–500 | 1000–1500 | 10–100 | $SO_4^{2-}$ = 100–150 | — | |
| Coke oven | 7.0–8.5 | — | 800–1200 | 200–7000 | — | $CN^-$ = 8.2–21 | — | |
| Pig iron cooling | 7–8 | — | 500–2000 | 500–3500 | 350 | $MnO_4^-$ = 60–100<br>$SO_4^{2-}$ = 20–650<br>Cr = 200–300 | — | |
| Pickling unit | 1.5–4.5 | — | — | — | — | $SO_4^{2-}$ = 200–2000 | — | |

effluent. Howe and Michael (1998) observed serious changes in soil chemistry in Northern Arizona as a result of irrigation with pulp mill effluent.[13] Also, the usage of pulp and paper wastewater for irrigation purposes will result in the contamination of food, while its use for washing and the consumption as raw vegetables such a lettuce, strawberries and cabbage may cause cholera, typhoid *etc.*

### 4.2.2 Textile Industry

Textile industries are major contributors towards the production of bulk amounts of wastewater as a huge amount of water is used for the colouring and finishing process. The effluent from the textile industry encompasses a variety of dyes mixed with various other contaminants in a variety of ranges. The coloured effluent released by these industries poses a serious threat to the environment; therefore, environmental legislation strictly obligates textile industries to treat these wastewaters prior to discharge into receiving water bodies.[14]

- **Sources**
  There are two major processes involved in the production of fibre in the textile industry, *viz.* dry and wet processes. In the wet process, a considerable amount of potable water is utilized which results in the formation of highly contaminated wastewater. The main sources of contamination in the textile industry are operations/processes such as sizing, de-sizing, scouring, bleaching, mercerizing, dyeing, printing and finishing. The dyeing process is a principal step in the textile industry which involves addition of colour to the fibre, yet different chemicals are used to enhance the adsorption process between colour and fibre. After the finishing process, dyes and chemicals becomes part of textile industry wastewater that pollutes soil, sediment and surfacewater.[15]
- **Characteristics**
  The effluent from the textile industry comprises a mixture of dyes, metals and other contaminants. The dye effluents possess certain characteristics such as a strong colour, a high pH, COD and BOD, and contain suspended solids, metals and mineral salts. The textile industry also releases an array of toxic and hazardous organic and inorganic compounds such as ammonia, aromatic amines (benzidine and toluidine), pigments and chlorine which can cause severe environmental and health issues.[16]
- **Environmental impacts**
  Textile industries releases millions of gallons of colourful wastewater containing organic and inorganic chemicals which are toxic and hazardous for the ecosystem. The occurrence of certain chemicals such as sulfur, nitrates, naphthol, chromium compounds and heavy metals such as Cu, Pb, As, Cd, Hg, Ni and Co collectively make the wastewater highly

toxic for the environment. The presence of colour and oil in wastewater causes an increase in turbidity and foul odour in the surfacewater.[17] This wastewater if discharged to surfacewater inhibits penetration of sunlight which is necessary for the photosynthesis of flora and fauna. Use of this wastewater for irrigation results in clogging of soil pores, eventually affecting the soil productivity. Chemicals evaporated from this wastewater get mixed with the atmosphere and are absorbed by our skin, which can cause allergic reaction.

### 4.2.3 Petrochemical Industries

The petrochemical industries are fundamental to industry, with an important role in enhancing any country's economy and offering support to other sectors such as energy, transportation and agriculture.[18] Wastewater is produced during various operations carried out in the petrochemical industry such as processing of raw materials, cooling water from boilers, factory rainwater and domestic sewage *etc.* A recent report demonstrated that ≈4.4 billion tons of petroleum products have been produced globally and ≈3–3.5 $m^3$ of wastewater is generated from the petrochemical industry per ton of petroleum refinery production. This wastewater contains a range of refractory, organic and inorganic pollutants, oil and grease which are detrimental to the aquatic ecosystem.[19]

- **Sources**
  Petrochemical wastewater is generally associated with oil-related industries. There are many sources of petrochemical wastewater that can originate from crude oil refinery plants, oilfield production, olefin processing plants, energy utilities, refrigeration *etc.*[20,21] Also, petroleum refinery wastewater produced during oil refinery processes yields >2500 refined products. This wastewater may emanate from cooling systems, hydro treating, distillation and desalting processes. Moreover, oilfield-produced wastewater, which is generated during the extraction of crude oil from oil wells, contains a high concentration of COD an artificial surfactant.[22]
- **Characteristics**
  Petrochemical wastewater includes organic and inorganic substances, oil and some other toxic compounds. Among these, oil and grease are major organic compounds and are the source of numerous other toxic compounds found in oil refinery wastewater such as phenolic compounds, PAHs and benzene. Moreover, oilfield-produced wastewater, which is generated during the extraction of crude oil from oil wells, contains a high concentration of COD and artificial surfactant. Oily wastewater is mainly comprised of four types of hydrocarbons, *i.e.* aromatic, aliphatic, asphaltenes, and oxygen, nitrogen and sulfur containing compounds. The pH value of oily sludge ranges from 6.6 to 7.5 depending upon the sources of crude oil, the methods applied and the reagents used.[23]

- **Environmental impacts**
  Wastewater discharged by the petroleum industry comprises large amounts of hydrocarbons, phenols, heavy metals and other toxic pollutants.[24] Among these, phenol is considered very harmful for humans and is known to be carcinogenic, mutagenic and teratogenic in nature. Phenol can cause mouth souring, skin irritation, diarrhoea, vision deficiency and darkening of urine in human. Benzene, toluene, ethylbenzene and xylene (BTEX) are a common part of crude oil and absorbance of these compounds through the skin results in anaemia and a decrease in platelets, whereas ethylbenzene can result in the liver or kidney damage if consumed.

### 4.2.4 Iron and Steel Industries

The iron and steel industries earn particular attention owing to their high consumption of material, energy requirements, and emission of $CO_2$ and particulate matter. The iron and steel industry is a water-intensive sector and also a major contributor to wastewater discharge. According to a World Steel Association (2018b) report, the average water intake for an integrated plant is 28.6 $m^3$ per tonne of crude steel, with average consumption of fresh water being 3.3 $m^3$.[25] The data clearly reveal the huge consumption of fresh water required by the iron and steel industry, and this trend is due to increase in the coming years which will ultimately causes a greater amount of wastewater release from these industries.

- **Sources**
  The production of iron from its ores involves an intense reduction reaction in a blast furnace. Production of coke from coal in coking plants requires water for cooling and for by-product separation. At this stage, cooling water becomes contaminated with various compounds such as phenol, cyanide and ammonia. The conversion of steel/iron into sheets, rods or wire requires hot and cold mechanical transformations which necessitate water as a coolant and lubricant. These are a few major sources of production of wastewater from the iron and steel industry.
- **Characteristics**
  Effluents from the iron and steel industry are loaded with toxic and hazardous pollutants with high COD and BOD, as well as suspended solids, PAHs, phenol, ammonia, cyanide, heavy metals *etc.*
- **Environmental impacts**
  Effluent from iron and steel industries contains obnoxious compounds as mentioned above that can condense in the aquatic system and contaminate land areas making them unsafe for public use. The direct discharge of steel plant effluent into receiving water bodies causes contamination, with an increase in total solids, reduction in pH (8.9 to 3.9)

and dissolved oxygen levels, presence of phenols, ammonia and sulfides. The general characteristics of pulp and paper, textile, petrochemical and iron and steel industrial wastewater are given in Table 4.3.

## 4.3 Laws and Regulations for Industrial Wastewater Treatment

The plethora of rules and regulations, laws, ordinances and limitations that regulate the discharge limits of industrial solid, liquid and gaseous waste represents an alarming challenge to anyone attempting to become an expert in the field of environmental guidelines. Every year these legal entities are published in hundreds of brochures; new laws are invented and passed by several local, state, country and federal governments and authorities. Prior to the 1950s, most US states had regulations forbidding the pollution of groundwater and surfacewater. For example, the Pennsylvania State Legislature approved the Clean Streams Act in 1937, which specifically prohibited the release of industrial waste into surfacewater and groundwater. In the early 1970s, the federal government got public attention for prosecuting industries for high levels of pollution. Before passing of the Federal Water Pollution Act (FWPCA) by Congress in 1948, only the Refuse Act of 1899 was accessible under which a discharger of pollutants could be accused. The FWPCA was amended in 1956 to create the Water Quality Act, 1965; the Clean Water Restoration Act, 1966 and the Water Quality Improvement Act, 1970. In the beginning of the 2000s, with the passage of 1972 amendments to the Clean Water Act, Public law 92–500 (PL 92–500) replaced all the language and amendments of the original 1956 act (Clean Water Act, 404).[41] Consequently, the establishment of all federal, local and state water pollution control laws and regulations continues in the form of PL 92–500 in the amendment of 1972 of the Clean Water Act. Before approval of these watershed amendments, water pollution control laws were mainly based on water quality standards and effluent limitations adapted to those standards. The level of treatment required for a particular industrial discharge directly depended on the cumulative capacity of the receiving water bodies. The approach was completely based on the fact that the "solution of pollution is dilution". Moreover, PL 92–500 has been modified numerous times since 1972 and it is a comprehensive law which is a tough task to summarize in a few sheets. Some of the significant requirements given in the act are described as follows.

- All industrial dischargers must possess a permit under the National Discharge Elimination System (NPDES). The permits have three essential parts: (1) effluent limitations, (2) compliance schedule, (3) monitor and report requirements.

- All industrial dischargers are required to treat of wastewater up to their minimum discharge limit. If any hazardous substances are present then additional obligations must be fulfilled.
- Penalties have been set for non-compliance.
- Industrial effluent discharged to publicly owned treatment works (POTWs) is controlled by Pre-treatment Regulations that are published in part 403 of PL 92–500.
- Provision for receiving waters of PL 92–500 includes all river streams, lakes, creeks, ponds, swamps, bogs and territorial sea in the range of 3 miles as well as drainage, ditches, wetlands and intermittent streams.
- Release of hazardous substances is controlled under distinct provision from discharge of conventional elements.
- Non-point sources of pollution such as storm water runoff from industrial spots is regulated.
- Development and application of section-wise waste treatment management plans are sanctioned.
- Water quality standards and implementation strategies for accomplishing those standards for water bodies are compulsory.
- If the industry is not able to meet the desired water quality while releasing into receiving water bodies then additional treatment must be adopted.
- Industries must acquire a discharge permit from the state environmental rules and regulations authority before an NPDES permit will be grant.

In accordance with the federal Clean Water Act, any state may administer the clean water law as amended. In this context, applications for discharge permits by the federal law (NPDES) and state law are done simultaneously.[42]

## 4.4 Conventional Methods for Industrial Wastewater Treatment

A number of conventional processes have been established in the area of industrial wastewater treatment. The main objective of all these processes is to improve the purity of water or lower the level of impurities through removal of toxic components; improve energy efficiency by adopting the most appropriate separation methods; work for environmental safety and compatibility to meet the guidelines and adopt sustainable techniques from an industrial point of view. In the area of industrial wastewater treatment, there are mainly three main methods of operation known as primary, secondary or tertiary treatment, which depend on the nature of the separation method selected and the results obtained from the particular method. In general, primary treatments are size-based separation processes carried out by means of physical techniques such as sedimentation, coagulation, flocculation and filtration. Secondary treatment generally comprises physicochemical or biological methods including extraction, reactive separation, advanced oxidation processes, membrane separation processes, activated sludge processes, aerated lagoon, trickling filters, anaerobic digestion *etc.* Final polishing of the effluent with removal of toxic/hazardous contaminants up to the desired level (>99% removal) can be attained wit tertiary treatment. Hence, the most commonly used conventional methods for industrial wastewater treatment are discussed in the following section.

### 4.4.1 Coagulation or Flocculation

Traditional coagulation methods involve destabilization of colloidal particles/substances present in the fluid by the addition of a metal salt compound such as aluminium sulfate and ferric chloride which neutralize or reduce the charge between particles. This reaction causes the formation of precipitates that facilitate the agglomeration of suspended particles which improves removal during sedimentation. Coagulation is one of the most commonly used methods in the treatment of effluent from industries. Nevertheless, usage of coagulants in wastewater treatment processes containing refractory chemicals is a complex problem and to date there is no solution available. In the case of flocculation, particle size is continually enlarged to form discrete particles through collision and interaction between added inorganic and organic polymers.[43] When discrete particles are flocculated into larger particles, they can be easily removed/separated by filtration, floatation and straining processes. However, coagulation or flocculation processes alone are not the complete solution for the problems of industrial wastewater treatment. These methods only help to improve the performance of a treatment process and the use of additional treatment techniques is required.

### 4.4.2 Ion Exchange

Ion-exchange processes ares commercially employed techniques for wastewater treatment which involve reversible exchange of ions between a liquid and a solid. It is a water treatment method that facilitates removal of undesirable ionic pollutants from water through exchange with other non-objectionable ionic substance. This method is a cost-effective process as it usually involves low cost materials and it is very proficient for the removal of heavy metals from contaminated water. The mechanism of ion-exchange in the case of acid removal is carried out by the protonation of inorganic compounds on a weak base resin by the proton of the acid and consequent addition of an anion through electrostatic interaction, which can be understood by following reactions:[44]

$$\mathrm{R + H^+ \rightarrow RH^+}$$

$$\mathrm{RH^+ + A^- \rightarrow RH^+\,A^-}$$

where $\mathrm{A^-}$ represents the anion of the acid, R is a resin, $\mathrm{RH^+}$ and $\mathrm{RH^+\,A^-}$ is protonated species and acid salt of the resin, respectively.

Ion-exchange resins are water-insoluble solid materials that can attract positively or negatively charged ions from an electrolyte solution and release other ions having the same charge in equal amount into the solution. The positively charged ions in cationic resins (hydrogen and sodium ions) are replaced with positively charge ions (nickel, zinc, copper). In the same manner, the negative ions in the resins (hydroxyl, chloride) are exchanged with negatively charged ions (chromate, nitrate and sulfate).

### 4.4.3 Membrane Filtration

Membrane filtration has attracted significant attention in the treatment of wastewater containing inorganic substances. It involves pressure-driven filtration with the help of small pores which aid in the removal of contaminants. This technique is capable of specifically removing inorganic contaminants like heavy metals and organic contaminants, suspended solids *etc.* Depending upon the size of the particle, a membrane filtration technique can be categorized as ultrafiltration (1–100 nm), nanofiltration (1 nm), microfiltration (0.1–10 μm) and reverse osmosis (0.1 nm). Ultrafiltration normally employs a permeable membrane for the separation of heavy metals, macromolecules and suspended solids based on the pore size and molecular weight of the compounds, whereas in reverse osmosis pressure is applied to force a solution through a semipermeable membrane which retains the solute on the other side and allows the passage of solvent but not the metals.[45] In comparison to the other conventional techniques, membrane filtration processes are more energy efficient, easy to operate and yield high-quality products. The environmental effect of this process is very low as no toxic chemicals are used which require a discharge stage and there is no heat generation. However, membrane filtration techniques possess their own limitations that should be kept in mind before applying them for wastewater treatment in any industry.

### 4.4.4 Advanced Oxidation Processes

Advanced oxidation processes have been commercially used for the removal of refractory pollutants that are difficult to remove by other conventional techniques. These processes are mainly employed for the treatment of highly hazardous and non-biodegradable wastes. Although a variety of Different catalyst and reactor configurations are used for oxidation processes, photo-Fenton and Fenton oxidation are mostly applied for industrial wastewater treatment. Advanced oxidation processes are carried out through generation of hydroxyl radicals and other oxidant species to degrade organic compounds present in wastewater.[46] The hydroxyl radical breaks organic molecules by extracting a hydrogen atom *via* the addition of a double bond for ultimate conversion into carbon dioxide and water.

This process generally has high operating costs. However, the oxidation products formed are less complex in nature and can subsequently be easily treated by biological methods.

## 4.5 Biological Methods for Industrial Wastewater Treatment

Biological treatment is a significant and essential part of any wastewater treatment plant which helps to treat wastewater coming either from a municipality or industries that contains a mixture of impurities such as organic, inorganic, heavy metals *etc.* Biological treatment methods are a cost-effective process in terms of capital investment and operating cost in comparison to other physicochemical processes such as chemical oxidation, extraction, membrane separation, electrochemical treatment, adsorption and absorption *etc.* The huge demand for the development of such processess that could meet the stringent discharge standards led to the implementation of a range of biological treatment processess in recent years. The main objective of a biological treatment process is to treat the soluble organic matter present in wastewater that often needs pre-treatment by physical methods for the removal of solids prior to biological treatment. Biological degradation of waste is accomplished by the combined activity of microorganism such as bacteria, algae, fungi, protozoa and rotifers. Biological processes are categorized according to the primary metabolic pathways carried out by the dominant microorganism active during the treatment process. As per the availability of oxygen, biological treatment processes are mainly classified as anaerobic, anoxic and aerobic. Anaerobic treatment occurs in the absence of oxygen and mainly assists in sulfate reduction and methanogenesis processes. Biological processes that occur in the presence of molecular oxygen which use aerobic respiration for the generation of cellular energy are known as aerobic processes, whereas an anoxic process is generally carried out in the absence of free molecular oxygen and in the presence of bound oxygen that produces energy through anaerobic respiration. A brief discussion about aerobic and anaerobic modes of biological treatment is given in the following section:

### 4.5.1 Aerobic Process

Biological treatment of industrial wastewater using an aerobic activated sludge process has been carried out for decades. A high amount of substrate conversion is achieved in aerobic wastewater treatment with less maintenance and monitoring of the operation being required. However, a large amount of sludge generation is the major limitation of this process. The aerobic process involves oxidative degradation of carbonaceous substances to provide the energy required for the proliferation of the microorganisms which as a biocatalyst to carry out the process. The bacterial cells can be called as "biochemical reactors" in which heterotrophic organisms oxidize organic substances to produce carbon dioxide and water with the help of oxygen. The aerobic process can be efficiently operated by keeping the following points in mind (WEF manual, 2008).[47]

- The concentration of essential nutrients (nitrogen and phosphorus, trace metals) in wastewater should be properly maintained.
- An adequate supply of oxygen should be provided to enable aerobic respiration.
- The growth rate of microorganism or monitoring of biomass concentration should be given proper consideration.
- The optimum environmental conditions such as pH, temperature must be checked regularly for efficient biological degradation.
- The food to microorganism and C : N : P ratio must be assured for the growth of bacterial cells.

As mentioned earlier, the most common aerobic process is the activated sludge process which generally involves aeration of wastewater, separation of solid–liquid ensuing aeration and release of clarified effluent. A number of variations in the activated sludge process are practiced by the various industries, for instance a contact tank can be substituted with an aeration tank, provision of carried media or a physical surface for the attachment of microorganism and variation in reactor configuration. The activated sludge process creates a huge amount of sludge which necessitates further treatment and processing prior to final disposal.

### 4.5.2 Anaerobic Process

The problems associated with aerobic processes with regard to excessive sludge generation, the need to meet environmental standard regulations and the rising energy cost of conventional treatment processes, have led in recent years to the development of anaerobic processes. These involve anaerobic fermentation in association with the formation of biogas, alcohols, organic acids and ketones. Biogas is a by-product in anaerobic fermentation processes which is generally used to meet the energy requirements. In general, biogas is comprised of methane and carbon dioxide in a ratio of 1 : 1 to 3 : 1 along with hydrogen sulfide and trace amount of nitrogen and hydrogen. The major factors that affect the growth of anaerobic microorganism include pH, temperature, redox potential, residence time and composition of essential nutrients. In the process of anaerobic fermentation for the production of methane, there are three kinds of microorganism involved in the degradation of organic substances, *i.e.* acidogenic, acetogenic and methanogenic bacteria. Initially, biopolymers are hydrolysed through the process of acidogenesis to produce soluble monomers, which is followed by the formation of acid and the simultaneous production of hydrogen and carbon dioxide, a step described as acetogensis. At this point only, formation of methane occurs through the reaction of hydrogen with carbon dioxide. A number of approaches are available to enhance the retention and recycling of the biomass produced, which serves as a catalyst in the various steps of the anaerobic process. Internal retention (biomass retention) is the most significant method adopted in anaerobic wastewater treatment for decoupling of retention time for the liquid substrate, which can be understood by considering following steps depending on the particular method and reactor involved:

- sedimentation – Upflow anaerobic sludge blanket reactor (UASB)
- filtration – membrane anaerobic bioreactor, rotor fermenter
- immobilization by means of adsorption – fixed bed reactor, anaerobic film reactor, fluidized bed reactor, stirred tank reactor with suspended carrier materials, hybrid UASB/fixed film reactor
- biomass cycling
- sedimentation by chemical/physical methods – anaerobic contact process (flocculation), centrifugation
- flotation

The major limitation associated with this process is the scale-up problem of anaerobic wastewater treatment; specific provision should be made for that.

## 4.6 Management Strategies for Industrial Wastewater Treatment

Management of industrial waste is a very difficult problem which affects the entirety of processes carried out in industry starting from the manufacturing process through to waste minimization. In general, the management systems adopted by various industries are completely based on the hierarchy of waste generation. The hierarchy gives priority for the solution of problems related to waste generation as follows: minimization of waste/pollution prevention > recycling/reuse > toxicity reduction > disposal. Practical application of this hierarchal approach to pollution prevention through evaluation of waste reduction and discharge at the source, prior to assessing recycling processes and treatment programmes, epitomizes the chemical industry's success in dealing with volatile organic carbon sources by executing the guidelines set out by the Toxic Substances Control Act (TSCA) air pollution regulations of 1976. As per the United States Environmental Protection Agency (USEPA) guidelines and the Hazardous and Solid Waste Amendments (1984), the successful management of industrial waste is governed by a complete understanding of the manufacturing process and not just a survey of the waste produced.[48] The chief elements of these guidelines include:

- clearly define the problem and construct written goals
- acquire top management support in order to find a solution to the problem
- product characterization and identification of process modifications that can aid waste reduction

- waste characterization
- create options for waste minimization and make it a priority to obtain a solution
- evaluate waste minimization treatment options periodically
- build a cost allocation system in order to refer disposal cost back to the production unit
- obtain feedback for the evaluation of waste minimization techniques and encourage suggestions for improvement.

The USEPA effluent standard approaches for selected point sources intended for the minimization of wastewater and pollution prevention are demonstrated in Table 4.4.

**Table 4.4** Wastewater minimization approaches used by the USEPA for particular point sources.

| Point source | Approach for wastewater minimization/pollution prevention |
|---|---|
| Iron and steel manufacturing | Zero discharge for the process which will not produce wastewaters, disposal of wastewater through coke quenching process, high degree of recycle of forging process by means of oil–water separation, usage of multimedia filtration for the treatment of blowdown, control of emission scrubbers in coke quenching |
| Leather tanning and finishing | Reduction in the usage of water |
| Mining of minerals and processing | Zero discharge of wastewater as no usage of water in any process, control of runoff and rainfall |
| Extraction of oil and gas | Waste minimization by the reduction in oil spillage, separation of deck drainage from oil leaks |
| Paint formulation | Recycling of solvents, high degree of water washing of equipment, cleaning of floor |
| Pesticide chemicals | Pollution prevention in order to obtain minimal discharge of wastewater, sweeping/vacuum drying of area before cleaning with water, reuse of the rinsate of the containers |
| Pulp and paper | Reduction in the flow activities such as frequent recycling of pulp and paper machine white water by the use of gravity strainers, reprocessing of deinking wash water after flotation clarification |
| Rubber manufacturing | Flow reduction with the use of dried-air pollution equipment, reuse of solutions in wet-air pollution equipment, exclusion of soap-solution discharge by recycling and reuse of water, elimination of latex solution discharge by curbing and sealing of drains |
| Steam electric power generation | Control in the usage of chemicals to reduce the total residual chlorine concentration for the prevention of cooling-tower fouling, reduction in the concentration of toxic pollutants resulting from the utilization of chemicals to maintain the cooling tower |

The management strategy for the treatment and control of industrial waste needs to be assimilated at the beginning of the process itself. Benefits of a well-implemented management strategy includes lower operating cost, enriched product quality, improved production, reduced responsibilities and successful regulatory compliance.

## 4.7 Conclusion

This chapter provides an overview and outline of wastewater originating from various industries with their sources, characteristics and the environmental impacts associated with the particular industry. The rules and regulations governing the discharge of industrial wastewater according to different authorities is also addressed. Various conventional methods available for the treatment of industrial wastewater are discussed. From an economic point of view, biological treatment processes have proved to be very efficient for the successful treatment of industrial wastewater containing a variety of toxic pollutants. In addition to this, management strategies for pollution and the prevention of industrial waste are also summarized. Advanced treatment techniques including hybrid methods (physical and biological) should be adopted for the efficient treatment of industrial wastewater to reduce the health and environmental hazards.

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CHAPTER 5

# *Introduction to Industrial Wastewater and Allied Treatment Technologies*

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## 5.1 Introduction

Water pollution refers to contamination of natural water bodies like lakes, rivers, oceans, aquifers, and groundwater, resulting in the degradation of aquatic ecosystems and death/disease all over the world. Causes of water pollution include natural phenomena like volcanic eruptions, earthquakes or landslides, algal blooms, storms, and anthropogenic activities like industrialization and urbanized living. The chief sources of water pollution can be described as point sources and non-point sources. Point sources can be referred to as contaminants that are released into waterways from discernible single sources, for instance a pipe/ditch from a factory or a municipal drain. Non-point source pollution arises from cumulative diffuse sources from

Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

various points of pollution, like typical chemical leachates from fertilizer-treated farms/fields. Water pollution levels can be determined through analysis of polluted water samples using physical, chemical and biological tests through measurement of turbidity, biological oxygen demand, chemical oxygen demand, nutrients, metals, *etc.* Common types of wastewaters resulting in water pollution are the result of domestic, municipal, agricultural and industrial activities.[1,2] Controlling water pollution requires apposite infrastructure and management plans. Requisite infrastructure includes wastewater treatment plants like sewage treatment plants and industrial wastewater treatment plants. This chapter focuses on explaining sources of industrial wastewaters, treatment techniques and the associated challenges.

## 5.2 Sources of Industrial Wastewater

Industrial wastewaters are those released by industrial/commercial processing plants, which need to be treated appropriately before being discharged and/or disposed of. Industries that are significantly responsible for industrial wastewater production include oil and gas, metal and mining, textile, pharmaceutical, and food and agricultural industries. The content, volume/quantity, quality of organic materials and presence of recalcitrant compounds in industrial wastewaters determine if they are biodegradable, and whether they can be reused after treatment for any purpose, if at all. Due to the difficultly in tracking toxic compounds and their fate, combined with the need to use complex and expensive treatment methods to remove them from wastewater, it is advisable to consider the implementation of cost-effective cleaning methods in industries (such as the replacement of toxic recalcitrant compounds with others that are less harmful or not harmful at all) and, also to raise awareness in society to reduce the use of such types of compounds.[3] Industrial pollutant-containing wastewaters are commonly deposited semi-treated or untreated (in some cases) into the receiving water bodies present in the vicinity. Such pollutants commonly contain pathogenic microbes, phosphorus and nitrogenous compounds, hydrocarbons, heavy metals, and other organic materials, which result in eutrophication, and are associated with health hazards.[4]

Certain industrial pollutants are serious polluters, but effluents from food and agricultural industries are loaded with biodegradable and recyclable pollutants which can be efficiently mitigated in spite of the heavy loads. Pollution issues have a strong impact on the population. Coloured effluents discharged by pulp/paper and textile mills are perceived as a sign of serious pollution to the associated water bodies. All industrial activities are energy and water consuming and in turn release polluting chemical-loaded effluents. Combating pollution caused by these wastewater effluents through treatment methodologies is very challenging.[5] Before aiming for proper and effective treatment strategies, we must consider the various sources of industrial wastewaters, the chief types of pollutants released by them and their impacts on environmental well-being and human health.

Metal finishing and mining industries produce composite hydroxides of metals like iron, steel, magnesium, nickel, zinc, copper and aluminium; such wastewaters should be treated following mandatory regulations before being released into natural ecosystems. During the production of iron/steel, water is used for cooling and lubricating operations, and for separation of by-products, while becoming contaminated with pollutants like ammonia, cyanides, benzene, naphthalene, anthracene, phenols, cresols, rinsed off waste acids (hydrochloric acid, sulfuric acid, *etc.*) and hydraulic oils.[6,7] The textile industry is known to processes billions of pounds of laundry every year, using chemicals and large amounts of water, yielding wastewater streams laden with oil/grease, lint, sand particles, grit, nitrogen, phosphorous, organic matter and heavy metals traces of chromium, arsenic, copper, zinc, *etc*. which can harm environmental ecosystems and human health.[8] Petroleum refineries/plants produce wastewaters laden with pollutants like oil, grease, suspended solids, ammonia, chromium, phenolic and sulfide compounds. Oil and gas fracking wastewaters contain salts and high concentrations of sodium, magnesium, iron, barium, strontium, manganese, methanol, chloride, sulfate, hydrocarbons like benzene, toluene, ethyl benzene, xylene *etc.*[9] Fossil-fuel power stations like coal-fired plants discharge wastewaters heavily laden with metals like lead, mercury, cadmium and chromium, arsenic, selenium, and other nitrogenous compounds.[10] Water purification/treatment plants discharge waters loaded with by-products such as trihalomethanes, haloacetic acids, biosolids, heavy metals and household-based synthetic/organic compounds.[11] Food processing and agricultural needs result in wastewater streams containing pesticides, insecticides, fertilizers, animal wastes, and other organic waste materials.[12] Milk processing industries are one of the world's essential industries; they produce huge loads of wastewater as water plays a chief and huge role in dairy farms and cheese manufacturing. Water is essential in bulk throughout stages like cleaning, washing, skimming, disinfecting, sanitizing, heating/cooling, and other miscellaneous manufacturing operations.[13] Textile industries are another sector which generate huge amounts of wastewaters during activities like colouring and finishing of textiles. The significant effluents are composed of biodegradable and/or non-biodegradable chemicals like azo dyes, dispersants, levelling agents *etc.*, and are capable of modifying the physical/chemical/biological natures of the receiving waters, leading to detrimental health/environmental hazards.[14] Emerging pollutants include dangerous chemicals and/or compounds that can enter the environment, and as a result are detrimental to human health. They are termed as ‘emerging’ due to the ever-increasing rising levels of concerns regarding their regulation. Various kinds of emerging contaminants like personal care products, endocrine disruption compounds, pharmaceutical compounds and allied transformed products occur at trace levels in post-treated wastewaters because even wastewater treatment plants are sometimes inefficient in mitigating such trace levels of contaminants. Hence, the re-entry of such traces of emerging contaminants

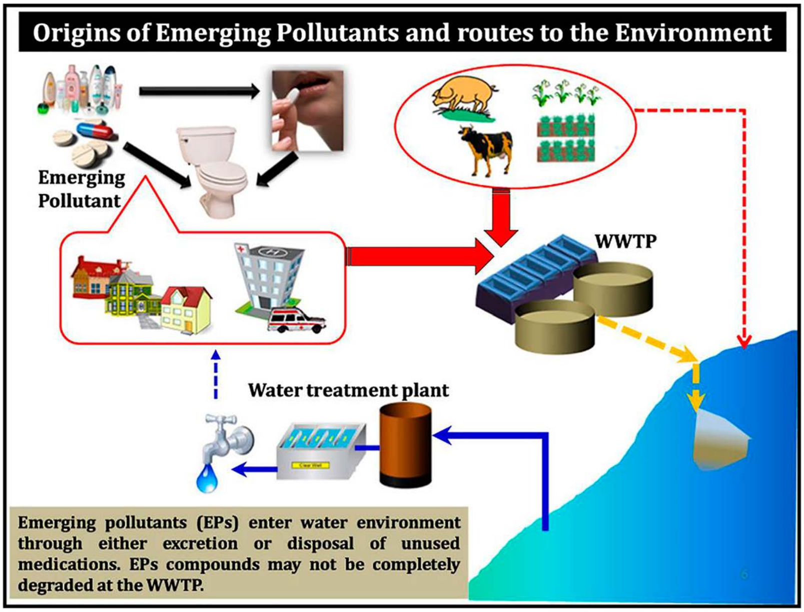

**Figure 5.1** Schematic depiction of the origins of emerging pollutants from sources like medicines, cosmetics, agricultural and animal husbandry wastes. These polluted waters reach wastewater treatment plants (WWTPs), with the processed waters being dumped into large water bodies, and such pollutant traces find their way eventually into tap waters for human consumption. Reproduced from ref. 15 with permission from Elsevier, Copyright 2019.

is of a serious threat for human health and water bodies. Therefore, advanced treatment techniques apposite for the removal of such emerging contaminants are essential in designing wastewater treatment plants. Figure 5.1 shows sources of emerging pollutants and their eventual routes into the environment.[15]

Based upon the source the kind of wastewater treatment to be used can be determined through usage of various technologies, which can chiefly be classified as conventional and advanced.

## 5.3 Treatment of Industrial Wastewater

### 5.3.1 Conventional Methods

Conventional methods for wastewater treatment are targeted to improve its quality before it is released into the environment; this is intended to restrain polluted waters from fouling cleaner water resources within the vicinity. Conventional wastewater treatments are adopted in primary and secondary stages. Primary treatment involves pretreatment of wastewater using grit chambers and sedimentation tanks, and other means like coagulation, precipitation, filtration using sand and adsorption using activated carbon, in order to remove larger and suspended solid particles. Secondary treatment of wastewater includes chemical and biological treatment methods using either aerobic or anaerobic methods, and is designed to remove the dissolved organic matter and nitrogen- and phosphorus- based nutrients. Secondary treatment processes are based on the organic matter content of the wastewaters, and biological means are preferred. Low organic loads in wastewaters can be treated through aerobic means using methods like activated sludges, trickling filters, rotating biological contactors *etc.* Wastewater with higher organic contents need higher levels of biodegradation, and must be treated using the more efficient anaerobic bioprocesses. During anaerobic digestion there is also generation of energy (methane gas), along with production of lesser sludge. Four processes occur sequentially during anaerobic digestion, including hydrolysis (breakdown of complex organic matter into simpler sugars, aminoacids), acidogenesis (sugars converted into organic acids), acetogenesis (organic acids converted to acetic acid, carbon dioxide, hydrogen, water) and methanogenesis (methane production and wastewater treatment).[16,17] The activated sludge process is a traditional biological method for wastewater treatment, where microbial communities are chiefly instrumental in the biodegradation process. Through adaptation, biostimulation and bioaugmentation, microbial populations can be augmented resulting in effective decontamination of the wastewater pollutants through biological means.[18] There are various kinds of activated sludge processes *e.g.* a complete mix activated sludge process, the series/plug flow method, tapered/extended aeration, step-feed activated sludge, contact stabilization, oxidation ditches, *etc.*19 Trickling filters are the earliest, simple biological and simple filters, with a layered bed of stones or ceramic material or hard coal, or corrugated plastic sheets, through which wastewater is made to drip. Here microorganisms develop as biofilms (zoogleal films) upon the filter surface and aerobically decompose the organic matter trickling over them. As the biofilm thickens with the advent of time, due to depleted oxygen levels for the biofilm microbes, an anaerobic environment is created causing the microbes to slough off, resulting in the formation of a new film to aid in biodegradation. Biological filters can serve as a complete secondary wastewater treatment unit.[19,20] Rotating biological contactors employ rotating discs to trap/hold biofilms, and have features like voluminous organic matter removal, solid retention, hydraulic resistance *etc.* Compared with other biofilm processes, they have lower energy requirements and can biologically remove phosphorus, nitrogen and organic matter.[21] Treatment of industrial wastewater discharges and reuse of decontaminated wastewater for various applications in several sectors is shown in Figure 5.2.[22]

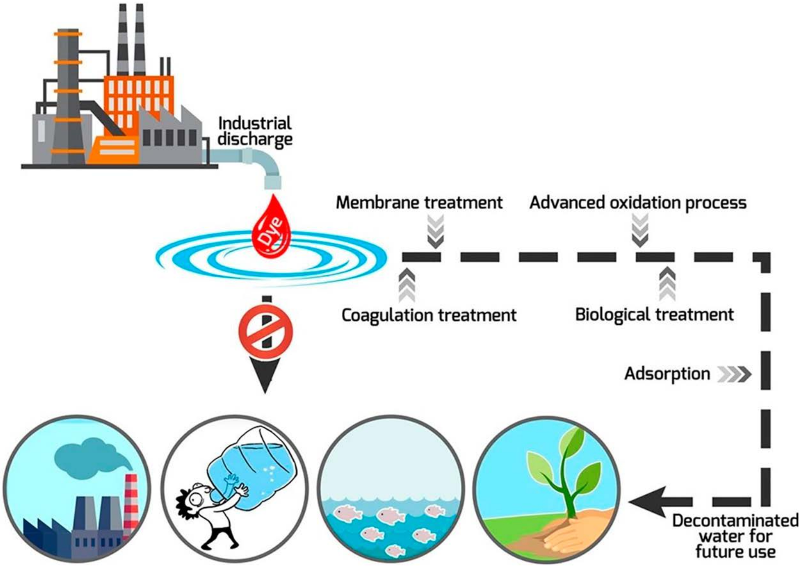

**Figure 5.2** A schematic depiction of discharge of wastewaters from a factory sewer (point source of pollution), various wastewater treatment methods, and myriad applications of decontaminated wastewaters are represented. Reproduced from ref. 22 with permission from Elsevier, Copyright 2018.

## 5.3.2 Advanced Bioprocesses

### *5.3.2.1 Biohydrogen Production*

Wastewater treatment processes can be used for the biological generation of hydrogen using acidogenic fermentation, dark fermentation and photofermentation. During the acidogenic phase of anaerobic digestion, hydrogen is released with low yields, while dark fermentation can enhance hydrogen production. Photofermentation utilizes organic acids (as substrate) occurring in wastewater effluents (treated by anaerobic digestion and dark fermentation), converting them into hydrogen and carbon dioxide, thereby generating additional energy from the semi-treated wastewater. Biohydrogen production from industrial wastewaters (cheap substrate) can be operated on a large scale using emerging strategies by analysing various operational lab-scale parameters. Challenges/limitations associated with biohydrogen production commonly include a dearth of biohydrogen producers, limited substrate conversion, biomass washout, low productivity and metabolite accumulation. Upgrade strategies for overcoming such limitations include proper optimization of operating conditions, pretreating the inoculum for selective enrichment of hydrogen-producing microbes, immobilization of microbes to prevent washout in bioreactors, and process integration (dark and photo-fermentation) to mitigate accumulation of metabolites and augment hydrogen yields. However, commercialization is still challenging due to the high installation costs.[23–25]

### 5.3.2.2 Anammox Process

Industrial wastewaters from petrochemical, pharmaceutical, agricultural fertilizers and food industries contain huge amounts of ammonium and other nitrogenous compounds. During anaerobic digestion almost all nitrogenous compounds are bioconverted into ammonium, which needs to be treated owing to its hazardous nature. Ammonium oxidation (anammox) treatment can be accomplished by nitrifying and denitrifying bacteria, which aid in its bioconversion into molecular nitrogen, by utilizing oxygen. Commercial bioreactors like sequencing batch reactors and fluidized bed reactors can be used to remove nitrogen from wastewater. The efficiency of anammox operations integrated with wastewater treatment plants can be increased by increasing the nitrogen loading rates of anammox bioreactors, reducing the hydraulic retention times and increasing ammonium concentrations.[26] Partial denitrification coupled with anaerobic anammox biofilters can be applied in activated sludge processes for nitrate-laden wastewater treatment, reportedly with 74.6% nitrogen removal using *Candidatus brocadia* as the dominant microorganism. Moreover this advanced technique was found to be feasible for wastewater treatment, also saving aeration consumption and carbon source supplementation, and reducing sludge production.[27] Research on anammox processes have been delimited to laboratory scales, hence online-monitoring systems coupled with automatically controlled operational factors using artificial intelligence techniques are likely to promote anammox processes at pilot and industrial levels.[28]

### 5.3.2.3 Advanced Oxidation

Advanced oxidation processes are widely used for wastewater treatments as they can be integrated with other processes with ease; using this technique hydroxyl/sulfate radicals are generated in quantities necessary for the removal of refractory organic matter, organic contaminant traces, inorganic pollutants and/or for increasing the extent of wastewater biodegradation as a pre-treatment before biological treatment. Advanced oxidation of effluent organic matter from biologically treated secondary effluent wastewaters can evidently generate reusable water streams.[29] Other methods like photocatalysis and photo-Fenton can be used as tertiary effluent treatment methods for detoxifying urban wastewater streams with recalcitrant contaminants and highly dissolved organic carbon contents.[30] A UVC (ultraviolet radiation C)-coupled advanced oxidation process can be used for concomitantly removing microcontaminants like acetaminophen, caffeine, carbamazepine, trimethoprim, sulfamethoxazole, diclofenac and pathogens from wastewaters at a pilot plant scale.[31] The application of nanoparticles as nano-catalysts in ozone-based advanced oxidation processes for wastewater treatment has revealed that a combination of ozonization and nano-catalysts could resolve the problems encountered during wastewater treatment.[32]

### 5.3.2.4 Adsorption Onto Non-conventional Solids

Non-conventional/green adsorbents chiefly include products/by-products of biological (algae, bacteria, fungi, yeasts), forest (bark, sawdust, peat), agricultural (cotton, flax, hemp, polysaccharides, alginates) and industrial (red mud, sludge, seafood processing waste, nanomaterials) origin can be used to facilitate inexpensive adsorption processes. Such materials are preferred over conventional ones due to ample availability in large quantity, low cost and ability to complex with other materials; however research into their commercial application in large scale is still underway.[33] Removal of nitrate ions from effluent wastewaters has been reported through adsorption onto ‘micro-particles of shrimp shell waste’ which are abundant and ecofriendly adsorbents (animal origin).[34] Geopolymers like aluminosilicate solid wastes (industrial origin) can also be used as adsorbents or catalysts and filtration membranes during wastewater treatment due to their robust but simple and amenable mechanical properties.[35]

### 5.3.2.5 Membrane Bioreactors

Membrane bioreactor-based treatments involve a combination of microfiltration, ultrafiltration and membrane filtration, using biological degradation processes like activated sludge. There are two kinds of membrane bioreactors, *viz.*, a system consisting of a traditional stirred tank-reactor joined with a membrane separation unit; and membranes containing immobilized biocatalysts like enzymes, microorganisms and antibodies serving as supportive and separating units.[36] The total nitrogen and phosphorous contents are removed from industrial wastewaters using membrane filters by processes like nitrification and denitrification, with the aid of microorganism genera like *Nitrosomonas, Nitrosovibrio, Nitrobacter, Azoarcus, Dechloromonas, Pseudomonas, Acinetobacter, Aeromonas, Accumulibacter, Enterobacter, Moraxella, Klebsiella etc.* However, a few associated challenges include, identifying the precise bacteria (among complex communities) needed for nitrogen and phosphorus removal and their mechanisms, optimizing the requisite chemical/media composition and reactor configurations, and reclamating of treated wastewaters for potable reuse. Membrane bioreactor-based wastewater treatments yield comparatively better effluent quality over activated sludge processes, due to their higher mixed liquor suspended solid contents, longer sludge and hydraulic retention time, small footprint, good disinfection capacity, and the production of less sludge.[37] Integrated-membrane bioreactors like electro membrane bioreactors operate using the combined actions of biodegradation, electrochemical and membrane filtration, electro-coagulation, electrophoresis, electro-osmosis *etc.* for treatment of wastewaters. Using such integrated-hybrid technologies would help resolve various challenges like, treatment of high-strength industrial wastewaters, reduce the extent of membrane fouling, removal of recalcitrant contaminants, improve optimization effects, enhance cost-cutting strategies *etc.*[37–39]

## 5.4 Challenges in Watewater Treatments

Wastewater treatment methods are usually used for treating water so that it can be recycled carefully into natural ecosystems, however many challenges are faced during wastewater treatment, *viz.*, intensive power and energy consumption, staffing shortages at wastewater treatment plants, high expenditure for designing and managing treatment facilities for filtering and cleansing wastewaters in an ecofriendly way, and above all searching for disposal sites for the organic matter post-treatment, which is critical.[40] An integrated strategy of biological waste conversion by applying microalgae like *Neochloris oleoabundans* and *Chlorella vulgaris* in wastewater treatment plants has been reported. Various sludge waste feedstocks were optimized to achieve microalgal growth through photoautotrophy and heterotrophy, with simultaneous disposal of sewage sludge produced from wastewater treatment plants. Lipid production from microalgal fuel cells was also reported during cultivation. During such processes, typically sludge wastes from the wastewater treatment plants can be collected and optimized using suitable growth media for growing microalgae using either photoautotrophic growth or heterotrophic growth. The microalgal biomasses grown can be harvested, dried, lipids extracted from them, and such microalgal lipids can be used for the generation of energy. This concept can be termed the ‘generation of wealth from waste’. Figure 5.3 shows the application of microalgal cells in wastewater treatment plants for waste-energy conversion.[41] Urbanized wastewater treatment plants play a pivotal role in circular sustainability by integrating production of energy and resource recovery. Moreover, the developing wastewater industry can be driven by universal nutrient needs, accompanied by efficient water and energy retrieval from wastewaters. Wastewater treatment plants of public municipalities play a significant role in developing cities with sustainable futuristic views, branded by a circular flow of water, wastes, materials and energy. Wastewater treatment plants which were once regarded as conventional players in sludge and wastewater management, are now seen as factories that can be used in the recovery of energy and/or resources. Hence in the future, it is very likely they will be seen as significant role players in the technological development of SMART cities. SMART cities are urban areas which use various kinds of electronic methods and/or sensors to collect and monitor data, to manage assets, including resources like freshwater and services like wastewater/sewage treatment, efficiently.[42,43] Figure 5.4 shows a model of a wastewater treatment plant that is likely to be developed and operated in a SMART city.[42]

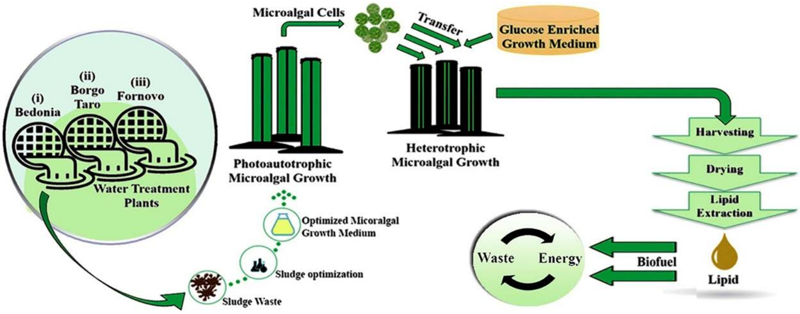

**Figure 5.3** Schematic depiction of integrated bioconversion of wastes using microalgal cells for treatment of wastewaters in wastewater treatment plants and production of bioenergy like lipids or biofuels. Reproduced from ref. 41 with permission from Elsevier, Copyright 2020.

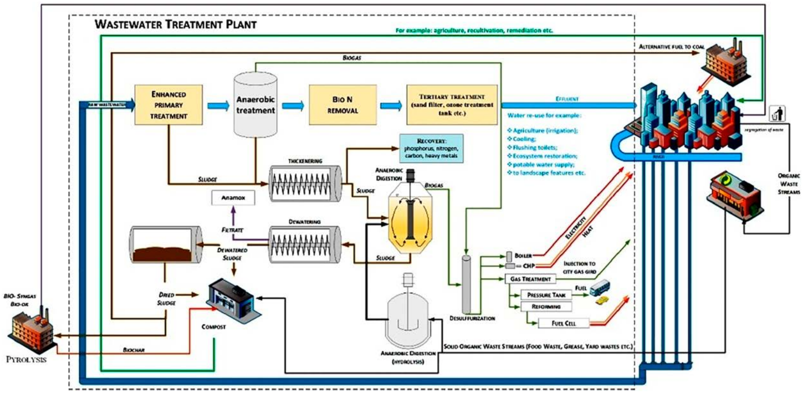

**Figure 5.4** Schematic depiction of futuristic designs of wastewater treatment plants in SMART cities with model features of operation including advanced versions of primary, secondary, tertiary treatments, anaerobic digestion, and reuse of processed wastewaters and reclaimed bioenergy for various applications. Reproduced from ref. 42, https://doi.org/10.3390/proceedings2110614, under the terms of the CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

Optimizing energy use plays a pivotal role in the running of wastewater treatment plants to enhance cost-cutting strategies, conserve energy, and combat global pollution caused by greenhouse gases. Such optimization can be achieved by synergizing energy-recovery and energy-saving technologies, in order to achieve self-sufficiency of wastewater treatment plants.[44] Most of the challenges faced during wastewater treatment can be handled by modelling the designs of wastewater treatment plants. A unique feature that must be considered during the typical design of any wastewater treatment plant is the sludge settling tank which can be 1D, 2D or 3D. 2D and/or 3D activated sludge models merged with computational fluid dynamics for wastewater treatment are particularly appropriate for conducting biochemical reactions within bioreactor plants. Advanced process control mechanisms which can use control algorithms, cascaded control systems, online-measurement-probes for various variables like ammonia/nitrate contents, chlorine, sludge contents, sludge blanket heights *etc.*, and several types of controllers can be used to combat the various challenges associated with wastewater treatment, in order to optimize the overall processes required for plant efficiency.[45,46] The other challenges that need to be researched and addressed during wastewater treatment and its reuse applications include institutional barriers, monetary allocations and public insight.[40]

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CHAPTER 6

# *Bioreactors: A Biological and Bioengineering Prodigy*

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## 6.1 Introduction

A bioreactor is a device that provides an optimal environment for the growth of microorganisms or for any biological reaction to occur. The main task is to attain this goal *via* design and optimization. This requires the integration of various fields of specialization and hence requires a multidisciplinary approach. When designing the physical entity of the bioreactor the inflow of gas, liquids and solids have to be taken into consideration in order to maintain optimal physiological conditions. Another parameter to be considered is that the physiological conditions of the bioreactor must favour the biological reaction, and the physical environment of the bioreactor must also be maintained under industrial conditions. As designing of the bioreactor is an integral part of the system, the design itself and the scale of the bioreactor have sometimes been regarded as a developmental stage, independent of the biological system that is inside it.

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

The bioreactor as an instrument has been known since ancient times and has been used for wine or beer making or for the preparation and production of food.[1] Over time, research in microbiology and advances in technology have enabled/paved the way for industrial biotechnological applications of microbes in the 20th century. In the early days of the 20th century industries for the production of glycerol, wine and beer making were established. The development of antibiotics represents another example of the integration of microbiological and industrial biotechnological advancement. These processes have evolved with time and have contributed significantly to the welfare of human civilization.[2] The production process was further extended to other products such as amino acids and organic acids[15] along with the incorporation of gene transfer, genetic engineering and recombinant DNA technology, all of which have contributed to significant technological and commercial advancement.[1,3] Thus, the present chapter deals with the various features and types of bioreactor, modelling, scale-up, scale-down and recent trends in the application of bioreactors. Further, the limitations and future prospect are also discussed enabling a better understanding of the bioreactor.

## 6.2 Understanding Bioreactors

The bioreactor is present both naturally and as a commercial product; examples of natural bioreactors include a pond, a termite gut and the stomach of a calf. The type of bioreactor however depends on various parameters such as stirrer, agitation *etc.* as discussed in the next section. With a commercial bioreactor the processes have to be optimized manually, with regard to the conditions for the organism (*i.e.*, sterility), inflow of gas and media component's, removal of gas and biomass, maintaining the physiological conditions, the production process, designing of the reactor and recovery of the product, each of which has to be designed and engineered with the utmost care to gain maximum product value with low input of cost and energy.[4]

## 6.3 Various Features and Types of Bioreactor

Among various features that play an important part in the bioreactor, growth of the desired culture and production of biomolecules is of the utmost importance. As cultures vary, the physiological conditions within the bioreactor too have to be modified for the cultures to grow optimally and requires immense technical designing of the bioreactor system, resulting in various types of reactors being designed and used industrially. Time is another crucial factor during the operation of a bioreactor, *i.e.* timing of the addition of the nutrients and removal of the mass from the bioreactor is very important for the its optimal functioning.

The various factors that are responsible for the proper functioning of a bioreactor are gas transfer in the submerged culture, mixing efficiency, supply of nutrients, liquid–solid transfer, heat transfer, sterility, selection of strain, scale-up procedure, rheology, homogeneity of culture, temperature, pH, inoculation of cells, kinetic relationships and composition of the media.[5,6] The integration and modification of these factors in the bioreactor along with the technical engineering has resulted in different types of bioreactor, *i.e.* stirred-tank, bubble, airlift, immobilized cells in a reactor, fluidized reactor with recycling of cells, solid-phase tray, rotary drum, agitated-tank, continuous screw, hollow-fibre, and wave bioreactor (Figure 6.1).

The design of the bioreactor has been integrated with technology (computers) for complex calculations, resulting in fast and efficient systems being developed. In the initial stage the cost of the systems was very high, which reduced the economic feasibility of the process. The integration of

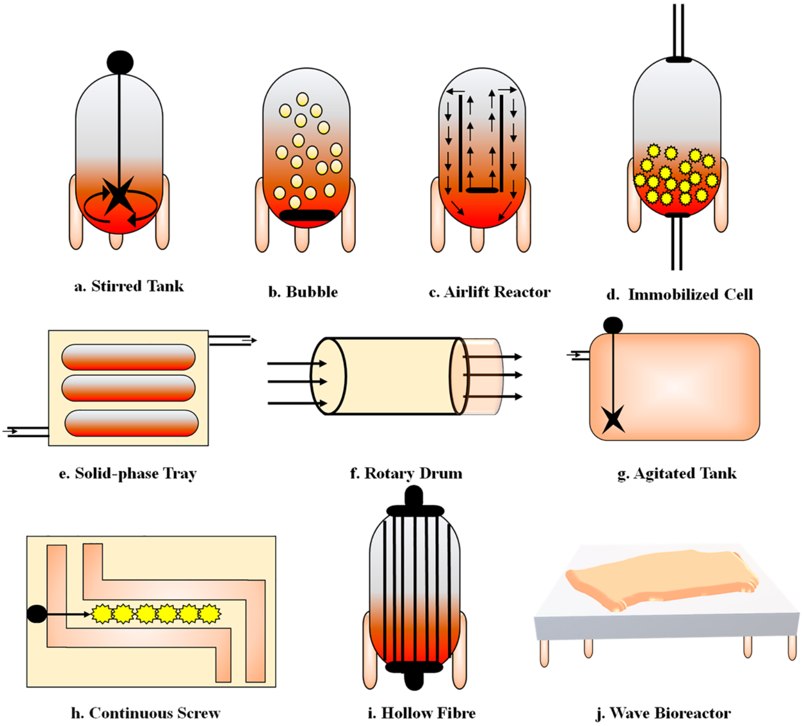

**Figure 6.1** Schematic representation of the various types of reactor: (a) stirred tank, (b) bubble, (c) airlift reactor, (d) immobilized cell, (e) solid-phase tray, (f) rotary drum, (g) agitated tank, (h) continuous screw, (i) hollow fibre, and (j) wave bioreactor.

technology and engineering has resulted in the design and development of different types of bioreactors that are cost effective and efficient, with lower mass production and pollution generation but with enhanced output (Figure 6.1). After the wave bioreactor was developed, a similar approach was used for the development of microbioreactors and microbio-chips with the use of low-cost polymeric materials.

Later MIT in Boston developed a concept of conceive–design–implement–operate (CDIO) based on a renewal of the conventional approaches to education, *i.e.* training and education, with concept-based approaches that allow detailed study of the major elements involved in the design and operation of a bioreactor[7,8] (Figure 6.2). In addition, statistical tools previously used for multivariate data analysis and factorial analysis were used for optimization of the design process, *e.g.* design of experiment (DoE). The other principles that have been applied are quality-by-design (QbD) and process analytical technology (PAT),[9,10] which suggest that quality should be linked to design and be considered in the design process. It should be noted that in the case of the biotechnology industry, the main parameter that has to be considered for the production of the desired product using a bioreactor is that the organism used to produce the end/desired product has to be transferred to the engineering domain. This key engineering factor should be addressed in the early development phases when upgrading the system from laboratory to industrial scale. Thus, to address these problems bioreactor systems needs to be designed with the involvement of new technologies, with consideration of optimization of the process parameters for the optimal production of the

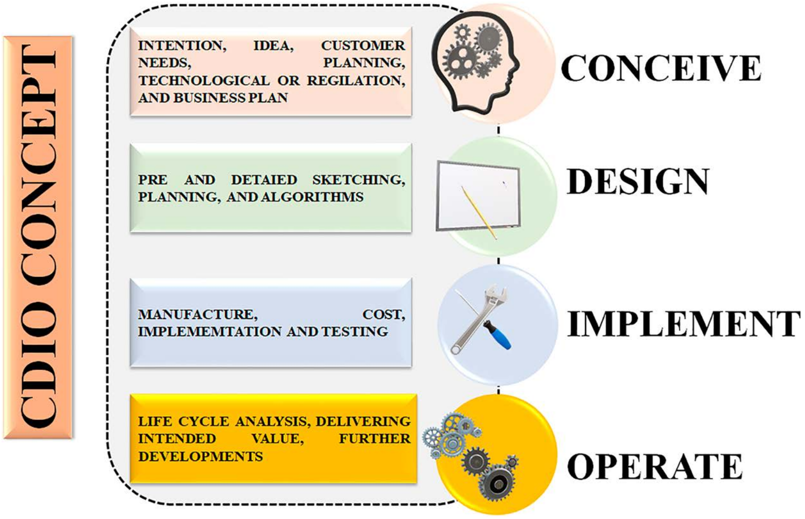

**Figure 6.2** Schematic representation of the conceive–design–implement–operate concept.

desired product and functioning of the system.[11–13] In addition, recovery of the product should also be integrated into the system in order to obtain the full benefit of the process.

## 6.4 Modelling of a Bioreactor

The modelling of a bioreactor requires the consideration of various parameters and depends on the major objective for which the bioreactor is to be used. The first step would be optimization of the process to achieve the desired goal and incorporation of an indicator to determine whether the change incorporated has resulted in a positive or negative impact on the system. The bioprocess is designed so that the desired amount of the product available after a predefined period can be attained with minimum cost being involved in the process. The following sections discuss a number of proposed models.

### 6.4.1 Basic Modelling

Modelling of a bioreactor depends on the conservation law which states that the measurable property of the physical system does not change with time as the system evolves.[14] The basic reaction equation in the case of a bioreactor involves the conversion process that is under consideration. The first parameter considered is the identification of the component ($A_i$) which changes in concentration during the process, the yield ($Y_{ij}$) of the various species ($i$) with the standard/reference species ($j$), rate of biochemical system ($\boldsymbol{c}$) of the concentration of all such species ($A_i$).[16] Additional information can be determined from the biochemical conversion rate ($\boldsymbol{R}$) and, as per the heuristic approaches, the essential parameters must be determined experimentally and the basic dynamic balance equation can be represented as follows where the summation of eqn (6.1) represents that more than one feed may be present in the system.

$$\left(\frac{\mathrm{d}c}{\mathrm{d}t}\right)=\boldsymbol{R}+\sum \mathrm{i}\left(\frac{Fi}{W}\right)\left(\boldsymbol{c}_{Fi}-\boldsymbol{c}\right) \tag{6.1}$$

where $Fi\ [t:h]$ represents the feed rates at which material, of concentration $\boldsymbol{c}_{Fi}$, is fed to the bioreactor and $W$ is the mass of the culture. In case of a fed-batch culture $W$ may vary with time due to feed added to the reactor and also due to loss from the system.

$$\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right)=\sum \mathrm{i}\,Fi \tag{6.2}$$

It has to be noted that $\boldsymbol{R}$ results in non-linear coupling between various equations and is due to the limitations associated with biochemical reactions that are associated with a change in the concentrations of the species involved. The other factor is the non-linear kinetic rate expression for the important components of the system. The actual reaction rate in the system that makes ***R*** cannot be modelled in a closed form as per the first principle and the rate expressions are correlations based on assumptions which are thought to be prevailing in the biochemical reaction system *e.g.* kinetic expression of the Monod equation

$$Rx = \mu X = \mu_{\text{max}} \frac{S}{K_{\text{m}} + S} X \tag{6.3}$$

In eqn (6.3) the values of $\mu_{\text{max}}$ and $K_{\text{m}}$ cannot be pre-determined but can be inferred after experimental analysis, also known as model parameter identification. The various factors in the Monod equation effect the systems of the bioreactor such as growth of the microorganism and formation of the product. Thus, more extensive study is required for better and enhanced representation of the kinetic behaviour.

### 6.4.2 Validation

The system/model that has been adopted must be validated first before its use and consist of using fresh process data. If the data does not include any new assumptions then the model response and test data are compared based on Gaussian error criteria. The variance ($V$) or root mean square deviation value represents a better model if the values are smaller. It has been stated that the excellence of the model relies on its intricacy, thus the variance can be a function of number of free parameters ($m$) as a result the systems theory which states that $V(m)$ can be represented as:[17]

$$V(\text{m}) = V_{\text{N}} + V_{\text{F}} + V_{\text{B}} \tag{6.4}$$

Where, $V_{\text{N}}$ is variance of noise superimposed on the model output, $V_{\text{F}}$ represents the uncertainty in the output due to the determination of the model parameters on the basis of a necessarily limited amount of test data and $V_{\text{B}}$ represents the bias *i.e.* uncertainty in the model structure that was unrecognized/neglected in the process mechanism. The parameters $V_{\text{N}}$ and $V_{\text{F}}$ rely on the data ($N$) used for validation and at its very high value $V_{\text{B}}$ will be dominating if no error is present in the data. Further, the term $V_{\text{F}}$ can be estimated as in eqn (6.5):

$$V_{\text{F}} \approx V \frac{m}{N} \tag{6.5}$$

From the representations, it can be stated that the components of the process that are not possible to model *via* a mechanistic understanding should be assessed *via* expressions that have been chosen carefully using bias functions. Thus, with better representation a smaller number of data would be required for the validation and would be beneficial form a work and economic viewpoint in developing practical models.

### 6.4.3 Hybrid Models

In case of the above-mentioned models the Monod equation was best, although the bias limits the quality of the model and for better models alternatives have to be designed, *e.g.* black-box kinetic models.

#### *6.4.3.1 Black-box Kinetic Models*

In the case of black-box models the best model selected should have more flexibility and complexity. The non-linear functions can be represented using artificial neural networks (ANNs), where the nodes are characterized by response functions as per the averaged input. Here any variable can be added or taken into account if it has a significant impact on the system, however the addition of irrelevant parameters should be avoided as this reduces the quality of the model. In the case of black-box models these factors have to be fitted to the experimental data as well, a method referred to as the training procedure. It should be noted that in the case of a linear system the representation is simple and simple statistical techniques can be used to determine the interrelationships among various quantities. However, in the case of a biological/non-linear system the representation is more complex. In 1997, Hiden *et al.*[18] proposed that principal component analysis (PCA), which is usually applied for linear systems, could be used for non-linear systems as well. Later a technique, *i.e.* the influence analysis technique, was proposed that can easily be used with PCs.[19] The ANN is more effective when used with factors that cannot be modelled on a mechanistic basis, the process parameters that as been derived from mathematical models (physically derived) the model must be used, though the addition of free parameters would reduce the model quality. The solution would be to divide the process into two parts, *i.e.* modelled parts and the not well understood parts. The models where various parameters are represented using various models are known as hybrid models, *e.g.* combination of a mechanistic model with adata driven model, and these models are easy to operate as well. The black-box model and ANN has the disadvantage that it can only be used in areas of state space, *i.e.* areas from which the extended data were used for the training and validation. On the other hand, in case of designing and optimization studies the areas in the state space have to be explored that have insufficient/no data. In addition, kinetics that are more suited for extrapolation can be used.[20]

#### *6.4.3.2 Knowledge-based Techniques*

Knowledge-based techniques allow qualitative heuristic knowledge to be exploited. The biochemical production process is a very complex process taking into consideration a biochemical conversion process that cannot be applied to the present process model under study. As all factors cannot be considered in a system the very first step would be to characterizing a process, *e.g.* time. It is stated that models based on heuristic knowledge and data are termed grey and black box, respectively, and the mathematical models are purely based on a mechanistic approach. Both the black and the grey box have to be used in such a way that the process/representation selected consist of the minimum number of free parameters for the system to be characterized in the most accurate way. If, moving a step ahead, the fuzzy rule is applied for defining the basis of a function in a problem specific way, the behaviours of the system can be deduced more precisely.[20,21]

### 6.4.4 Balance Regions

When considering the modelling of a bioreactor in terms of chemical engineering, the balance volume of a the stirred-tank bioreactor is considered to be uniform. Failure to justify this assumption results in division of the reaction mass into small compartments that at the individual level have to be uniform, followed by integration of the compartments for it to be considered as an entire reactor. Integration is a complex process and detailed information about the system and exchange of materials and energy is required, the execution of which is a very complex. Thus, for the ideal stirred bioreactor the volume balance is considered uniform throughout the entire culture, though this has not been true for most of the large-scale reactors, as has been observed by Steel and Maxon,[22] Manfredini *et al.*,[23] Oosterhuis and Kossen[24] and Larsson *et al.*[25] It should also be noted that inhomogeneity in modelling results in an undermodelling error. The errors obtained from neglected mechanisms are compensated by other parameters and are distributed unpredictably across these values, resulting in a bias in the parameters. Thus, at large scale these parameters become unreliable. Thus, the properties related to transport should be considered in more detail.[20]

### 6.4.5 Bioreactor Fluid Dynamics

The three prime matters of concern in the case of fluid dynamics are transport properties, mass transfer and heat removal. In the case of transport properties, the important factor is the mixing to ensure a uniform/homogenous environment in order to provide the desired conditions for the optimal production of the desired product. In the case of mass transfer, the transfer of oxygen from gaseous to liquid phase occurs and is dependent on the agitation system of the bioreactor. In case of aerobic microorganisms oxygen plays an integral part in the development of the biomass, which ultimately impacts the production of the desired end-product. After this requirement has been met, lastly the heat removal has to be considered,[26] and both mass transfer and heat removal are fluid dynamics dominated processes. Heat production is directly proportional to oxygen consumption and thus more oxygen consumption and higher transfer rates lead to an increased requirement to remove the heat. As broad temperature gradients are undesirable in bioreactors, as organisms grow under a narrow temperature range, thus temperature is a key factor in the operation of a bioreactor. Other parameters to be considered are fluid dynamic reactor models and practical approach. In the case of fluid dynamic reactor models the mass and momentum balance are considered and are described by the Navier–Stokes equation system. This system suffers limitations if meaningful date is not available and if the data does not provide accuracy or is not relevant, although the development of computational technologies has helped improve calculations based on the Navier–Stokes equation system.[27] Lastly, with regard to practical approach, two major aspects that are considered are mixing and mass transfer.[20]

### 6.4.6 Bioreactor Operation

Bioreactors in industry are kept under surveillance and the operator may modify the recipe in the system if deviations are observed. These systems usually do not require a model but if deviations in inoculum size or composition of substrate are observed the system becomes sensitive to the change. The statistical software that helps enhance the reproducibility of the data is known as statistical process monitoring (SPM)/statistical process control (SPC). The SPM uses a data set based on statistical correlation and the operator is advised about the intended course of action manually if it deviates from the normal course of action. In addition, methods to improve the productivity may also be advised.[28] The other batch reactor operator consists of open loop control where optimization is from one run to the next, and in the case of a hybrid model the reaction rate is determined and the data obtained is used in the optimization of the next batch, resulting in batch-to-batch optimization. Thus, after running a few batches runs an optimized system would be developed.[20]

## 6.5 Scale-down and -up of a Bioreactor

The industrialization of the bioreactor is an integral step in a bioprocessing system, and knowledge of both scale-down and -up is integral along with the sensitivity of the process parameters. Numerous parameters have to be considered for the industrialization of the bioreactor, such as type of reactor, fluid dynamics, and the response of the biological system to physical and chemical changes in the process parameters. One of the major limitations of the scale-up process in the case of fed-batch is the formation of various concentration gradients in the bioreactor at the point of feed addition, inlet of gas or any other controlling agent, and this gradient depends on the input of global and local power in the gas–liquid phase of the system/bioreactor. Scale-up of the system is very important from an industrial perspective and also its robustness, to ensure its effectiveness and adaptability if transferred from one facility to another. Scale-up can be applied to factors such as type, size and miscellaneous construction parameters but cannot be applied to input of power, the tip of the stirrer, concentration of dissolved $O_2$ and transfer of $O_2$. The parameters specific to the scale-up process in a bioreactor vary and should be individually considered with respect to fluid phase and response of cells/microorganisms under heterogenous cultivation conditions.[29] In the case of a scale-down approach the most common acceptable approach was fed-batch that was used for the production of baker's yeast. Scale-down of a bioreactor can be divided into three parts: phase 1, initial studies of mixing behaviour and spatial distribution phenomena; phase 2, evolution of scale-down systems based on computational fluid dynamics; and phase 3, recent approaches considering hybrid models. On the other hand, in the case of scale-up the parameters considered are dissolved oxygen concentration, contemplation of similarities and dimensionless numbers, shear rate and cell physiology.[29]

### 6.5.1 Scale-down Phases 1, 2 and 3

In the case of scale-down phase 1 the mixing and spatial distribution is studied and the various engineering parameters such as input of power and transfer of $O_2$ using a two and five compartment model have been reported by Oosterhuis and Kossen[30,31] Using theoretical and experimental data of large-scale cultivation it was observed that the circulation in between the compartments was strongly influenced by the aeration rate at various regions of the bioreactor.[32–35] In the case of phase 2 it has been stated that the microbes in the reactor respond to cyclic perturbations and kinetic studies based on single pulses also contribute to the development of scale-down systems. The computational fluid dynamics approach has been used for the development of the scale-down systems.[25] Lastly, in the case of phase 3 metabolic models and response behaviour in combination with fluid dynamics were used to determine the gradients formed in all parts of the bioreactor.[36–38] An area of major concern is the development of perturbations in microwell plates under nutrient limiting conditions in a fed-batch system, although microvalves coupled with microwells[39] or a biocatalyst-based feed system have been developed which has made the development of the system easier and feasible.[40–42] Further, insight into the time kinetics of the cellular response along with the development stage in the case of single-cell analysis will be obtained from fluorescence-based gene reporter systems in the future. An understanding of network analysis and determination of flux will help enhance the cellular response further, and tailored scale-down reactors are also required to provide a better understanding of the system, along with the integration of new tools to characterize large-scale bioreactors.[29,43,44]

### 6.5.2 Scale-up

The major problem faced in scaling up a bioreactor is maintaining homogeneity with respect to the key parameters both mechanically and economically. Scale-up of bioreactors has been studied in detail with respect to stirred-tank bioreactors and single-use-orbital shakers.[45,46] Further, various parameters that effect scale-up of a bioreactor are type of microorganism, characteristic features of the substrate and end product, the mode of the process, dissolved $O_2$ concentration, similarities and dimensionless numbers, shear rate and cell physiology.[29]

### *6.5.2.1 Various Parameters Considered during Scale-up*

The most important parameter in a bioreactor consisting of aerobic microorganisms is the concentration of dissolved $O_2$, which has been described earlier in the chapter.[47] The distribution of $O_2$ from gaseous to liquid phase increases in the presence of a stirrer due to dispersion and has been intensively studied over the past few years.[47,48] For dimensionless numbers, the similarities between different scales are estimated. In such cases the volumetric ratio of the key parameters is kept constant while using dimensionless numbers in the case of scale-up.[49] The shear rate of the bioreactor is increased at the tip of the stirrer in order to limit the reduction of the volumetric power input, resulting in a different gradient being created at the top and at the tip of the stirrer.[50] As a dimensionless study does not suffice for both scale-up and ultimately scale-down processes, cellular physiology is very important in industrial production using a chemical process.[51,52] Lastly, it has been stated that the integration of cellular metabolism and physiological state to a dimensionless study is a better approach for general analysis of the process. In addition, better analysis of the physiological state of the microorganisms and the application of online sensors in a bioreactor will allow the attainment of higher-resolution physiological and morphological images of the cultures or even single cells.[29]

## 6.6 Recent Trends in the Application of Various Types of Bioreactor

The various type of bioreactor studied in the literature has been reported for multitudinal applications and has contributed significantly to the betterment of life. Bioreactors have been used effectively in bioremediation, production of alcohol-based products, production of proteins, desalination of saltwater, nitrification, composting and biohydrogen production (Table 6.1).

## 6.7 Limitations and Future Prospects

The major limitation faced by bioreactors is the need for an understanding of systems biology, and is thus a major area that can be exploited. Detailed information about behavioural changes when shifting from laboratory to large scale is very crucial for the development of an efficient system. Thus, the integration of "omics" and data interpretation can be employed for a

**Table 6.1** The various types of bioreactor reported in the literature.

| No | Type of bioreactor | Application | Reference |
|---|---|---|---|
| 1. | Stirred-tank bioreactor | Production of aryl alcohol oxidase | 53 |
| 2. | Stirred-tank bioreactor | Manufacture of human CAR-T cells | 54 |
| 3. | Stirred-tank bioreactor | Bioethanol generation | 55 |
| 4. | Bubble-free membrane bioreactor | Production of protein | 56 |
| 5. | Bubble column bioreactor | Bio-oil conversion | 57 |
| 6. | Bubble column bioreactor | Ethanol production | 58 |
| 7. | Jet loop-airlift bioreactor | Simultaneous removal of carbon and nitrogen from soft drink | 59 |
| 8. | Hybrid airlift bioreactor | Nitrogen removal | 60 |
| 9. | Airlift bioreactor | Gas-phase trichloroethylene removal | 61 |
| 10. | Upflow immobilized cell bioreactor | Biotreatment and bacterial succession with fludioxonil wastewater | 62 |
| 11. | Immobilized-cell stirred-tank bioreactor | Ethanol fermentation | 63 |
| 12. | Fluidized bed bioreactor filled with immobilized cells of *Bacillus subtilis* | Partial desalination of seawater | 64 |
| 13. | Non-sterile stirred fluidized bioreactor. | Degradation of pharmaceuticals | 65 |
| 14. | Inverse fluidized bed bioreactor | Treatment of synthetic municipal wastewater | 66 |
| 15. | Fluidized bed bioreactor | Partial nitrification | 67 |
| 16. | Rotary drum bioreactor | Bioremediation of mercury-polluted agricultural soil | 68 |
| 17. | Rotary drum bioreactor | Maturity and stability assessment of composted tomato residues and chicken manure | 69 |
| 18. | Rotating bioreactor | Composting palm tree residues | 70 |
| 19. | Hollow fibre bioreactor | Simultaneous pharmacokinetic and pharmacodynamic evaluation of test compounds | 71 |
| 20. | Hollow fibre membrane bioreactor | Biohydrogen production | 72 |

**Table 6.2** Major limitations and solutions for bioreactors.

| No | Limitation | Solutions |
|---|---|---|
| 1. | Studies lacking | • For a better understanding of the system a detailed study of systems biology has to be performed.<br>• A detailed behavioural study has to be performed for scale-up |
| 2. | Model adaptations | Hybrid models provide better results over single models |
| 3. | New technologies | The use of “omics” can allow better understanding of the system |
| 4. | Integrated approach | The integration of system biology and engineering can be fruitful |
| 5. | Design and implementation | The designing of the bioreactor should be cost effective and productive when implemented at commercial scale |

better understanding of the system. The integration of bioanalytical systems biology and engineering tools are lacking and thus future research based on these aspects has to be conducted to ensure efficient working of the system. The bioprocess industry, bioremediation sector and biotechnological sectors have their own limitations with respect to the intrinsic features and properties of both biological systems and bioreactors. Thus, as stated above, an integrated approach and hybrid models would enable a better understanding of the system, its design and implementation[15,73,74] (Table 6.2).

## 6.8 Conclusion

Bioreactors have been studied and much development has been attained with the advancement of time, although they remain an area with tremendous research potential. Scale-up has been a major step forward and its limitations can be addressed with an integrated approach where systems biology, omics and engineering tools can function together for the design of efficient bioreactors. Research must be carried out in the areas that are lacking, so that the limitations can be identified and rectified. Development of a model that is both cost-effective and practically feasible is necessary. Thus, the bioreactor is a system that meets the current need to ‘go green’ and can be used for improving living standards along with providing sustainable, green technology.

## Conflict of Interest

All authors declare no conflict of interest.

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## CHAPTER 7

# Challenges in Industrial Wastewater Treatment Using Biological Reactors

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## 7.1 Introduction

Numerous industrial products, such as pesticides, chemicals, pharmaceuticals, fertilizers, textiles, processed foods, and other essential goods, are used by society to improve living standards. Industrialization in various sectors offers goods and facilities to society that generate waste during and after use, in the form of wastewater, solid residues, and gaseous emissions. Unfortunately, these wastes are being released into the environment causing a deterioration of natural resources and environmental pollution.[1] A significant portion of the water used in industries turns up as wastewater that contains a significant amount of pollutants, which differ

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

depending on the type of industry. The release of industrial wastewater and toxic pollutants into the environment may create various hazards.[2] The adverse effects of various industrial effluents on human health and the environment are presented in Table 7.1. Thus, all efforts must be made to reduce water usage, and wastewater must be treated up to the standards that ensure it can be reused or safely discharged into the environment. Industrial wastewater contains several pollutants such as inorganic dissolved salts, suspended solids, organic matter, petroleum hydrocarbons, surfactants, heavy metals, and detergents, which may vary from industry to industry. The occurrence of pollutants in discharged effluent may adversely affect receiving water bodies and humans, animals, plants, and aquatic life.[3]

**Table 7.1** Effects of industrial wastewater constituents on human health and the environment.[3] Reproduced from ref. 3 with permission from Springer Nature, Copyright 2019.

| Pollutants | Adverse effects |
|---|---|
| **Alkalinity** | It may cause animals and humans health issues and affect aquatic life. Loss of soil productivity if the water is reused for irrigation purposes. |
| **Heavy metals** | Cause allergic reactions, respiratory tract irritation, skin rashes, neurotoxicity, gastrointestinal disorders, Minamata disease, and fluorosis. Adverse effects on aquatic flora and fauna. |
| **Inorganic dissolved salts** | Interfere with water reuse in industries and irrigation purposes and water supplies. Phosphorus and nitrogen cause eutrophication. The excess algal growth depletes oxygen and gives bad odour and taste. |
| **Pathogens** | Pathogenic microorganisms cause several waterborne diseases such as typhoid, polio, cholera, dysentery, hepatitis, *etc.* |
| **Agrochemicals** | They are highly poisonous, cause Parkinson's disease, and affect seed germination. They can also affect the nervous and respiratory systems and the liver of animals. |
| **Petroleum products** | They are harmful to aquatic life, soils, animals, plants, and human life. Oil spill on the water surface reduces the light transmission and obstructs the photosynthesis of aquatic plants. |
| **Phenols** | Phenols are toxic and impart unpleasant odour. Nitrophenyl is carcinogenic to humans. It also affects the reproduction of aquatic organisms. |
| **Surfactants** | Inhibit the self-purification process of water. Also harmful to aquatic organisms. |

Industries take advantage of various production plans and strategies to reduce water usage and wastewater volume. Physicochemical methods of wastewater treatment can only partially remove the organic content of the wastewater. Therefore, most industrial effluents go through a biological treatment unit for organic matter removal, with or without a pre-treatment step. Industrial wastewaters are much stronger than domestic sewage in terms of organic content, depending on the industry type. Industrial wastewater chemical oxygen demand (COD) exhibits a vast variation from 500 to as high as 100 000 mg $L^{-1}$.[4] As biological processes can remove organic and inorganic contaminants this has led to the integration of biological processes into many industrial wastewater treatment systems.[1] The biotreatment of industrial wastewater mainly depends on the wastewater characteristics.

Microorganisms in biological units consume the organic contents in industrial wastewater to fulfill their energy requirement for growth and maintenance. The pollutant removal mechanisms from wastewater through a biological process are absorption, adsorption, and biodegradation. Microorganisms produce enzymes such as oxidoreductases, peroxidases, laccases, cellulolytic enzymes, amylases, and proteases that play an essential role in treating industrial wastewater.[3]

## 7.2 Industrial Wastewater Composition and Treatability

Industrial wastewater varies in its composition, depending on the nature of the industry, and contains a particular combination of pollutants. It can be characterized in terms of their physical (suspended solids, temperature, colour, and odour), chemical (organic and inorganic), and biological (pathogens) characteristics.[3] The characteristics of pollutants in various industrial wastewaters are presented in Table 7.2. Wastewater characterization is the first criterion for selecting and designing a suitable biological treatment process.[2] The following factors are necessary for the wastewater to be treated biologically.[5]

- Biodegradability: the ability of the wastewater to be treated by microorganisms. Wastewater containing organic matter is mostly treated through biological processes.
- Treatability: suitability of the wastewater to be treated with biological processes.
- Nutrient availability: the biological system requires balanced nutrients that can be utilized by the microorganism for its reproduction and growth.
- Toxicity: toxic constituents (such as heavy metals, pesticides, and nano-particles) are toxic to microorganisms and the inhibition of microbial activity can inhibit biological treatment.

Table 7.2 Characteristics and major pollutants of various industrial wastewaters.[2,3] Reproduced from ref. 3 with permission from Springer Nature, Copyright 2019 and from ref. 2 with permission from Elsevier, Copyright 2014.

| Industry | Wastewater characteristics | Pollutants |
|---|---|---|
| **Pulp and paper mill** | High concentration of suspended solids, BOD, COD, inorganic dyes, chlorinated organic compounds, sodium hydroxide, sodium carbonate, sodium sulfide, and bisulfites and wooden compounds such as lignin, cellulose, hemicelluloses | High concentration of chemicals such as sodium hydroxide, sodium carbonate, sodium sulfide, bisulfide, elemental chlorine, chlorine dioxide, calcium oxide, HCl, organic halides, toxic pollutants, lime mud, wood processing residuals, traces of heavy metals, pathogens |
| **Tannery industry** | High concentrations of chlorides, tannins, chromium, sulfate, sulfides, synthetic chemicals such as pesticides, dyes, and finishing agents, heavy metals, toxic chemicals, lime with high dissolved and suspended salts, BOD, COD, and other pollutants | Organics, heavy metals such as Cr, ammoniacal nitrogen, acids, salts, sulfides, suspended solids, dyes, fats, oil |
| **Distillery** | Colour, odour, high concentrations of total solids (TS), TDS, TSS, BOD, COD, ammonical nitrogen, phosphorus, potassium, calcium, magnesium, alkalinity, chloride, melanoidin, and large variations in pH | Glucose, polysaccharides, ethanol, glycerol, amino acids, proteins, caramels, high concentration of salts, organic matter, sulfates |
| **Sugar mill** | Brown colour, burnt sugar-like odour, high ash or solid residue, oil and grease, a high percentage of dissolved organic and inorganic matter of which 50% are present as reducing sugars with high BOD, COD, TS, TDS, and TSS | Floor washing waste, sugar cane juice, molasses |
| **Textile industry** | High colour content with COD and BOD, a wide variety of dyes, natural impurities extracted from fibres, and other products such as acids, alkalis, salts, sulfide, formaldehyde, phenolic compounds, surfactants, and heavy metals | Complex mixture of salts, acids, heavy metals, organochlorine-based pesticides, pigments, dyes, PAHs |
| **Pharmaceutical industry** | Pharmaceutically active compounds, high BOD, COD, TSS, TDS, TS, and high concentrations of acids, phenol, chlorides, nitrogen, sulfate, oil, and grease | Polycyclic aromatic hydrocarbons (PAHs), arsenic trioxide, chlorambucil, epinephrine, cyclophosphamide, nicotine, daunomycin, nitroglycerin, melphalan, physostigmine, mitomycin C, physostigmine salicylate, streptozotocin, warfarin over 0.3%, uracil mustard, halogenated/nonhalogenated solvents, organic chemicals, sludge and tars, heavy metals, test animal remains |
| **Oil refinery/petroleum industry** | Oil, grease, polyaromatic hydrocarbons (PAH), benzene, toluene, ethylbenzene, xylene, phenols, ammonia, hydrogen sulfide, and suspended solids with high BOD and COD | Oil, acid, soda sludge, hydrogen sulfide, lead sludge, hydrocarbons, spent filter clay, ethylene glycol, 1,4-dioxane |

## 7.3 Biological Processes for Industrial Wastewater Treatment

Physical, chemical, and biological processes or a combination of these processes have been widely used to eliminate organic matter from wastewater. The biological approach has attracted much attention due to its economic and ecological superiority. It (anaerobic or aerobic) is suitable for the treatment of wastewater containing organic matter. In biological treatment, the organic matter serves as nutrition for bacteria, rotifers, fungi, ciliates, or other microorganisms.[6,7] The cellular enzymes disassemble complex organic molecules into new cells.[4,8] Several combinations of biological systems (aerobic and anaerobic) used in wastewater treatment are shown in Figure 7.1. The oxidation or reduction of organic matter is carried out in reactors through a process categorized as aerobic/anaerobic and suspended/attached growth.[1]

### 7.3.1 Aerobic Biodegradation

Aerobic bacteria require oxygen to convert food into energy. Bacteria and fungi produce enzymes that help in the oxidization of organic pollutants and release energy, carbon, and nutrients, which can be used for the growth of microorganisms. A considerable number of microorganisms produce different types of enzymes that help to degrade organic pollutants.[9] Figure 7.2 shows the process of aerobic treatment for wastewater containing organic matter. In the aeration tank, microorganisms convert organic materials present in wastewater into new microbial cells, $H_2O$, and $CO_2$. Organic nitrogen is converted into nitrate or ammonium ion, and organic phosphorus is transformed into orthophosphate.[8,10] The aerobic process can be further subdivided into two processes: suspended growth and attached growth.

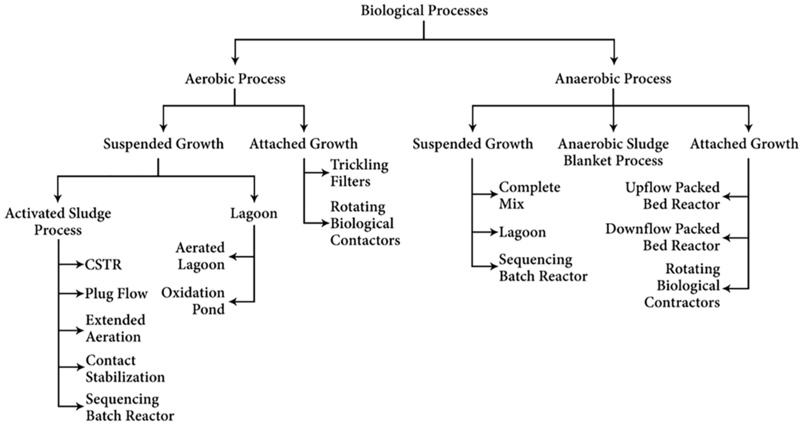

**Figure 7.1** Aerobic and anaerobic processes used to treat organic wastewater. Reproduced from ref. 26 with permission from McGraw Hill LLC, Copyright 2003.

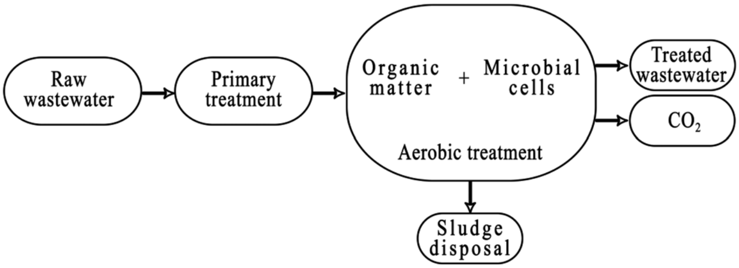

**Figure 7.2** Schematic representation of organic removal by an aerobic process.

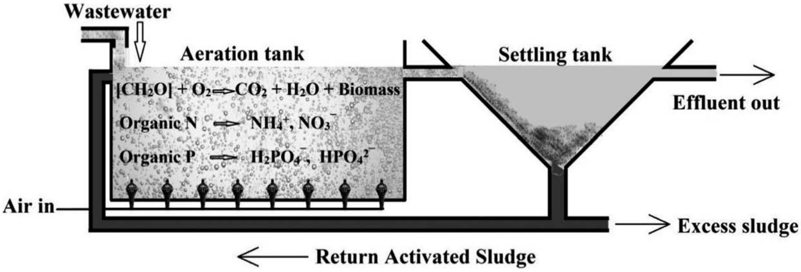

**Figure 7.3** Schematic diagram of an activated sludge process. Reproduced from ref. 10 with permission from Taylor and Francis Group, Copyright 2001.

### *7.3.1.1 Aerobic Suspended Growth System*

Suspended growth systems have a diverse group of microbes suspended as flocs in the liquid mixture that includes the wastewater being treated.[11] A mechanical mixer or sparger aids in providing contact between microorganisms and wastewater. The flocs are an aggregate of microorganisms and are accountable for organic pollutant removal. In this system, the wastewater and microbial flocs are continuously mixed to provide uniform concentrations of all constituents throughout the reactor. The different suspended growth biological reactors used for wastewater treatment are described below.

**7.3.1.1.1 Activated Sludge Process.** The activated sludge process (ASP) is a suspended growth process used for both municipal and industrial wastewater treatment.[2] Biologically active sludge and wastewater are mixed in an aeration tank and kept in suspension and contact until the desired treatment efficiency is achieved. Bacterial cells are an integral part of wastewater treatment. They are generally mixed with wastewater in the aeration tank and form flocs. The flocs settle down in a settling tank, and a portion of solids is recycled to the aeration tank to keep the biomass level near to a fixed value[6] while the remaining fraction is discarded as excess sludge, as shown in Figure 7.3. Some modifications in the activated sludge process are explained below.

**7.3.1.1.2 Continuous Stirred-tank Reactor (CSTR).** The particles that enter the tank are immediately dispersed throughout the reactor body. In this system, settled wastewater and recycled sludge are introduced from the influent points in the aeration tank, as shown in Figure 7.4a. The input and output flows are continuous. Complete-mix reactors are also known as CSTR or continuous-flow stirred tank reactors (CFSTR).[5] The reactor's working volume is constant, and organic concentration, solids concentration, and the oxygen demand are kept uniform throughout the tank by continuous mixing.[8,12]

**7.3.1.1.3 Contact Stabilization.** The return sludge is mixed with raw wastewater in a small contact tank. Rapid organic matter degradation occurs due to the adopted microorganisms in the tank.[7] The wastewater and sludge then move on to the stabilization tank, where microbes metabolize the pollutants.[11,13] Compared with conventional ASP, the aeration tank is comparatively small. The bulk liquid is separated in the clarifier and proceeds to the stabilization tank,[7] as shown in Figure 7.4b.

**7.3.1.1.4 Extended Aeration.** Using long aeration times (24–48 h), a biological reactor can operate in the endogenous respiration zone to produce less sludge than a normal plant.[14] It is generally used without primary settling.[15] All of the substrate is oxidized and converted into energy; thus, very little excess biomass

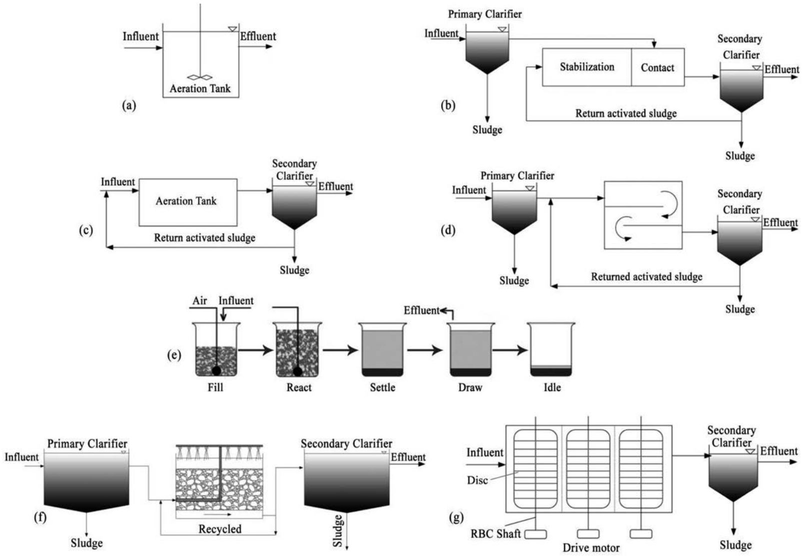

**Figure 7.4** Various aerobic suspended and attached growth biological reactors.[19,65] (a) Continuous stirred-tank reactor (CSTR), (b) contact stabilization, (c) extended aeration, (d) plug flow, (e) sequencing batch reactor, (f) trickling filter, and (g) rotatory biological contactor. Reproduced from ref. 65 with permission from Elsevier, Copyright 2021 and from ref. 19 with permission from Taylor and Francis Group, Copyright 2013.

is produced. The accumulation of non-biodegradable material is discarded on a regular basis from a secondary clarifier.[16] The extended aeration process requires high aeration energy and a relatively large aeration tank and is hence most adaptable to a small plant.[17] A schematic diagram is shown in Figure 7.4c.

**7.3.1.1.5 Plug Flow.** In plug flow systems, the tank shape is generally narrow and long with a width to length ratio of at least 1 : 12.[1,15] Both return activated sludge and the feed are added at the beginning of the tank,[18] as shown in Figure 7.4d. The liquor flows through its length, and a little longitudinal mixing occurs in a plug flow tank.[19] The lack of longitudinal mixing reduces the ability to handle shock loads.[15] All fluid elements have the same residence time in the reactor.

**7.3.1.1.6 Sequencing Batch Reactor (SBR).** Most of the biological treatment processing of wastewater is achieved by using two tanks, one for mixing/aeration and one for solids–liquid separation. SBR allows both operations to be performed in a single tank,[20] as shown in Figure 7.4e. The tank is filled with raw wastewater and active sludge biomass and mixed/aerated until the desired BOD is achieved. The aeration is stopped to separate solid and liquid, and treated wastewater is decanted from the SBR.

### *7.3.1.2 Aerobic Attached-growth System*

In this system, microorganisms are grown and attached to a bed of extremely porous medium, forming a slime layer into which wastewater is permeated.[8,21] Several attached growth biological reactors are discussed below.

**7.3.1.2.1 Trickling Filters.** Trickling filter is an aerobic attached-growth process widely applied to treat organics-containing wastewater, as shown in Figure 7.4f. The organic matter is adsorbed onto a slime layer and metabolized by microbes.[7] The outer area of the slime layer consists of aerobic microorganisms that degrade the organic matter aerobically. The continuous growth of microorganisms in the slime layer results in oxygen depletion due to an increase in slime layer thickness, which creates anaerobic conditions near the surface of the medium. These microorganisms die and are washed off by flow.[12] This phenomenon is known as sloughing.[5,12]

**7.3.1.2.2 Rotating Biological Contactor (RBCs).** Rotating biological contactors consist of a series of parallel discs made of plastic attached to a metal shaft. The metal shaft is connected to both ends of the tank that contains the wastewater.[22] As the discs rotate, only a portion of the discs assembly is immersed in the wastewater,[23] as shown in Figure 7.4g. The attached microbes absorb organic material and other nutrients from the wastewater while the discs are immersed. The degradation occurs when the discs are in the air, which provides the necessary oxygen for biodegradation of absorbed organic materials.

## 7.3.2 Anaerobic Biodegradation

Anaerobic processes are supported by a diverse and large group of microorganisms that require neither oxygen nor nitrate for their survival.[24] Insoluble organic pollutants break down into soluble substances (amino acids and sugars) in the anaerobic process. Acid-forming microorganisms convert amino acids and sugars into organic acids, which are further converted into $CO_2$ and $CH_4$ by methane-forming bacteria.[9] Figure 7.5 shows the anaerobic treatment of the organic matter. There are two types of anaerobic wastewater treatment systems: attached and suspended growth, as for aerobic wastewater treatment systems.

### *7.3.2.1 Anaerobic Suspended Growth System*

The anaerobic microorganisms are kept in suspension by gentle mixing in the suspended growth system. The major anaerobic biological reactors used for wastewater treatment are described below.

**7.3.2.1.1 Complete Mix Anaerobic Reactor (CMAR).** Complete mix reactors are made up of a tank with a mixing system. CMAR without sludge recycling is appropriate for wastewater with a high concentration of dissolved or solid organic matter. The hydraulic retention time (HRT) and solids retention time (SRT) are equal and are in the range of 15–30 days. A schematic diagram is shown in Figure 7.6a.

**7.3.2.1.2 Contact Anaerobic Reactor.** This system is similar to an anaerobic CMAR except that the reactor biomass is separated in the clarifier provided downstream. A portion of the biomass is recycled and has a hydraulic retention time of 6–12 hours. A schematic diagram is shown in Figure 7.6b. Solids separation and thickening are achieved by gravitational settling before sludge recycling.

**7.3.2.1.3 Anaerobic Sequencing Batch Reactor (ASBR).** ASBR is a suspended growth process system in which reaction and solid–liquid separation occur in the same reactor, as shown in Figure 7.6c. The operation of an ASBR

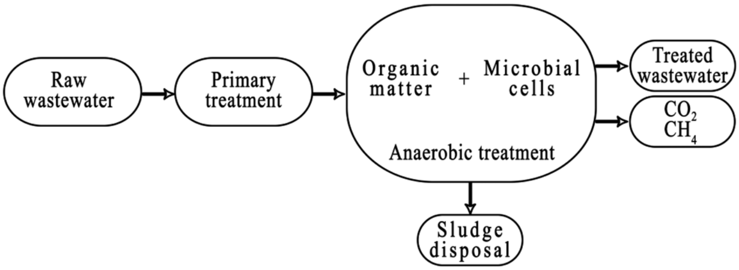

**Figure 7.5** Schematic representation of organic removal by an anaerobic process.

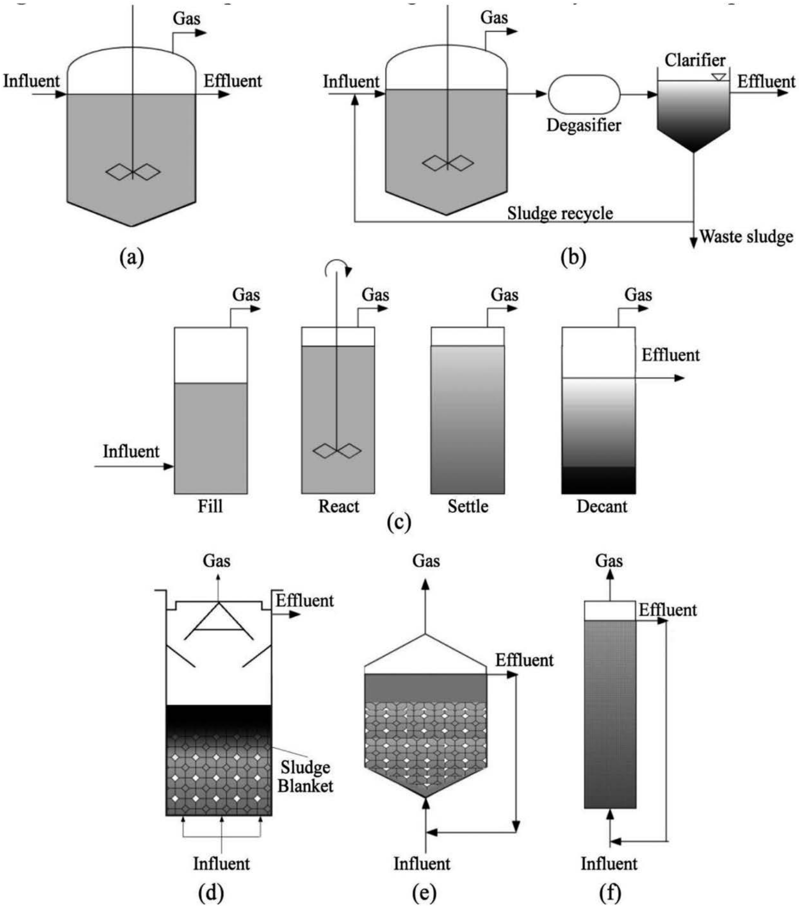

**Figure 7.6** Various anaerobic suspended and attached growth biological reactors.[65] (a) Complete mix anaerobic reactor, (b) contact anaerobic reactor, (c) anaerobic sequencing batch reactor, (d) UASB, (e) UPBR, and (f) AFBR. Reproduced from ref. 65 with permission from Elsevier, Copyright 2021.

is divided into four steps: (1) feed/fill, (2) react/mix, (3) settle, and (4) decant.[19] Intermittent mixing for a few minutes in each hour is required to provide uniform distribution of substrate and contact between substrate and biomass.

**7.3.2.1.4 Upflow Anaerobic Sludge Blanket (UASB) Reactor.** A UASB system is comprised of granular beads (1–2 mm in diameter) containing anaerobic microbes. These active beads are developed within the anaerobic reactor.[25] As wastewater is induced to flow up through the anaerobic sludge blanket, as shown in Figure 7.6d, hydrodynamic drag causes the blanket to be fluidized or expanded.[6] The structures of the sludge blanket are dense and thick enough to be carried up by the influent. Organic matter degradation occurs in the sludge blanket by anaerobic microorganisms, after which treated effluent is discharged from the top.[19] Gas is collected in the hoods and removed.[12]

### 7.3.2.2 Anaerobic Attached Growth System

**7.3.2.2.1 Upflow Packed-bed Reactor (UPBR).** An anaerobic packed-bed reactor comprises a basin filled with an immobile solid medium on which microbes grow and attach. The wastewater flows into the solid medium and comes into contact with the microorganisms.[12] In a UPBR, the wastewater can be fed in either downflow or upflow mode, as shown in Figure 7.6e. The most common packing materials are stones and plastic media of different shapes.[26]

**7.3.2.2.2 Anaerobic Fluidized-bed Reactor (AFBR).** In AFBR, the medium is much heavier (*e.g.* sand), and the wastewater upflow velocity is higher (to fluidize the heavier medium).[26] A schematic diagram is shown in Figure 7.6f. The raw wastewater is fed through the bottom of the reactor and flows up through the solid medium. The upflow velocity serves to fluidize the bed, allowing water and organic molecules to take a tortuous path through the bed. The organic matter and other solid materials are attached to microorganisms and sand within the reactor.[19] The upflow velocity of the wastewater helps to keep the microbial film from growing too thick and from bridging between grains to form blockages to flow. The treated wastewater flows upwards, and collective gas devices collect the gas generated during the operation from the top.

Aerobic biological processes are commonly used to treat organic wastewaters. In contrast, anaerobic treatment is based on resource recovery and utilization while still achieving wastewater treatment.[27] The difference between aerobic and anaerobic process is presented in Table 7.3.

**Table 7.3** Comparison of aerobic and anaerobic treatment.[27] Reproduced from ref. 27 with permission from Elsevier, Copyright 2009.

| Feature | Aerobic | Anaerobic |
|---|---|---|
| **Organic removal efficiency** | High | High |
| **Effluent quality** | Excellent | Moderate to poor |
| **Organic loading rate** | Moderate | High |
| **Sludge production** | High | Low |
| **Nutrient requirement** | High | Low |
| **Alkalinity requirement** | Low | High for certain industrial waste |
| **Energy requirement** | High | Low to moderate |
| **Temperature sensitivity** | Low | High |
| **Start-up time** | 2–4 weeks | 2–4 months |
| **Odour** | Less opportunity for odours | Potential odour problems |
| **Bioenergy and nutrient recovery possibility** | No | Yes |
| **Mode of treatment** | Total (depending on feedstock characteristics) | Essentially pre-treatment |

## 7.4 Advanced Biological Wastewater Treatment Technology

Advanced biological reactors came into the picture to overcome limitations by providing cost-effective installation and efficient operation and sludge separation. The advantages of advanced biological reactors are low sludge production, excellent effluent characteristics, small area requirement, and highly effectiveness in industrial wastewater treatment.[28]

### 7.4.1 Membrane Bioreactors (MBRs)

The MBR is an advanced wastewater treatment technology based on ASP and membrane separation that is used for both industrial and municipal wastewater treatment. MBRs comprise either an aerobic or anaerobic system with suspended biomass, and membranes are used for liquid–solid separation. In an MBR, the solid–liquid separation process is based on filtration through a membrane. The size of the membranes falls in the micro- to ultrafiltration range (0.01–0.4 μm). Due to variations in pore size, membranes efficiently retain all solids, including colloidal material and bacteria.[8] Based on the membrane position, there are two main MBR processes available: submerged or immersed (iMBR) and sidestream (sMBR), as shown in Figure 7.7. MBRs are operated in two modes: pumped (positive pressure) and air-lift (vacuum pressure), the latter being almost exclusively used for immersed systems and the former for side streams. In the case of iMBR, sludge separation takes place within the reactor and it does not require a recycling unit. The iMBR needs a large membrane area compared with the sMBR, and it works at low *trans*-membrane pressure and low fluid crossflow velocities and, hence, less energy requirement and low cost of operation are achieved.[18,29] MBR treatment applies to numerous sectors, including municipal, industrial, and water reclamation. MBRs have been used for palm oil mill effluent, pharmaceuticals, textile, hospital, and organophosphate pesticides wastewater treatment, *etc.*[28,30–34]

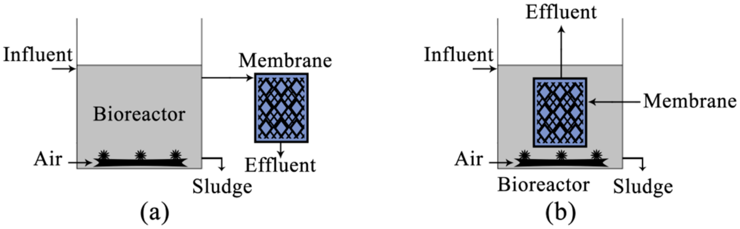

**Figure 7.7** MBR process configuration.[66] (a) Sidestream MBR, and (b) immersed MBR. Reproduced from ref. 66 with permission from Springer Nature, Copyright 2018.

### 7.4.2 Moving-bed Biofilm Reactor (MBBR)

An MBBR process was established in the late 1980s in Norway.[19] In recent years, several modifications have been carried out on MBBRs, such as aerated and anoxic reactors, which require small areas.[35] In this system, the biomass is grown on a small carrier as a biofilm (made up of polyethylene) and operated as a completely mixed and continuous flow system. The carrier elements have a high surface area that provides sufficient space for biomass growth. The cylindrical shape is preferable as a carrier element with a diameter of 7–22 mm.[6,36] Mechanical agitation is needed to mix these elements with wastewater in an anaerobic reactor, whereas aeration is used in the aerobic reactor. No sludge is recycled here.[37] A screen across the outlet is used to prevent the medium from leaving the aeration tank.[36] The variations in MBBR are presented in Figure 7.8. An MBBR can be set up in a smaller tank than a clarifier-coupled ASP system. Multiple MBBRs can be sequenced in a series without any intermediate return sludge system or pumping facility. MBBRs contain a biofilm carrier, which is up to 67% of the liquid volume. Between two MBBRs, screens are usually installed that allow the flow of effluent to the next MBBR while retaining biofilm carriers. The significant advantage of the MBBR process is compactness (in terms of area) and high volumetric treatment capacity.[8,38]

### 7.4.3 Granular Sludge Technology (GST)

Aerobic granulation is also known as aerobic granular sludge technology (GST). The granulation is an agglomeration of cells involving physical, chemical, and biological actions that transform into a regular shape.[39,40] Granules are densely packed with mixed consortia of millions of self-immobilized microorganisms per gram of biomass.[41] The regular and dense granules structure provides high biomass retention, excellent settling properties, and the ability to treat high-strength wastewater. The diverse and strong microbial community structure undertakes biodegradation of

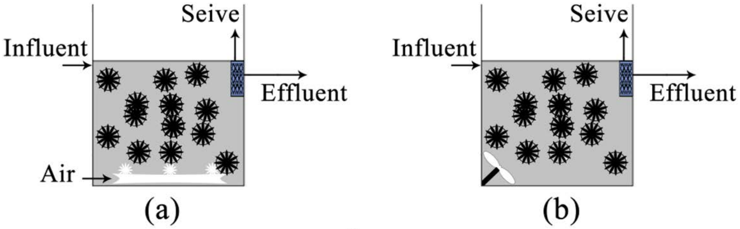

**Figure 7.8** Variation in the MBBR processes:[66] (a) aerobic, and (b) anaerobic. Reproduced from ref. 66 with permission from Springer Nature, Copyright 2018.

the organic matter present in the wastewater and nutrient removal. The main drawback is the long start-up period required (typically 2–8 months) and disintegration of granules (due to low-strength organic wastewater). Several conditions must be met for granule formation, such as diffusion force, cell mobility, gravity force, thermodynamic forces, hydrodynamic force, Brownian movement, van der Waals forces, cellular membrane fusion, bacterial community, extracellular polymers, *etc.* and growth of cellular clusters. Filamentous microorganisms are the backbone of the granulation process.

## 7.5 Challenges in Industrial Wastewater Treatment Using Biological Processes

Industrial wastewaters are mostly treated in an anaerobic reactor due to the high COD level, energy generation potential, and low sludge production. Anaerobically treated effluent contains solubilized organic matter, which is not safe for discharge. Therefore, effluent from anaerobic treatment requires further aerobic treatment, indicating the requirement for anaerobic–aerobic systems to meet effluent discharge standards.[27] Several combinations of aerobic and anaerobic reactors have been used for treating industrial wastewater, as presented in Table 7.4.

Biological treatment aims to eliminate organic matter from wastewater with a small share of nitrogen and phosphorus removal. The increasing number of small-scale industries/animal farms in urban areas has increased the chance of wastewater being discharged into sewers. Pollutants in discharged wastewater hamper the treatment efficiency of a treatment plant. Table 7.5 shows the various parameters influencing industrial wastewater treatment operations. The following studies show the impact of industrial wastewater on the treatment efficiency of the biological units of a treatment plant.

### 7.5.1 Agrochemical Wastewater

Contamination of the hydrosphere by pesticides is due to industrial discharge and extensive use of agrochemicals that somehow find their way into the natural environment, such as like the freshwater and marine system. An aerobic reactor (at 22 ± 2 °C) and an anaerobic reactor (at 30 ± 2 °C) can treat vydine (25 mg $L^{-1}$)-containing wastewater efficiently in the presence of glucose (as a carbon substrate). Firstly microorganisms acclimatize to the pesticide conditions and then start to degrade it. The aerobic and anaerobic reactor's acclimation periods are ≈172 and 230 days, respectively, removing >96% of pesticide. After acclimatization to vydine, the aerobic and anaerobic biomass utilizes vydine for biomass build-up, minimizing the toxic effects of vydine, which improves the reactor efficiency. Un-acclimatized biomass removes less vydine (25%) than acclimatized biomass (95% after 32 days).[42] Similarly, other aerobic and anaerobic SBRs treat herbicide [soproturon

**Table 7.4** Anaerobic–aerobic systems using high-rate bioreactors.[27] Reproduced from ref. 27 with permission from Elsevier, Copyright 2009.[a]

| Reactor | Wastewater | Influent COD (mg $L^{-1}$) | OLR (kg COD/$m^3$ d) | Total COD removal (%) | Anaerobic COD removal (%) | Aerobic COD removal (%) | Total HRT (h or d) | Anaerobic HRT (h or d) | HRT (h or d) |
|---|---|---|---|---|---|---|---|---|---|
| **UASB + CSTR** | Wool acid dying WW | 499–2000 | — | 83–97 | 51–84 | — | 3.3 d | 17 h | — |
| **UASB + CSTR** | Cotton textile mill WW | 604–1038 | — | 40–85 | 9–51 | — | 5.75 d | 30 h | 4.5 d |
| **UASB + CSTR** | Simulated textile WW | 4214 | 1.01–15.84 | 91–97 | — | — | 19.17–1.22 d | — | — |
| **2 UASBs + CSTR** | Food solid waste leachate | 5400–20 000 | 4.3–16 | 96–98 | 58–79 | 85–89 | 5.75 d | 1.25 d | 4.5 d |
| **UASB + CSTR** | Pulp and paper industry effluent | 5500–6600 | 16 | 91 | 85 | — | 11.54 h | 5 h | 6.54 h |
| **UASB + CSTR** | Pharmaceutical industry WW | 3000 | 3.6 | 97 | 68–89 | 71–85 | — | — | — |
| **UASB + ASP** | Olive mill WW + municipal WW | 1800–4400 | 3–7 | 95–96 | 70–90 | >60 | 28.3 h | 14.7 h | 13.6 h |
| **UASB + ASP** | Starch industry WW | 20 000 | 15 | — | 77–93 | 64 | 5 d | 1 d | 4 d |
| **UASB + ASP** | Municipal WW | 386–958 | — | 85–93 | 69–84 | 43–56 | 6.8 h | 4 h | 2.8 h |
| **UASB + AFB** | Synthetic textile WW | 2000–3000 | — | — | — | — | 2.7–32.7 h | 1.4–20 h | 1.3–12.7 h |
| **UASB + AFB** | Synthetic textile WW | 2700 | 4.8 | 80 | 50 | 60 | 20 h | 10 h | 10 h |
| **RBC + SBR** | Mixture of cheese whey and dairy manure | 37 400–65 700 | 5.2–14.1 | 99 | 46.3–62.6 | 93–95 | — | 2–5 d | — |
| **RBC + SBR** | Screened dairy manure | 39 900–40 100 | 8.2–26.8 | 98 | 18.7–29 | 86–87 | — | 1–4 d | — |
| **FFB + FFB** | Slaughter house WW | 400–1600 | 0.39 | 92 | — | — | 4.7–7.3 d | 1.2 d | 3.5–6.1 d |
| **EGSB + aerobic biofilm reactor** | POME | 35 000 | 10 | 95.6 | 93 | 22 | — | 3 d | — |
| **UBF + MBR** | Synthetic WW | 6000–14 500 | 7.2 | 99 | 98 | — | 1 d | — | — |

(*continued*)

**Table 7.4** (*continued*)

| Reactor | Wastewater | Influent COD (mg $L^{-1}$) | OLR (kg COD/$m^3$ d) | Total COD removal (%) | Anaerobic COD removal (%) | Aerobic COD removal (%) | Total HRT (h or d) | Anaerobic HRT (h or d) | HRT (h or d) |
|---|---|---|---|---|---|---|---|---|---|
| **UASB + aAerobic solid contact system** | Municipal WW | 341 | 2.6 | — | 34 | — | 3.53–6.2 h | 3.2 h | 0.33–3 h |
| **UASB + RBC** | Domestic sewage | 640 | — | 84–95 | 35–47 | 52–56 | 6–13.5 h | 3–6 h | 3–7.5 h |
| **CSTR + Activated sludge** | Green olive debittering WW | 23 500 | 0.47 | 83.5 | 37.4–48.9 | 73.6 | 55 d | 50 d | 5 d |
| **AFFFBR + ASP** | PTA effluent | 5000 | 4–5.0 | 96.4 | 64–62 | 90 | 23–27.2 h | 1–1.2 h | 22–26 h |
| **AnFB + airlift suspension reactor** | Complex industrial WW | 3800 | 25–30 | — | 60–65 | — | 3.4–4.3 h | 1.4–1.8 h | 2–2.5 h |
| **Hybrid bioreactor + ASP** | Oil shale ash dump leachate | 2000–4600 | — | 75 | 20–40 | 60–80 | 8.8 d | 62 h | 150 h |
| **Packed column reactor + ASP** | Textile industry WW | 800–1200 | — | 50–85 | 30–65 | 40–90 | 22–82 h | 12–72 h | 10 h |

[a] AFB, aerobic fluidized bed; AFFFBR, anaerobic fixed film fixed-bed reactor; AnFB, anaerobic fluidized bed; ASP, activated sludge process; CSTR, continuously stirred-tank reactor; d, day; EGSB, expanded granular sludge bed; FFB, fixed-film bioreactor; h, hour; HRT, hydraulic retention time; OLR, organic loading rate; POME, palm oil mill effluent; PTA, purified terephthalic acid; RBC, rotating biological contactors; SBR, sequencing batch reactor; UASB, upflow anaerobic sludge bed; UBF, upflow bed filter; WW, wastewater.

**Table 7.5** Influenced parameters during various industrial wastewater treatments.[a]

| Reactor type | Volume | COD (mg $L^{-1}$) | Wastewater | Pollutant (mg $L^{-1}$) | HRT (h) | SRT (d) | Parameters | Reference |
|---|---|---|---|---|---|---|---|---|
| **SBR** | 30 | 3450 ± 65 | PWW | AMP, ERY, TET, KAN, and CIP | — | — | Reactor performance, ARB, Zeta potential, and relative hydrophobicity | 67 |
| **SMBR** | 8 | 3551 ± 252 | PWW | Sulfonamides, tetracyclines, and fluoroquinolone | — | — | Removal of bulk organic matter and nutrients, removal of antibiotics, biomass characteristics | 68 |
| **Anaerobic biofilter reactor** | 13.40 | 3000 | Coal gasification | Phenol (0–800) | 96 | — | Reactor performance, methane production, microbial community analysis | 48 |
| **Activated sludge plant** | 208 | 1045 | OMWW | Organic matter | 10 | — | Reactor performance, SOUR, microbial analysis | 69 |
| **Erlenmeyer flasks** | 0.25 | 75 000 | OMWWl | Phenol | — | 30 | Isolation and identification of bacterial strains, microbial consortium stability and process performance, bacterial community structure, phytotoxicity assessment | 70 |
| **AnMBR and AeMBR** | 4 & 2.5 | 2000 | TWW | Real wastewater | 48 | 60 | Reactor performance, Filtration characteristics of anMBR and aeMBR, optical profilometer and SEM-EDS analyses, dominant bacterial consortia | 31 |

(*continued*)

**Table 7.5** (*continued*)

| Reactor type | Volume | COD ($mg\ L^{-1}$) | Wastewater | Pollutant ($mg\ L^{-1}$) | HRT (h) | SRT (d) | Parameters | Reference |
|---|---|---|---|---|---|---|---|---|
| **SBR** | 2 | 140 | TWW | Dye, COD, TDS | — | 7 | Absorption, COD, and TDS parameters | 71 |
| **EGSB** | 1.47 | — | PWW | Amoxicillin (19.7–214.7) | 20 | — | Reactor performance, diversity, and abundance of bacteria | 72 |
| **MBR** | 36.2 | 900 | POME | Real wastewater | 15 | 60 | Reactor performance, EPS characterization, microbial community | 30 |
| **SBBR** | 8.5 | 85 | MWW | CTC (0–35) | — | — | Performance of SBBR, microbial activities in SBBR, 3D-EEM, microbial community analysis | 73 |
| **Column reactor** | 20 | 1250 | SWW | COD, nitrate, nitrite, ammonia, phosphate | — | — | Performance of reactor, 3D-EEM, Particle size distribution, and ammonia oxidation ability | 74 |
| **SBR** | 10 | 11 500 | POME | COD | 12 | — | Performance of SBR, determination of growth kinetic | 75 |
| **SBR** | 3.5 | 1650–2450 | TWW | COD | 72–120 |  | Reactor performance and kinetic study | 76 |
| **SBR** | 10 | 1200 | EPWW | $CN^-$, Zn(II) | 72–240 | — | Effect of dilution rate of EPWW, effect of HRT | 53 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **SBR** | 155000 | 260 | DWW | — | 12 | 107 | Organic matter and nutrients removal, biomass, and microbial communities analysis | 77 |
| **SBR** | 3 | 228–418 | PWW | — | 12 | — | Effect of influent pH, activities of AOB and NOB, sludge concentration and settle ability | 78 |
| **UASB** | 18 | 3000–6000 | PWW | — | — | — | Treatment efficiency, microbial community by PCR-DGGE profiling | 79 |
| **SBR** | 9 | 5417 | PWW | — | 240 | 45 | Effect of initial COD and SS concentrations, bacteria inactivation and toxicity reduction, process applicability | 80 |

[a] 3D-EEM: Three-dimensional excitation-emission matrix; AMP: ampicillin; AnMBR and AeMBR: anaerobic and aerobic membrane bioreactor; AOB: ammonia-oxidizing bacteria; ARB: antibiotic-resistant bacteria; CIP: ciprofloxacin; $CN^-$: cyanide; COD: chemical oxygen demand; CTC: chlortetracycline; DWW: domestic wastewater; EGSB: expanded granular sludge bed; EPS: extrapolymeric substance; EPWW: electroplating wastewater; ERY: erythromycin; HRT: Hydraulic retention time; KAN: kanamycin; MBR: membrane bioreactor; MWW: mariculture wastewater; NOB: nitrite-oxidizing bacteria; OMWW: olive mill wastewater; PCR-DGGE: polymerase chain reaction–denaturing gradient gel electrophoresis; POME: palm oil mill effluent; PWW: piggery wastewater; SBBR: sequencing batch biofilm reactor; SBR: sequencing batch reactor; SMBR: sequencing-batch membrane bioreactor; SOUR: Specific oxygen-utilizing rates; SS: suspended solid; SWW: slaughterhouse wastewater; TC: tetracycline; TDS: total dissolved solid; TWW: textile wastewater; UASB: up-flow anaerobic sludge blanket; Zn(II): zinc.

and 2, 4-dichlorophenoxyacetic acid (2,4-D)]-containing wastewater supplemented with glucose. However, SBRs have failed to remove isoproturon throughout the operation, although after an acclimation period of 30 (aerobic) and 70 (anaerobic) days, the reactor can remove 2,4-D altogether. The aerobic reactor can remove up to 700 mg $L^{-1}$ 2,4-D without causing any inhibitory effect on an aerobic SBR. On the other hand, the anaerobic SBR could degrade 120 mg $L^{-1}$ of 2,4-D.[43] Microbial cells degrade pesticides and utilize them as a carbon source for their growth and maintenance. The gradual decrease in peptone (from 300 mg $L^{-1}$ to 0) allows the microorganisms to degrade chlorophenols [4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP)] mixtures. Microbial communities shift from peptone degradation to chlorophenols degradation. 5-Chloro-2-hydroxymuconic semi-aldehyde (CHMS) is a degradation product of 4-CP that accumulates in bacterial cells.[44] A member of the *Ralstonia* genus within *Betaproteobacteria* can utilize nitrophenol (80–320 mg $L^{-1}$) as the sole carbon source aerobically.[45] Chlorpyrifos (CPS), 3,5,6-trichloro-2-pyridinol (TCP), methyl parathion, and carbonfuran can also be used as sole carbon and energy sources for the bacteria obtained from sludge.[46]

### 7.5.2 Coal Gasification Wastewater

Coal gasification processes discharge many toxic pollutants such as phenolic compounds, pyridine, cyanide, and long-chain alkanes. A membrane bioreactor (MBR) with intermittent aeration is used to treat coal gasification wastewater. The intermittent aeration has a minor effect on organic matter removal; however, chloride, nitrite, and sulfate reduction significantly decrease. Furthermore, increasing non-aeration time increases nitrate removal. The relative abundance of the genera in MBR sludge is greater for *Roseibaca* (62.1%) and *Desulfarculaceae* (9.3%). Intermittent aeration influences the functions, behaviours, richness, and diversity of the microbes in MBR sludge.[47] The biomass in an anaerobic biofilter reactor can maintain its methanogenic activity while treating up to 280 mg $L^{-1}$ of phenol-containing coal gasification wastewater. However, an increase in phenol concentration causes irreversible inhibition of anaerobic microbial activity. Moreover, the occurrence of phenol in influent increases the portion of small-sized anaerobic granular sludge (from 10.2% to 34.6%) in the reactor. Coal gasification wastewater also affects the abundance of *Chloroflexi* and *Planctomycetes* due to its toxicity and causes shifts in the microbial community.[48]

### 7.5.3 Dairy Wastewater

Dairy wastewater contains high organic matter content (COD and BOD), including fats, sugars, and protein in colloidal form. An SBR treating dairy wastewater exhibits excess filamentous growth that causes operational problems, especially during settling. A combination of an anaerobic-micro-aerated feeding pattern reduces filamentous overgrowth and transforms it into aerobic granules to overcome the problem. The reactor reducess COD (94%), nitrogen (95%), and phosphorus (83%) during dairy wastewater treatment.[49] In urban areas, sewage treatment plants often receive dairy wastewater. The presence of dairy wastewater (13% volume) affects the organic matter, nitrogen, and phosphorus removal efficiency of an SBR reactor.[50]

### 7.5.4 Electroplating Wastewater

Electroplating wastewater contains a broad range of heavy metals such as Cd(II), Cr(III), Fe(III), Ni(II), Zn(II), and many others,[51] which may enter the wastewater treatment systems and exert toxic effects on the microorganism of the treatment system. Cu(II) (>1 mg $L^{-1}$) has adverse effects on autotrophic and heterotrophic microbial activities; moreover, autotrophic bacteria are more sensitive to Cu(II) than heterotrophic bacteria. The Cu(II) concentration (5 and 3 mg $L^{-1}$) inhibits the COD reduction and nitrification efficiency of an anoxic/oxic membrane bioreactor (A/O MBR). Furthermore, an increase in Cu(II) concentration (10 and 5 mg $L^{-1}$) severely inhibits COD reduction and the nitrification process. Cu(II) (1 mg $L^{-1}$) can accelerate extra-polymeric substance (EPS) production, which protects the cells from Cu(II) toxicity, while higher Cu(II) concentrations inhibit EPS production.[52] Moreover, the presence of $CN^-$ and Zn(II) in electroplating wastewater inhibits microbial growth and nitrifying bacteria activity, especially *Nitrobacter* sp. However, $CN^-$ and Zn(II) do not affect heterotrophic and denitrifying microbial growth and activity.[53] The settling properties of sludge are impaired by copper dose, resulting in a lower settling velocity of sludge due to damaged bacterial cells.[54] Before Cu(II) addition, the sludge volume index (SVI) for the activated sludge process was in the range 290–400 mL $g^{-1}$. It significantly changed to a value of 126 mL $g^{-1}$ within 10 days of Cu(II) addition (20 mg $L^{-1}$).[55] The addition of 40 mg $L^{-1}$ of Cu(II) slightly decreased the SVI value. However, a further increase up to 80 mg $L^{-1}$ led to a significant decrease in SVI.[56] The SVI value changed (from 200 to 108 mL $g^{-1}$) with the addition of 16.05 mg $L^{-1}$ of iron in the anoxic process.[57] Ni(II) exposure at 1 and 10 mg $L^{-1}$ decreased the SVI; moreover, long-term exposure increased the suspended solids (SS) concentration in effluent with a low SVI value.[58]

### 7.5.5 Mustard Tuber Wastewater

Mustard tuber wastewater contains a high organic load, a high level of nitrogen, and high salinity. A sequencing batch biofilm reactor (SBBR) effectively treats saline mustard tuber wastewater and reduces COD (86.48%) and total nitrogen (86.48%) at 30 g $L^{-1}$ NaCl during 100 days of operation. The increase in the salinity of the wastewater (10 to 30 g $L^{-1}$ NaCl) does not affect the reactor performance but reduces the microbial community structure in the SBBR; thus, populations of halophilic bacteria increases. High salinity inhibits nitrite-oxidizing bacteria (NOB), partial nitrification, and denitrification processes.[59]

### 7.5.6 Palm Oil Mill Wastewater

Palm oil mill effluent is characterized by its high organic content, lignin, tannins, lignin-derived compounds, and humic acids, contributing to its dark colour. The treatment of palm oil mill effluent in an MBR causes a considerable change in the microbial community structure. During the treatment process, phyla *Proteobacteria* (19–23%) and *Chloroflexi* (11–13%) are the dominant members of biofilm under operational condition. In comparison, *Proteobacteria* (18%) and *Planctomycetes* (16%) were found to be dominant in biofilm under static and non-operational conditions.[30]

### 7.5.7 Pharmaceutical Wastewater

Pharmaceutical wastewater contains various drugs, antibiotics, endocrine disrupters, hormones, *etc.* An antibiotic aim to inhibit bacterial growth; hence, it directly affects its target bacterial species. The treatment efficiency of an ASBR decreases while treating a mixture of erythromycin- and sulfamethoxazole-containing wastewater. Furthermore, COD reduction and methane production also decrease with increased antibiotic concentrations in influent wastewater. These antibiotics cause an inhibitory effect on enzyme activity and metabolic reactions of microorganisms that eventually contribute to a decrease in reactor performance. An increase in antibiotic combination dosages also decreases antibiotic removal efficiency.[60] The continuous addition of carbamazepine (90 $\mu g\ L^{-1}$ in the feed) in a submerged MBR causes more severe membrane fouling and increases the supernatant's protein content. Carbamazepine in influent inhibits respiration rate and increases sludge floc size.[61] The exposure of fluoxetine (FLX) to aerobic granular sludge in an SBR affects the removal of carbon, nutrients, and phosphate. The microbial community adapts to the continued exposure of FLX, and phosphate removal efficiency improves.[62] The addition of oxytetracycline (OTC) (0–12 $mg\ L^{-1}$) reduces the nitrogen and COD reduction efficiency of an anoxic–aerobic SBR. The specific oxygen uptake rate (sOUR), specific nitrate reduction rate (SNRR), specific ammonium oxidation rate (SAOR), and specific nitrite oxidation rate (SNOR) decrease due to OTC toxicity. However, microbial cells try to protect themselves; hence EPS contents increase. The presence of OTC depletes or weakens some microbes in the reactor. In contrast, a few bacteria become predominant due to OTC toxicity.[63] Similarly, SAOR, sOUR, SNRR, and SNOR decrease in the presence of florfenicol (FF) in a sequencing batch biofilm reactor (SBBR). High FF concentrations inhibit COD reduction and nitrogen removal and increase EPS production. FF concentration causes variations in the microbial community and affects the nitrification process by decreasing *Nitrosomonas* and *Nitrospira* populations.[64]

## 7.6 Summary

Industrial wastewater is much stronger than domestic sewage and contains a high content of organic and inorganic pollutants. Biological treatment units receive the pretreated or raw wastewater based on the treatability and composition. Industrial wastewater characteristics change with industry type and their operational strategies. The microorganisms of biological units are susceptible to toxicity. Most industrial wastewater contains toxic pollutants that affect microbiological parameters like the population and microbial community structure and sludge activity. Contamination of industrial wastewater with high pollutant concentrations causes a significant decrease in organic matter, nitrogen, and phosphorous removal efficiencies in a biological system. Sometimes heavy metals in wastewater cause irreversible changes in biomass, which further contribute to the failure of the treatment plant. High organic content loading favours filamentous growth, which causes sludge bulking problem, thereby hindering treatment plant operation. Even a trace amount of pharmaceutical compounds can cause a treatment plant operation failure due to its toxicity. In many cases, biological processes have been proved to be effective; however, the presence of inhibitory compounds in industrial wastewater requires an acclimatization period for the microorganisms to increase their tolerance to toxicants and improve industrial wastewater treatment capacity.

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CHAPTER 8

# *Challenges in Designing and Operation of a Bioreactor for Treatment of Wastewater*

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## 8.1 Introduction

Development across the world has resulted in soil contamination, and pollution of groundwater, sediments, surface water, and air with dangerous and poisonous chemicals, which is one of the chief problems currently being investigated by globally approved research. Providing hygienic and inexpensive water to meet human needs is the outstanding task of this century. The production of waste has increased due to world industrialization, and hence, contamination problems have worsened. Overall, groundwater characterizes about 98% of the accessible freshwater across the globe and thus, guarding and reinstating groundwater is an issue of extraordinary prominence. The supply of water competes with the reckless rising demand, which is worsened by the growth of population, climatic change globally, and deterioration of water quality. This prevalent problem presents a substantial methodical and monetary challenge. Worldwide, an enormous number of products are being manufactured and disbursed, resulting in tons of wastewater annually,

Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

and the consumption of substantial quantities of natural resources.[1] Consequently, there is a requirement for a broader range of economical, *in situ* remediation tactics, such as bioremediation. Biological treatment is an essential part of several wastewater treatment plants.[2] The commercial benefit of biological treatment, rather than processes like chemical oxidation and thermal oxidation, with regard to its operating costs, has ensured its role in many integrated wastewater treatment plants.[3]

A bioreactor offers a manageable environment, providing the biological, biomechanical and biochemical necessities to fabricate the engineered product. As the purpose of a bioreactor is to generate a chosen bio-product, it is important to carefully screen the reaction parameters such as overall mass transfer, shear stress, velocity, heat transfer, *etc.* Refined and comprehensive designing of a bioreactor with exclusive performance is vital in the creation of valuable biotechnological products from natural as well as genetically engineered cell systems. The mass transfer behaviour in bioreactors must be understood in order to improve reactor design, modelling tools and reactor operation, which are important for increasing the rate of reaction, optimization of throughput rates and minimization of cost.

A bioreactors can mostly be described as a container that employs a biological catalyst's activity in order to achieve a preferred conversion. It usually delivers a biochemical as well as biomechanical atmosphere with a range of nutrients and transfer of oxygen into the cells.[4] Diverse designs of bioreactor have been industrialized to provide to an extensive range of substrates, products and biocatalysts.

Conventional chemical reactors and bioreactors have differences in the level to which they provide maintenance and regulate biological activity. As microorganisms are sensitivite and not as stable as chemicals, the bioreactor system must be sufficiently robust to deliver an advanced degree of control over the process limitations and impurities. The bioreactor must operate under specific defined conditions that are advantageous for the activity of the microorganisms activity. Maintenance of the desired biological activity as well as minimization of undesired activities are definite challenges as microorganisms can mutate and thus modify the biochemistry of the reaction and the physical properties of the organism.[5] The current chapter describes the major existing challenges of industrial wastewater treatment and how advanced biological processes can deal or are dealing with them. A short description of the basics of bioreactors, the role of bioreactors in wastewater treatment, conceptual design and approaches for bioreactor design, the challenges associated with the designing and operation of a bioreactor, fouling control strategies, and reuse and the recovery of wastewater using membrane bioreactors are all discussed in detail.

## 8.2 Basics of a Bioreactor

Bioreactors are a key component in the process of industrial conversion of biochemicals, in which the treated resources are biotransformed through the action of microorganisms and other components such as enzymes.[6]

This is the core of numerous biotechnological systems that are utilized for agricultural, industrial, environmental, and medical purposes. In certain cases, this method is applied for production of biomass, *e.g.* single-cell protein, microalgae, Baker's yeast and animal cells; for the formation of metabolites, *e.g.* ethanol, organic acids, antibiotics, pigments and aromatic compounds; and in substrate transformation such as steroids or even for active cell production of *e.g.* enzymes.

A bioreactor comprises a multifaceted system of fittings, pipes, sensors, and wires and is exposed to operating problems. Its elementary features include headspace volume, foam control, agitator system, temperature and pH control system, oxygen delivery system, cleaning and sterilization system, sampling ports, and lines for charging and emptying the reactor.[7] The headspace volume is the operational volume of a bioreactor, *i.e.* the portion of its entire volume that is occupied by the media components, microorganisms, and gas bubbles; the volume that is left is the headspace. Usually, the working volume is ≈80% of the total reactor volume, although it depends on the foam formation rate during the working of the reactor.

$$\text{Headspace volume} = H_t(\text{Total volume of the reactor}) - H_i(\text{Working volume of the reactor})$$

The agitator system comprises an impeller, peripheral power drive and baffles for extreme mixing and amplified rate of mass transfer by the maximum liquid in the layers of the bubble boundary. It delivers sufficient shear that is required for bubble breaking. A Rushton turbine type impeller is used in most microbial fermentations. The air delivery system comprises an air inlet, a compressor, a sterilization system, an air sparger and an exit air sterilization system to avoid impurities. The foam control system is an indispensable component of a bioreactor as unnecessary formation of foam leads to congested air exit filters and forms pressure in the reactor. The temperature control system includes a heat transfer system and temperature probes. Heating is delivered by electric heaters and steam is produced in boilers, whereas cooling is delivered by cooling water formed by cooling towers. The pH control system includes nullifying agents to control pH and they should be non-toxic and non- corrosive while diluting in the media components. Sampling ports are utilized to inject nutrients, water, salts *etc.* into the bioreactor. The cleaning and sterilization system is critical to avoid contamination. Thermal sterilization is provided by steam, which is a preferable option for economic reason as well as easy sterilization of large-scale equipment. Chemical sterilization is usually favoured for heat-sensitive equipment. Radiation sterilization is achieved by UV rays for solids and X-rays are used for liquids.[8]

## 8.2.1 Mode of Operation

The mode of operation of a bioreactor can be categorized as a batch process, a continuous process or a fed-batch.

#### *8.2.1.1 Batch Process*

In a batch process microorganisms are inoculated in the disinfected culture medium after sterilization. Throughout this reaction, the concentration of microbial cells, micronutrients, macronutrients and products diverge with time. Fermentation takes place for a given time period required for the production of product.[9] The culture medium is aerated to provide an uninterrupted oxygen flow to encourage aerobic cultivation. The various phases of a batch process are lag phase: when the culture medium is inoculated with a fresh culture, the growth of microbial cells starts after a definite time period; log phase, commonly known as exponential phase: the number of cells doubles per unit time and when the number of cell of this reaction is plotted on a logarithmic scale as function of time, a curve with a continuously increasing slope is obtained; stationary phase: there is no net increase or reduction in cell number but the cell functions keeps on going; and death phase; if the incubation of cells is sustained even after the microbial population has reached the stationary phase, the cells die and death occurs due to cell lysis.

Batch bioreactors are easy to operate and encompass a tank that is proficient in carrying out structured reactions and the tank is furnished with an agitator to mix the reactants sideways, with heating and cooling systems, and the pH of the reactants are controlled by a pH controller. Such reactors are usually jacketed for steam heating or cooling supplies and are fitted-out with baffles and a sparger for aeration. The impeller is linked to an external motor, which drives the stirrer system. The agitator as well as the seal leads to contamination and therefore a shaft is passed into the bioreactor through a set of aseptic seals.[10] The impeller blade's design, the depth of liquid and speed of agitation help in determining the efficiency of agitation. Significant variables that affects the process of mixing and the rate of mass transfer are types of stirrer, number of stirrers, speed of stirrer, and the rate of gas flow. Batch bioreactors are used for suspension of solids, homogenization, aeration of liquid, dispersion of gas–liquid mixtures and heat exchange. The pH of the fermentation medium, concentration of the media components, and amount of dissolved oxygen can be controlled. Batch bioreactors are flexible systems that can be used for various products and have less risk of contamination or mutation of cells due to the comparatively short growth period, and a lower capital investment requirement compared with continuous processes for the same bioreactor volume.

The batch reactor is assumed to be well stirred with uniform concentration distribution across the reactor. Hence, $\frac{\mathrm{d}(VC)}{\mathrm{d}t} = Q_{\mathrm{in}} \cdot C_{\mathrm{in}} - Q_{\mathrm{out}} \cdot C_{\mathrm{out}} + R \cdot V$, where, $\frac{\mathrm{d}(VC)}{\mathrm{d}t}$ is the rate of mass accumulation in the control volume, $Q_{\mathrm{in}}$ is flow rate into the system, $Q_{\mathrm{out}}$ is the flow rate out of the system, $C$ is the concentration of substrate, $R$ is the rate of the reaction, and $V$ is the volume of the substrate. The in-flow and out-flow stream rates are zero, *i.e.* $Q_{\mathrm{in}} - Q_{\mathrm{out}} = 0$.

Hence, $\frac{(VC)}{\mathrm{d}t} = R \cdot V$ if the reactant volume changes significantly, $\frac{\mathrm{d}C}{\mathrm{d}t} = R$ if the reactant volume remains constant, and $R = k \cdot C$ where $k$ is the rate constant and $C$ is the concentration.

### *8.2.1.2 Continuous Process*

Fresh fermentation medium is uninterruptedly added in the continuous process and both the products as well as the culture are detached at the same rate, thus preserving persistent nutrient concentrations and cells throughout the process.[10] This process is often used for high-volume production; for reactions using gas, liquid or soluble solid substrates; and for processes that involve microorganisms with great mutation-stability. A common example of a continuous process reactor is a chemostat. In a continuous stirred-tank reactor, also known as a back-mix reactor, the reactants are mixed well and the liquid is constantly introduced and removed from the reactor. In a run through, mechanical agitation is essential to attain unchanging configuration and temperature. A culture medium is constantly fed into the bioreactor to sustain the steady state. The reaction variables and regulator parameters remain stable, creating a constant time state within the reactor and the result is uninterrupted production and output of the desired product. It necessitates huge volume reactors to get the anticipated results. This type of reactor is extensively applied for industrial purposes and in the treatment of wastewater. It can yield reliable product value using inflexible functioning parameters, although these bioreactors consume more energy because of the mechanical pumps.

The material balance for this reactor gives $\frac{\mathrm{d}(VC)}{\mathrm{d}t} = Q_{\mathrm{in}} \cdot C_{\mathrm{in}} - Q_{\mathrm{out}} \cdot C_{\mathrm{out}} + R \cdot V$. If the reactor volume is constant and flow rates of the in-flow and out-flow streams are the same, then $\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{1}{T}\left(C_{\mathrm{in}} - C_{\mathrm{out}} + R\right)$. The parameter $T = \frac{V}{Q}$ is called the mean residence time of the continuous stirred tank reactor (CSTR). The steady state of the CSTR is described by setting the time derivative $\frac{\mathrm{d}(VC)}{\mathrm{d}t} = 0$ and $Q_{\mathrm{in}} \cdot C_{\mathrm{in}} - Q_{\mathrm{out}} \cdot C_{\mathrm{out}} + R \cdot V = 0$. Conversion of reactant '$X$' is defined for a steady-state CSTR where $X = \frac{\left(Q_{\mathrm{in}} \cdot C_{\mathrm{in}} - Q_{\mathrm{out}} \cdot C_{\mathrm{out}}\right)}{Q_{\mathrm{in}} \cdot C_{\mathrm{in}}}$.

### *8.2.1.3 Fed-batch Process*

This process is an amalgamation of both batch and continuous processes. Supplementary nutrients are added gradually to the reactor as the biological reactions are ongoing, so as to acquire improved yields and advanced selectivity lengthways while regulating the temperature of reaction. The products are reaped at the termination of the production cycle as in a batch bioreactor.[10]

## 8.2.2 Types of Bioreactor

The different bioreactors used for various applications are based on distinct design and operational characteristics and inclued plug flow reactors, bubble column and air lift bioreactors, packed and fluidized bed bioreactors, membrane bioreactors, photo-bioreactors, rotary drum reactors, mist bioreactors *etc.*

### *8.2.2.1 Plug Flow Reactor*

The plug flow reactor is also described as a tubular or piston- flow reactor. It is a container that allows continuous and unidirectional flow in a steady state. The fluids flow like solid plugs or pistons, with the same reaction time for each substance at a specified tube cross-section. The fluid is assumed to flow as plugs in a tubular reactor, with equal reaction time over the reactor cross-section. Substrate concentration and microorganisms differ throughout the reactor. It functions similarly to a batch reactor as it delivers a great initial driving force which decreases with the reaction.[11]

Plug flow in a tube is an ideal-flow hypothesis in which a fluid is well mixed in a circular direction. The velocity of the fluid is expected to be a function only its axial position in the tube. If '$A_c$' is the reactor cross sectional areas and '$\Delta z$' is a thin disk with tiny thickness representing reactor volume, then the material balance for the volume element is as follows:

$$\frac{\mathrm{d}(Vc)}{\mathrm{d}t} = Q_{\text{in}} z \cdot C_{\text{in}} - Q_{\text{out}} z + \Delta z \cdot C_{\text{out}} + R \cdot \Delta V$$

Where, $\frac{\mathrm{d}(Vc)}{\mathrm{d}t}$ is the rate of mass accumulation in the control volume, $Q_{\text{in}}$ (flow rate into the system) = $Q_{\text{out}}$ (flow rate out of the system) = $Q$, $C_{\text{in}}$ is the concentration of the stream at the disk inlet $(z)$, $C_{\text{out}}$ = concentration of the stream at disk outlet $(z + \Delta z)$, $R$ is the rate of reaction, and $V$ is reactor volume. When, dividing the above equation by $\Delta V$ and taking the limit as $\Delta V$ goes to zero yields, $\frac{\mathrm{d}C}{\mathrm{d}t} = -\frac{\mathrm{d}C \cdot Q}{\mathrm{d}V} + R$, and if the tube has constant cross section, '$A_c$', then velocity, '$v$' is related to volumetric flow rate by $v = \frac{Q}{A_c}$, and axial length is related to tube volume by $z = \frac{V}{A_c}$. The equation can be rearranged as $\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{-\mathrm{d}(Cv)}{\mathrm{d}z} + R$ or $R = \frac{\mathrm{d}C}{\mathrm{d}t} - \frac{-\mathrm{d}(Cv)}{\mathrm{d}z}$.

### *8.2.2.2 Bubble Column Reactor*

This is an easy to scale-up and unpretentious types of reactor.[12] It consist of a tubular vessel equipped with a gas sparger that thrusts gas bubbles into a liquid phase. It has outstanding characteristics of heat and mass transfer. It demands low maintenance and low cost of operation because of the absence of moving parts and compactness, high durability of the catalyst, and online catalyst accumulation and withdrawal. It is used in fermentation and biological wastewater treatment.[14] Though the manufacture of bubble columns is simple, the design is efficient and a good understanding of multiphase fluid dynamics is required for scale-up. The design of the bioreactor is governed by heat, mass transfer and mixing characteristics and chemical kinetics of the system.[13]

### *8.2.2.3 Airlift Bioreactor (ALB)*

An airlift bioreactor can be described as a tower reactor that uses compressed gas expansion for mixing and is used for both free as well as immobilized cells; it is thus suitable for bacteria, yeast, fungi, plant, and animal cells. The fluid volume is distributed by an inner draft tube that helps in refining the oxygen transfer and aligning shear forces in the reactor.[15] The air flows up the riser tube and forms bubbles of exhaust gas that is freed from the top of the column, then the degassed liquid flows through a down-comer and the product is released from the tank bottom. The process of sparging is carried out either from inside or outside the draft tube. In lack of agitation, the reactor needs little energy for an efficient system. It has an enhanced rate of mass transfer as the oxygen solubility is improved; this is achieved with controlled flow and well-organized mixing with a decent residence time.[16]

### *8.2.2.4 Packed Bed Bioreactors*

These bioreactors are comprised of a bed of packing which is made up of polymer, ceramic, glass, or natural material, and is available in a range of shapes and sizes which allows fluids to flow from one end to the other. The immobilized biocatalyst is packed in the column and is fed with nutrients either from the top or bottom. The fluid contains dissolved nutrients and substrates that flow through the solid bed. The rate of flow of fluid and residence time are well-ordered to increase or decrease contact of substrate with the bed.[17]

### *8.2.2.5 Fluidized Bed Reactor*

Fluidized bed reactors constitute a packed bed with small particles size, and hence the problems of clogging, high liquid pressure drop, channeling and bed compaction experienced with packed bed reactors are avoided. The reactor operates at uniform particle mixing and temperature gradients and is a continuous process; the cells are immobilized small particles that move with the fluid. The smaller particle size enables a higher rate of mass transfer, oxygen transfer and nutrients to the cells. The concentration of biocatalyst can be higher and washout limitations of free cell systems can be overcome. The cross-section area is prolonged near the top to decrease apparent velocity of fluidizing liquid to a rate below the terminal velocity of the particles, in order to avoid elutriation (process of separation of particles). The efficiency of a fluidized bed reactor hinges on the particle attachment that are upheld in interruption by an upward flow rate of the fluid that needs to be treated.[18]

### *8.2.2.6 Membrane Bioreactors*

Membrane bioreactors are mostly built by the installation of external structures, *i.e.* the membrane modules are placed outside the bioreactor and recirculation of biomass is through a filtration loop.[19] Membrane bioreactor technology is progressing quickly around the world both in research as well as for commercial applications and is typically used to treat industrial wastewater, domestic wastewater and specific municipal wastewater.

In the context of water and effluent treatment, membrane bioreactors includes an activated sludge process combined with membrane separation to collect the biomass. Consequently the actual pore size is usually <0.1 µm, and the membrane bioreactor efficiently produces a clear and considerably disinfected effluent. Furthermore, it concentrates up the biomass and decreases the required size of the tank and also improves the efficiency of the biological treatment process.[20] Membrane bioreactors allow high concentrations of various liquors and suspended solids with low production of excess sludge, and achieve high elimination efficiency of biological oxygen demand, chemical oxygen demand in water reclamation. However, membrane fouling is a considerable obstacle to the extensive application of membrane bioreactors. The use of a membrane bioreactor in the large-scale treatment of wastewater will require fewer membranes.[19]

## 8.3 Role of Bioreactors in Wastewater Treatment

Extreme and unreasonable utilization of resources, devastation of whole ecosystems, forced extinction of animals and plants, generation of toxic wastes are all interconnected, uncontrolled phenomena that occur under the pretext of aiding mankind. Unquestionably, the generation of gaseous, liquid and solid wastes is an inevitable result of industrial, agricultural and domestic activities. Nonetheless, human activity having an impact on the environment must be diminished to safeguard justifiable quality of life and, ultimately, for survival itself. Though conservation of resources, proper utilization, and balanced human population numbers throughout the entire ecosystem would have the utmost effect on planet sustainability, reduction in waste generation, improved treatment and waste utilization will continue as a vital component of a complete approach for the conservation of the quality of the environment.

The centuries old biochemical process for wastewater treatment is biological wastewater treatment. Even nowadays, as the amount of discharged industrial effluents is on the rise and the forms of pollutants entering the effluent streams is expanding, wastewater treatment processes are increasingly being examined and experimented on across the globe. It is anticipated that wastewater treatment can be paired with the utilization of waste. In these situations, it is constantly proposed that effluent remediation and treatment processes be developed that can be achieved economically and with a high level of energy efficiency.

Numerous waste streams are responsive to biological treatment, either by degrading harmful materials with reduced environmental consequences, or, by progression to valuable products by means of natural, selected or engineered microorganisms and microbial enzymes. When this is not possible, then microorganisms can be used for concentrating heavy metals in quite diluted waste streams for disposal by other means. Biological wastewater treatment can be performed where the waste occurs, like in bioremediation of contaminated soil in the field.[21] On the other hand, for the treatment of wastewater, the contaminated substance can be treated in the bioreactors. The improved environmental panels in the bioreactor contribute to a complete and cost-effective wastewater treatment.[22]

Municipal wastewaters, industrial wastewaters and concentrated slurries of biodegradable organics have been treated mainly by aerobic or anaerobic biological processes.[23] Activated sludge reactors with microbial cells suspended in the wastewater, immobilized biofilm reactors like the rotating disc contactor and the trickle filter, or anaerobic tanks, are well recognized bioreactors in the treatment of wastewater. The biological treatment of liquid effluents can also be achieved using the activated sludge method, and the process can be intensified by better application of low volume, high-rate airlift and deep shaft bioreactor technologies.[24] These work as stand-alone treatment units and are used to improve the performance of conventional plants.

Airlift reactors are agitated by air injection into the riser, and the up-flow of air as well as wastewater occurs in the riser. Most gases leave the liquid in the head region of the reactor[24] and gas-free wastewater continues to circulate through the down-comer. In deep-shaft systems, gas injection is transferred from the riser to the down-comer as soon as the reactor is started in the airlift mode. The overall gas content in the down-comer remains lower than in the riser so the down-comer gas injection point is arranged accordingly; thus, by maintaining a circulatory pattern the lower density riser fluid moves up the riser and the denser liquid in the down-comer flows downward. Rapid biological oxidation of pollutants is allowed at high turbulent flow and is combined with good oxygen absorption in the reactor.

Other developments in the treatment of wastewater is biological removal of phosphate. Conventional activated sludge (AS) wastewater treatment processes characteristically remove <40% of phosphate from the water and the treated effluent can cause eutrophication. To avoid this situation, chemical additives are utilized to remove phosphates through precipitation. As a substitute, biological phosphate removal technology has been developed to achieve up to 90% elimination of phosphate in AS plants by integrating advanced phosphate removal phases. The final clarification stage is connected with the incoming wastewater from the anaerobic initial stage, for the removal of phosphate. The process is monitored by aerobic stages in the plug flow type bioreactor.[25] The phosphates can be removed without any additives through a combination of biological and chemical mechanisms. The removal of phosphate can be achieved by a vital step in the design and operation of the treatment process, depending on the characteristics of the raw wastewater.

Membrane bioreactor (MBR) technology is a fresh technology used for reuse and treatment of wastewater. This advanced technology is a combination of a biologically activated sludge process with membrane filtration[26] and is currently an extensively used and accepted treatment for wastewaters. The conventional activated sludge (CAS) process cannot manage deprived sludge settle-ability and hence does not allow a high mixed liquor suspended solids (MLSS) concentration to be maintained in biological reactors. Complete removal of solids is a significant process in disinfection; high rate and high efficiency of organic removal are attractive features regardless of the type of wastewater to be treated.[27] This MBR technology is also applied in situations where the quality of effluent surpasses the competency of CAS. Although, due to extra strict regulations, MBR capital and operational costs exceed those of conventional processes, and lack of space can prevent the addition of new treatment units to upgrade from CAS to MBR, the use of MBRs is essential in order to improve treatment performance. Along with improved understanding of developing contaminants in wastewater, biodegradability, and new regulations, MBR may grow into an essential up-gradation of existing technology to fulfill legal requirements in wastewater treatment plants (WWTP).

The treated water and microorganisms are separated by a porous membrane having pore diameters of 0.02–0.4 μm, in the MBR process. The quality of the treated wastewater from the Membrane Bioreactor is similar to the quality of the treated water from a tertiary wastewater treatment plant, because of the high selectivity of the membrane, it blocks the passage of activated sludge flocs and living microbes. A new technique has been designed for the separation of treated water from activated sludge without a sedimentation tank, through the installation of an ultrafiltration membrane external to the bioreactor when the mixed liquor is recirculated across the membrane surface. It is a pressure-driven process and is known as "external, recirculated, or side-stream" conformation. In external MBRs, the concentrated sludge excluded by the membrane module is reprocessed in the MBR.[28] A hollow fibre (HF) type membrane has been developed and is an advanced method that involves the direct installation of the membrane into the activated sludge tank, which makes permeation easier through the application of a suction pressure. The final approach is more feasible and economic and is known as a "submerged or immerged" method and requires very high energy for recirculation of the mixed liquor.[29]

The configuration of submerged MBR is simpler in comparison to the external MBR, as it requires less equipment and low energy. The consumption of energy for filtration in submerged MBR is ≈10–25 times lower when compared to the external MBR. Mostly flat sheet (FS) and HF membrane modules are utilized in submerged MBRs, while tubular membranes are preferred for external MBRs. The packing density of an FS is 30–130 $m^2\ m^{-3}$ and for HF membranes is 40–259 $m^2\ m^{-3}$. The tubular membranes used in external MBRs are more expensive because of the low packing density. In addition, the procedure for membrane cleaning in submerged MBRs is easier in comparison to external MBRs. However, the operating flux in submerged MBRs is about four times less than for external MBRs. As an overall assessment, submerged MBRs have numerous advantages over external MBRs, although it should be noted that external MBRs are more robust and flexible.[30]

External MBRs function at a constant pressure and the permeation flux is reduced when fouling of the membrane takes place, whereas submerged MBRs function at a constant permeation flux and the trans-membrane pressure (TMP) surges when fouling of the membrane takes place. External MBRs are usually used in industrial wastewater treatment and small-scale municipal wastewater treatment systems, whereas submerged MBR are mostly used in municipal wastewater treatment plants. External and submerged MBRs can be operated under both aerobic and anaerobic conditions and anaerobic or anoxic compartments can be added to the systems to allow biological nutrients removal.

## 8.3.1 Comparison of Conventional an Activated Sludge Processes and an MBR

It is important to clarify the advantages of membrane bioreactor technology. One of the chief features is the separation of treated water from solid particles. In CAS, this is achieved through a sedimentation tank or a secondary clarifier. As the lighter fractions of activated sludge remain in the effluent, in most of the cases the sedimentation tank does not produce high quality-treated effluent. Nevertheless, the quality of the treated effluent from an MBR can be compared with the effluent from tertiary treatment plants because of the use of membranes which have <0.1 μm pore size.[31]

In both CAS and MBR processes, the quality of the treated wastewater is based on the metabolic features of the microorganisms. MBRs still have advantages over CAS, due to their operation with high MLSS concentrations and the settling conditions in the secondary clarifiers. On the other hand, MBRs can be operated with high MLSS concentrations, by bacterial degradation or endogenous decay to reduce waste sludge production.[31] Another significant features that make an MBR more advantageous is that it works at a longer sludge retention time (SRT), mostly >20 days, in comparison to the SRT for CAS of mostly 5–15 days. Higher SRT reduces sludge generation and results in less waste sludge.

Even though MBR has advantages it still it is has some disadvantages, primarily from high operation costs and membrane fouling problems; fouling of the membrane is the greatest disadvantage in MBR as it reduces the water quantity and quality while increasing the operating costs by 60%.[32]

## 8.4 Conceptual Design and Approaches for Bioreactor Design

Bioreactors provide the possibility of constantly monitoring and controlling environmental conditions during the reaction period, along with the additional benefit of providing a closed system. They are a critical and essential component in the development of new processes. Appropriate selection and design of an efficient bioreactor system justifies the capital investment by assuring its economic viability. Appropriate process engineering control methods have been industrialized to give a measureable understanding of mass transfer. Advanced procedures for gas transfer, maintenance of pH, sensors and actuators detecting temperature, optimal feeding and cell quantification are significant tools for process engineering. As bioreactors require temperature control, it is necessary to select the appropriate temperature control device depending on the specific need of every application by computing the heat load. The bioreactor type required depends on the cells morphology, shear tolerance, and the growth and production behaviour of the culture.

Aerobic membrane bioreactor technology was developed for industrial application in the early 1990s. It is considered to have multiple advantages when compared with conventional activated sludge processes, such as fast start-up of the reactors,[33] small footprint, high efficiency of chemical oxygen demand (COD) and removal of total suspended solids; in order to improve the quality of treated water, it has a high rate of organic loading without any loss of biomass, control over solids retention times and hydraulic retention times, maintenance of concentrations of high mixed-liquor suspended solids *etc.*[34,35] Additionally, when bio-filters are compared with membrane bioreactors, the latter are more competent and can deal with the accumulation of biomass and work at higher inlet concentrations.[36] The benefits of a membrane bioreactor can be upgraded by functioning in anaerobic conditions.[37] Consequently, this technology is receiving great attention from both researchers as well as industrialists. The major drawback of aerobic and anaerobic membrane bioreactors is membrane fouling, which leads to a decrease in membrane permeation fluxes and, thus, increases costs and prevents their commercialization.[38]

### 8.4.1 Energy Recovery in MBRs

Anaerobic membrane bioreactors play a crucial role in energy recovery because of the ability to produce methane from a large fraction of the organics in wastewaters.[40] Anaerobic membrane bioreactors can transform ≈98%

of the influent COD into biogas;[39] furthermore, because of the low growth of anaerobic microorganisms, very little sludge production is detected in these systems. Commonly, anaerobic membrane bioreactors are proficient in producing biogas, which consists of 80% or even 90% methane that can be burnt to produce electric power, with a net energy gain for the wastewater treatment plant.

### 8.4.2 Treated Wastewaters from Membrane Bioreactors

The treatment of wastewater has been studied for a long time but there have been only a few technical studies that have dealt with pilot scale anaerobic membrane bioreactors.[41] In the studies reviewed, anaerobic membrane bioreactors were used to treat an extensive variety of wastewaters ranging from municipal wastewaters and raw domestic wastewaters, to white waters from pulp and paper mills or petrochemical effluents. Concerning municipal wastewaters specifically, both conventional membrane bioreactors and anaerobic membrane bioreactors are operated under similar conditions and end up providing similar soluble COD elimination efficiencies, and the anaerobic membrane bioreactor simultaneously avoids costs required for aeration.[42] However, anaerobic membrane bioreactors cannot retort effectively when considerable fluctuations in wastewater composition occur, as the biomass ends up being incapable of adapting to the environment; henceforth, under these conditions, steady state may never be reached in the system. Toxicity is usually described in terms of toxic levels, as most of the compounds are toxic if present at a sufficiently high concentration. However, the impact of toxicity can be minimized by design measures, for example application of long submerged bioreactors, as is the case for anaerobic membrane bioreactors. In general, the use of an aerobic membrane bioreactor may be more sensible for wastewaters having high a of toxic level; although, application of control methods like dilution below the toxic level, or the removal of the toxin before the application of the anaerobic treatment can lead to a safe process with anaerobic membrane bioreactors as well.[43]

Furthermore, with respect to low organic content wastewaters, it is worth operating at ambient temperatures because the low methane production may not be able to cover the heating costs; although, even operation at ambient temperatures seems to be theoretically feasible. Anaerobic membrane bioreactors can be successfully operated at concentrations of high mixed liquid suspended solid.[44]

### 8.4.3 Operating Conditions and Performance of Membrane Bioreactors

Membrane bioreactors function at extended solid retention times and high concentrations of mixed-liquor suspended solids. The solids retention time standards can alter from 5 to 30 days for the treatment of municipal wastewater treatment in a membrane bioreactor.[45] Higher solid retention times can be appropriate depending on the characteristics of the wastewater. In terms of membrane fouling, it was recommended that the optimum solid retention time should be kept between 20 and 50 days.[46] Higher values of solid retention time allow membrane bioreactors to be operated at a higher rate of volumetric organic loading and lower ratios of food to microorganism. These operational conditions make membrane bioreactor processes denser in comparison to the other processes. Maximum operating fluxes in submerged membrane bioreactor processes for municipal wastewater are usually between 25 and 30 L $m^{-2}$ $h^{-1}$, athough these values are kept between 5 and 15 L $m^{-2}$ $h^{-1}$ for the treatment of industrial wastewater.[47] From the point of view of wastewater reuse, characteristic effluent COD and BOD concentrations are usually below 30 and 5 mg $L^{-1}$, respectively. Total nitrogen exclusion in a membrane bioreactor is ≈30% higher than in other process, and effluent $NH_3$–N and total nitrogen concentrations are normally below 1 and mg $L^{-1}$, respectively.[48]

### 8.4.4 Membrane Materials and Modules Used in Membrane Bioreactors

Many membrane materials and configurations have been used for membrane bioreactor technology. Polymeric materials, such as polyvinylidene difluoride, polyethersulfone, polyethylene, polypropylene, and polysulfone are usually used for membrane production. Polymeric membranes are mostly hydrophobic; though, they can be altered to have hydrophilic features before use and are commonly employed in membrane bioreactor worldwide. Inorganic membranes like ceramics membranes are also appropriate for membrane bioreactors as they are more durable than polymeric membranes under diverse thermal and chemical conditions.[49]

### 8.4.5 Fluxes and Membrane Area of Membrane Bioreactors

The membrane design of fluxes is specified by membrane manufacturers for typical municipal wastewater treatment. The parameters used for the treatment of wastewater need to meet the values of the fluxes of the designed membrane. The number of membrane modules essential to treat influent is determined so as not to disrupt any of the restrictions given by the manufacture. Nonetheless, defining the required membrane area is not straightforward in the real world because the actual wastewater flow rate pattern complex as it varies based on the time, temporary weather conditions, season, types of the residence around the plant, existence of industrial sources *etc.* Furthermore, the size and the operation strategy of the equalization tank affects the flow rate to the membrane bioreactor. As a result, membrane reactors often have to be planned without all the required hydraulic data being available.

The rate of membrane fouling upsurges progressively below the sustainable flux. However, it surges exponentially as it surpasses the sustainable flux. The sustainable flux itself is a somewhat uncertain concept that is dependent on biological conditions, which are inclined to change depending on the running time of the membrane system under the manufacturer's guidelines, which do not guarantee successful operation. Consequently, the stability of the membrane system rises as the value of the membrane designed flux goes beneath the guideline. As a result of variable flow rate and the changing sustainable flux, it is not totally clear how well a membrane can accomplish its task during peak times of operation.

## 8.4.6 Membrane Design

### 8.4.6.1 *Sustainable Design Flux*

The sustainable flux is an unclearly defined concept, and is dependent on biological conditions of feed flow. The stability of the membrane system increases as the design flux falls below the guideline. Flux, permeability, clean frequency and protocol, and membrane aeration are important parameters concerning membrane operation, and therefore the maintenance of flow through the plant. Changing the sustainable flow rate may affect the performance of a membrane during peak time. Consequently, the area of the membrane should be determined depending on budget constraints and the acceptable level of risk.

### 8.4.6.2 *Determine Required Specific Air Demand Based on Membrane Area ($SAD_m$)*

Specific air demand based on membrane area ($\mathrm{SAD_m}$) is described as the flow rate of the scouring air per area of membrane. It is essential to aerate the membrane unit to scour solids. Consequently, the relationship between aeration and decline of flux is not properly understood and the value of membrane aeration is not theoretically clear; in most cases the aeration value is suggested by manufactures. A significant factor in energy demand in submerged systems is the demand for specific aeration, the ratio of $QA$ either to membrane area ($\mathrm{SAD_m}$) or permeating volume ($\mathrm{SAD_p}$), $\mathrm{SAD_m} = \frac{QA}{A_\mathrm{m}}$ where $QA$ is membrane aeration rate ($\mathrm{m^3\ h^{-1}}$) and $A_\mathrm{m}$ is total membrane surface area ($\mathrm{m^2}$) and $\mathrm{SAD_p} = \frac{QA}{J \cdot A_\mathrm{m}}$.

## 8.4.7 Design of an Aeration System

Aeration plays a key role in mass transfer on the membrane surface and it is crucial to design membrane module that allows efficient use of scouring air while maximizing mass transfer in the internal spaces of the membrane module.

Submerged membranes typically require coarse bubble aeration to remove foulants and sustain filtration capacity. The coarse-bubble aeration systems can have an impact on the overall turndown capabilities of a system, therefore it should be designed accordingly to reduce energy bills. In the case of a hollow fibre membrane, there is a random increase in the rising bubbles during fibre movement and this causes acceleration as well as deceleration of fibres in the liquid, which significantly increases the anti-fouling effect.

There is a portion of oxygen in membrane aeration that contributes in degradation of carbon and removal of nutrients. As in every aerobic biological systems, biomass contained in the MBR needs oxygen to achieve diverse chemical reactions. The exact amount of oxygen that is essential for the microorganisms in wastewater, is described by their specific demands. Carbonaceous biochemical oxygen demand (BOD) is the conversion of the carbonaceous organic matter in wastewater into cell tissues and various gaseous end products. Nitrogenous BOD is a nitrification process in which oxidization takes place to the intermediate product nitrite, which is converted into nitrate. Inorganic chemical oxygen demand (COD) describes the oxidation of reduced inorganic compounds within the wastewater.

## 8.4.8 Cost Benefit Analysis

A cost benefit analysis is an instrument to control helpful changes in plant design and operation. Binary indexes can be used to enumerate the impacts on cost and quality of effluent. The growth of the cost standard may be specific to each particular case, particularly when measuring variable operating costs. When designing a new wastewater treatment plant diverse alternatives of treatment and operating plans may be assessed with the help of the cost index and effluent quality index that presents the possible load of pollution to the receiving water body stated in kilograms of pollution per day.

### *8.4.8.1 Capital Cost*

Capital costs for membrane bioreactor systems ar inclined to be more than those for conventional systems with similar throughput due to the initial costs of the membranes. In certain circumstances, though, in particular cases, membrane bioreactor systems can have lower capital costs compared with the alternatives because membrane bioreactors requires less land and smaller tanks, that can reduce the existing costs. Cost of land, civil engineering, other electrical equipment and construction are excluded because they are all highly dependent on location.

### *8.4.8.2 Operational Cost*

Operating costs for membrane bioreactors are characteristically greater than those for conventional systems due to the higher amounts of energy utilized for scouring of air to reduce membrane fouling. The air desired for the scouring is twice that required to uphold aeration in a conventional activated sludge system. However, in membrane systems the residence time of sludge is lengthier than in conventional systems, partly offsetting the operating costs.

## 8.5 Challenges Associated with Design and Operation

### 8.5.1 Membrane Fouling

Deposition of soluble and particulate materials on the membrane surface and in the pores is known as membrane fouling. It is a chief and common disadvantage in membrane bioreactor processes. Fouling is the consequences of the interactions between ingredients of activated sludge and the membrane. According to the mode of operation, it decreases the flux at constant pressure in a membrane bioreactor.[50] Membrane bioreactors mostly function in constant flux mode and membrane fouling is measured by following trans-membrane pressure throughout the time taken for filtration. The trans-membrane pressure varies in a three-stage mechanism. The initial stage is limited to adsorption on the membrane surface and pore blocking, while the next stage is characterized by an exponential increase in the trans-membrane pressure which ends with a sharp increase; the last stage, *i.e.* trans-membrane pressure jump, is a sign of simple membrane bio-fouling and an urgent need for membrane cleaning.[51]

#### *8.5.1.1 Classification of Fouling*

Fouling of membranes cannot be described by a single mechanism, as it is a complex process in membrane bioreactor systems. Usually, fouling is classified as a reversible or irreversible process. Reversible fouling is the process in which the flux can be recovered after backwashing, air scouring, or relaxation. Reversible fouling can be divided into removable and irremovable fouling and flux can be recovered after a physical or chemical cleaning procedure. Nevertheless, flux is recovered after membrane cleaning using chemicals. Mostly, pollutants that are loosely bound can cause removable fouling in membrane bioreactors, while the pore clogging and tightly bound pollutants causes irremovable fouling. Formation of cake causes removable fouling and clogging of membrane pore causes irremovable fouling. Membrane fouling is permanent in irreversible fouling and hence the flux cannot be recovered.[52] Depending on the characteristics of the membrane foulants, fouling can be subdivided into organic, inorganic, or bio-fouling. Bio-fouling is the attachment of bacterial cells to membrane surface, and their multiplication leads to the production of bio-cake which is a layer that reduces the permeability of the membrane. The frontier between these types of fouling is not firm and overlapping is possible; these mechanisms may happen concurrently in which bio-fouling signifies 45% of overall membrane fouling.[53]

The initial step of membrane bio-fouling is the attachment that is governed by the capability of an individual cell to attach to a surface and depends on numerous factors like environmental, temperature, genes which encode the motility functions, nutrients *etc.* Further, the growth of microorganisms begins and leads to the formation of the biofilm layer which includes diverse types of microorganisms.[54] Cell growth will be accompanied by the production of organic substances called extracellular polymeric substances, such as polysaccharides, proteins, nucleic acids, and lipids, and these are excreted by the microorganisms. The chief role of the extracellular polymeric substances is to form a 3D matrix by binding the microbes together, which defines the microbial community of the biofilm. Adhesion of cells are also aided by the extracellular polymeric substances, which may be improved by polymeric interaction at high concentrations of extracellular polymeric substances or may be inhibited by electrostatic interactions at low concentrations of extracellular polymeric substances. Bio-fouling in membrane bioreactors is triggered by the deposition of microorganisms, colloids, and solutes on the membrane surface that leads to loss of membrane performance. Fouling of membranes can take place in a number of stages such as narrowing of pore, clogging of pore, and formation of cake. Clogging of pore depends on the blockage of the membrane pores, when the pores are blocked by particles which have sizes greater than the pore size of membrane, while the formation of cake depends on continuous deposition of foulants on the membrane surface.

#### *8.5.1.2 Types of Foulant*

Membrane fouling occurs at the physicochemical interface of activated sludge and membrane in a membrane bioreactor. Foulants represent a significant problem and it is desirable to resolve the issue of foulants binding on the surface or within the pores. To get an indication of the degree of membrane fouling, the components of activated sludge must be known. Activated sludge is made up of difficult materials and can be mostly fractionated into suspended solids, colloids, and soluble matter. The colloid matter in activated sludge and suspended solids are comprised of activated sludge flocs like microbial cells, individual cells, and debris. Every fraction of the biomass has some influence on fouling of the membrane.[55]

#### *8.5.1.3 Factors Affecting Membrane Fouling*

Though it is difficult to regulate the factors causing membrane fouling in membrane bioreactors because of the intricate relations between fouling factors, these factors can be discussed under four headings: the feed wastewater properties, activated sludge properties, operating conditions, and membrane materials and modules. Membrane fouling is directly related to activated sludge properties and hydrodynamic conditions in membrane bioreactor systems.

## 8.6 Fouling Control Strategies

### 8.6.1 Pretreatment of Feed Wastewater

The pretreatment of wastewater is a dynamic step in the membrane bioreactor operation. Though a membrane bioreactor could function with or without a sedimentation tank and prescreening, these features are essential for suitable and effective operation. Hairs, fibrous matters, lint, and debris passing along with water could clog or even damage the membrane module in a membrane bioreactor, so that even screens with a gap size of 2 mm were not satisfactory for the removal of waste materials from wastewater.[56]

Coagulation is an extensively used step for pretreatment both in water and wastewater treatment as it improves the rate of permeation by altering the characteristics of particles. It also prevents bio-fouling by lessening the concentration of bio-degradable organic matter in water. Aluminum-based, iron-based, commercial, and polymeric coagulants are commonly used in controlling the fouling of membranes. The success rate of coagulation is governed by the regularity of membrane cleaning, the nature of the feed water, the configuration and type of the membrane, and the expected water recovery. It is understood that residues from the process of coagulation have considerable bio-fouling potential and have a damaging effect on membrane performance. Therefore, membrane filtration or ultrafiltration can be applied as pretreatment methods rather using high levels of coagulants.[57]

### 8.6.2 Physical Cleaning and Backwashing

The cleaning of membrane is performed for the removal of foulants from the surface of the membrane. Cleaning is particularly used during the increase in transmembrane pressure. It can be categorized as physical or chemical cleaning; physical cleaning may be followed by chemical cleaning. It is also classified into *in situ* and *ex situ* cleaning based on whether the membrane module is within the membrane bioreactor. *Ex situ* membrane cleaning requires the removal of membrane modules from the membrane bioreactor, and a combination of physical and chemical cleaning can be supported. *In situ* membrane cleaning is usually preferred in membrane bioreactors. Physical cleaning involves air flushing, air bubbling, air sparging, $CO_2$ back permeation, sponge ball cleaning, forward and reverse flushing, and backwashing, and other types include ultrasonic, electrical fields, and magnetic fields.[58]

### 8.6.3 Cleaning

Chemical cleaning can be applied to irreversible fouling on the membrane surface. A number of the chemical agents used for membrane cleaning are acidic *e.g.* HCl, $HNO_3$, $H_2SO_4$, $H_3PO_3$, citric, oxalic; caustic *e.g.* NaOH, KOH, $NH_4OH$; complexing like EDTA; detergents like alkyl sulfate, sodium dodecyl sulfate, cetyl trimethyl ammonium bromide; enzymatic for example-α-CT, CP-T, peroxidase; disinfectants like NaOCl, $H_2O_2$, $KMnO_4$; and cleaning blends for example 4 Aqua clean®, TRiclean®, and Ultrasil®/Aquaclean®. Sodium hypochlorite is mostly used for chemical cleaning to eliminate organic-based compounds in most of membrane bioreactor plants.[56]

The caustic chemicals assist in the hydrolysis of foulants like proteins and saccharides. Surfactants in wastewater directly affect the hydrophobic connections between membrane and bulk solution, in order to prevent formation of biofilm. Enzymes promote hydrolysis, particularly proteases for protein hydrolysis and polysaccharases for polysaccharide hydrolysis. However, enzymes are costly enzyme activity is limited by pH, temperature and salt concentration. Citric acid is usually applied to eliminate inorganic substances like calcium, magnesium, carbonate, sulfate, silica, and iron that cause inorganic fouling in membrane bioreactors.[56]

### 8.6.4 Membrane Surface Modification

Traditionally, membranes that are easy to clean having low microbial affinity are usually favoured for bio-fouling control. Alterations of the bacteriostatic properties of membrane plays an essential role in avoiding bio-fouling.[59] Nowadays, novel technologies are engaged for prevention of initial microorganism attachment to membrane surfaces. Alteration of the properties of a membrane surface reduces the attachment of microbial cells, which is achieved through biocide treatment, blending of polymers, graft polymerization, and coating the surface of the membrane with antimicrobials. The chief problem are polymers that might alter the permeability of the membrane, its chemistry, and its pore size, leading to a modification in the overall performance of the membrane. The use of synthetic antimicrobial additives that are non-oxidizing and develop resistance with time is subject to environmental regulations and restrictions.

### 8.6.5 Optimization and Enhancement of Aeration

There are additional aspects of membrane module design and operating conditions of membrane bioreactor that affect bio-fouling. Spiral wound membrane is the most commonly used membrane module type in water and wastewater treatment plants. In this systemf bio-fouling may be prohibited by an amplified velocity or creating commotion near the surface of membrane. This may be achieved by the addition of fixed mixers to the system. Shear rate increase generates hard to remove biofilm which is undesirable and more compressed, hence the level of shear rate must be well studied in a pilot system before its application.

### 8.6.6 Biological Control Techniques

Minimum sensing inhibition is a novel method for the regulation of membrane bio-fouling. However, further investigation is needed to improve its efficacy and rate of success. Minimum number sensing is not the only biological way to supervise biofilm as use of bacteriophage can also be an efficient method for controlling biofouling. Biofilm formation is controlled by bacteriophage by infecting and lysing the host bacteria, thus decreasing the attachment of microbial cells to the surface of the membrane and improving membrane permeability. Periodically, numerous varieties of phages can be added during the mixing of bacterial species which are responsible for fouling. The use of bacteriophages in wastewater treatment plants is a challenge due to the specific characteristics of parasitic bacteriophages.

Another method for controlling bio-fouling is in its initial stage and requires considerable research before being used in *in vivo* studies. The adding of nitric oxide plays a significant role in scattering all varieties of bacteria accountable for formation of biofilm. Nitric oxide is insoluble in aqueous solution, therefore addition of a donor *i.e.* sodium nitroprusside, 3-morpholinosydnonimine, sodium nitrite, *S*-nitroso-*N*-acetylpenicillamine and diazeniumdiolate is more effective.

## 8.7 Reuse and Recovery of Wastewater Using an MBR

Currently, membrane bioreactors are robust, can be controlled simply and costs are quite reasonable. Also, they require less space, modest support in technical terms, and have the ability to achieve single step-easy elimination of pollutants. They can provide a crucial treatment process in municipal recycling and improve the quality of treated effluent, chiefly for the pathogenic microorganisms and removal of micro-pollutants. Further, membrane bioreactors can be used in several industries like tannery, laundry, textile, dairy, wheat starch, palm oil, beverage, and pharmaceutical.

A conventional membrane bioreactor should be combined with downstream units in order to remove low-molecular-weight compounds, which results in extraordinary capital cost as well as consumption of energy. In recent years, the combination of membrane bioreactors and reverse osmosis has been an encouraging step for the treatment of wastewater so as to attain drinking water of an acceptable standards. The process of reverse osmosis can efficiently remove TDS, $NH_4$–N, $NO_3$–N, and bacterial and viral cells. Experimental studies have indicated that this amalgamation is very successful at generating high quality water. The removal competences attained by the different systems were 91, 99, and 99% for TKN, phosphorus, and TOC, respectively.

The combination of a stimulated sludge process and forward osmosis is a comparatively new process. Forward osmosis membrane bioreactors offers high competency for the treatment of wastewater and its reuse. It has been shown that a forward osmosis membrane bioreactor can provide more than 99% organic carbon and 98% $NH_4$–N removal. Although forward osmosis membrane bioreactors have been mostly examined in laboratory-scale studies, a limited number of studies have been carried out with pilot-scale reactors.[60] Therefore, further research should be performed to study the application of real-scale forward osmosis membrane bioreactor systems.

## 8.8 Conclusion

MBR is a progressively widespread wastewater treatment process and the technology is well-developed and mature. It is considered to be the best available technology for industrial and municipal, wastewater treatment. Although, MBR technology has been used extensively across the globe for decades, MBRs are preferred over other treatment technologies, particularly when high effluent quality, easy retrofit and upgrade of old WWTP are the priority. The retention of activated sludge and wastewater constituents causes a reduction in the performance of membrane filtration. The competency of the filtration process in an MBR is defined by the filterability of the activated sludge and is determined by the connections between the biomass, the wastewater and the applied process conditions. Membrane fouling is a complex phenomenon because of the interdependency of the factors mentioned and the dynamic nature of the feed and biomass. Strategies applied for prevention and removal of membrane fouling lead to an increase in the operational and maintenance costs of the treatment system. Specifically, the high energy requirements arising from recurrent cleaning of membrane by air scouring remains a challenge in terms of consumption of energy and overall cost efficiency of full-scale MBRs.

## List of Abbreviations

| | |
|---|---|
| AS | Activated sludge |
| BOD | Biochemical oxygen demand |
| CAS | Conventional activated sludge |
| COD | Chemical oxygen demand |
| FS | Flat sheet |
| HF | Hollow fibre |
| MBR | Membrane bioreactor |
| MLSS | Mixed liquor suspended solids |
| SRT | Sludge retention time |
| TMP | Trans-membrane pressure |
| WWTP | Wastewater treatment plants |

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CHAPTER 9

# *Different Types of Advanced Bioreactors for the Treatment of Industrial Effluents*

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## 9.1 Introduction

Industries such as petroleum, pharmaceuticals, textile, food and other chemical process factories produce a large amount of wastewater that is discharged into freshwater bodies. Such wastewater consists of various contaminants like phenol, hydrocarbons, sulfides, and specific sulfur and nitrogen-containing compounds.[1] These water contaminants can have adverse effects on the environment, mainly on aquatic biota. The effective destruction of these toxic chemicals using biological methods has been intensively reported by environmental researchers and scientists in the last decades. The availability of clean and drinking water is limited in many areas of the world. The demand for large quantities of good water meet the needs of for the ever-increasing human population is encreasing.[2] In short, underdeveloped areas of the world are already facing a shortage of drinking water and water required for irrigation purposes in agricultural land.

Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

In contrast, in industrialized nations, the quality of the water available for people and commercial use will be an important issue in the coming years. In these conditions, the reuse of wastewater is the best route for beneficial purposes. A viable solution to solve these problems is the use of advanced bioreactors for effluent treatment.

### 9.1.1 Conventional Biological Treatments and Their Limitations

The activated sludge process has been commonly used as a vital process in conventional municipal wastewater treatment plants. It represents one of the most successful environmental technologies for over a century. Researchers have made significant progress with physicochemical manipulations, including optimizing reactor configurations and the use of abiotic conditions.[3] Still, there has been much less progress in understanding the ecology of the microbial communities. The activated sludge processes are dynamic biosystems, regularly exposed to different pulse and press disturbances, such as higher fluctuations in influent loads in terms of quality and quantity and environmental stressors such as climate. Wastewater treatment technologies such as chemical treatments, adsorption, membrane-based separation and biological treatment have made significant contributions to sustaining human society in the last decades. However, the ever-increasing demand for fresh and clean water push these conventional processes to their limits.[4]

Industrialization has result in a continuous increase in the emission of toxic effluents from various industries, which poses a severe threat to all living things because of their adverse effects. Nowadays, >10 000 types of dyes are produced as per the Colour Index, and global dye production is >700 000 tons per annum. Among all the dyes, an azo type of dye is the most crucial dyestuff due to its ease of preparation, better tinctorial strength and fastness properties, and the cheap and easy availability of the raw materials. Other classes of dyes include anthraquinones, aryl-carbonium, phthalocyanines, and poly-methines.[5] About 10% of dyes used in industry are released into the environment. It is a quite annoying fact that the presence of these synthetic dyes is harmful to the environment. The dissemination of dyes into water leads to coloured water, which is a visible public concern. This dispersion of dyes in water can block sunlight from reaching the bulk of the wastewater. As a result, the dispersed dyes reduce dissolved oxygen (DO) levels in the water. Dyes may also increase the biochemical oxygen demand (BOD) of the wastewater. A number of different techniques and methodologies have been developed to remediate these harmful dyes from industrial effluents. Generally, removing dye molecules is achieved *via* some chemical processes, physical separation or using biodegradation phenomena. Some techniques are widely employed, including oxidation, adsorption, biotreatment, electrochemical treatment, membrane filtration, and coagulation–flocculation. Each process has its advantages and limitations. It is not always possible to treat all types of dye wastewater with one technology. The proper choice of method depends on the quality of the industrial effluent, which depends on the nature of the dyes present in the effluent, its composition, and the impurities. There are three types of dyes: anionic, cationic, and non-ionic dyes with different chromophoric and auxochromic groups. The anionic dyes are highly soluble in water and difficult to treat with conventional methods. The biological processes are not good enough for the complete remediation of acidic and reactive dyes in wastewater. Nonionic dyes are known as disperse dyes; they do not easily get ionized in the water, and their fused aromatic ring structure makes them highly resistant to biodegradation. However, there are some cationic dyes like methyl blue, which can be quickly remediated by adsorption and advanced oxidation processes (AOPs). The severe impact of metals on human beings and the atmosphere has been of significant concern since the 1970s. Most metals are natural, generally found in the Earth's crust, and provide a background concentration. But it is the artificial sources that are of primary concern. Their presence in the environment raises the naturally low levels to potentially harmful concentrations.[6] The metals cannot be degraded; they persist in the environment and tend to accumulate throughout the food chain as living organisms readily absorb them. Some elements like copper, iron, chromium, zinc, and manganese perform physiological functions at low concentrations. If these elements are beyond their threshold concentrations, higher organisms, plants and microbes can suffer from acute toxicity. This has led to an increase in the stringency of the legislations. Therefore, environmental quality standards are set for metals under the EU Water Framework Directive (2000/60/EC). These standards are as per the risk posed, based on the severe impacts on the whole ecosystem and health. Some metals like cadmium, mercury, lead and nickel are priority water pollutants while chromium, copper and zinc are potentially primary pollutants. The metals are sometimes present in free form in the wastewater or attached to the suspended solids through surface-bound organic ligands or adsorbed onto an insoluble matrix component, like iron (III) oxide and aluminium oxide, or are present in inorganically bound soluble forms. Their speciation is dependent on the influent chemical oxygen demand (COD), influent metal concentration, pH and the alkalinity of the wastewater. Since the metals are non-biodegradable, their remediation by biological processes depends on physicochemical processes. The removal of the metals using biological methods can be carried out *via* adsorption of soluble metal by the bioreactor's activated sludge flocs or by the settlement of insoluble metal species with the sludge in a secondary settlement tank. Wastewater treatment plants produce a tremendous amount of sewage sludge as waste. This waste contains a high organic load, consisting of microbial aggregates with filamentous bacterial strains, organic and inorganic particles, extracellular polymeric compounds, and a quantity of water.[7] It can also contain some toxic substances depending on the type of industry. The disposing of such waste sludge accounts for ≈50% of the total costs of a wastewater treatment plant. Thus, disposal can have a severe impact on the environment and is regarded as public health hazards. Therefore, in the last decades, environmental researchers have been working on the development of various environmental and economically sustainable waste activated sludge management technologies such as aerobic and anaerobic stabilization methods. Anaerobic digestion is generally preferred over aerobic digestion. It has a lower impact on the environment; it can also supply part of the plant's energy requirement and be a viable alternative for conventional energy production. Many processes such as chemical, magnetic, thermal, mechanical, acoustic, electric, and hybrid pretreatment processes have been reported by researchers to enhance the dewaterability of sludge. Among these different processes, chemical conditioning was an effective treatment process for improving dewaterability performance.[8] Cationic polyacrylamide is one of the widely used chemical conditioners. It can significantly improve the sludge's dewaterability by flocculating fine colloidal particles to form a big floc thorough a mechanism of bridging and surface-charge neutralization. Treatment of activated sludge is the most commonly used technology in water resource recovery facilities to remove biological nutrients. This technology improves global water sanitation partially because of its reliability and robustness. But, it has some limitations, like higher pumping requirements and energy intensity, especially for removing nutrients such as nitrogen and phosphorous, higher generation of sludge, larger physical footprints, and associated settling issues.[9] Therefore, new technology like aerobic granular sludge technology has been reported widely in an effort to overcome the limitations of conventional biological processes.

## 9.1.2 Advanced Bioprocesses and Available Reactor Designs

Bioremediation is the bioprocess that removes water contaminants with the support of the bio-catalysts found at various levels in the ecosystem. It has benefits for the environment, human life, health and the economy.[10] This bioprocess requires minimum energy input and mild experimental conditions for the remediation of water contaminants. Sometimes, the process of bioremediation is superior to other physicochemical processes. Conventional wastewater treatment processes, such as the activated sludge process, treat the organics and suspended solids in effluent efficiently, but require a higher amount of energy. Nowadays, anaerobic digestion has been investigated as a more efficient process. It also produces methane as a value-added energy product in the process. The diverse microbial metabolism in anaerobic digestion has led to its amendment for energy production and for the production of certain chemically valuable products such as volatile organic compounds, alcohols, and hydrogen. This characteristic has become an inspiration in the search for renewable and non-traditional energy sources. The secondary treatment is generally described as wastewater treatment by a method involving a bioprocess with secondary sedimentation. Secondary treatment is simply a biological process for the treatment of industrial and other domestic effluents.

The settled wastewater is added into a well-designed bioreactor where organics are used by microbes such as bacteria, algae, and fungi under aerobic and anaerobic conditions. The bioreactor only performs well when the suitable microorganisms are selected to reproduce, using dissolved organics in the water as their energy source.[11] The bioconversion of the dissolved organics into thick bacterial biomass can fundamentally decontaminate the effluent. The treatment strategies enable the recovery of the nutrients and energy production as well. This can include a net profit, allowing the technology to gain traction on a broad scale.[12] Alternative technologies for wastewater treatment must achieve both recovery of energy and production of energy. It has been found that the anaerobic technologies can recover a measurable amount of energy from the organics (known as COD).[13] Phototropic technologies can enhance the effluent's chemical energy through the fixation of carbon dioxide during its growth and storage. Anaerobic processes are assumed to be less energy-intensive than aerobic methods because of a decrease in the wastage of the sludge and lack of an aeration facility. Some bioenergy products are still generated in anaerobic processes such as hydrogen, methane, or electrical energy production. The membrane-aerated biofilm reactor (MABR) is an emerging bioprocess in which gas-permeable membranes are employed as carriers of microorganisms in a bubbleless aerator. The membrane aerator is more useful than conventional bubble diffusers as it lowers the emission of the volatile contaminants and has low operating costs.

Besides, the large surface of the attached biomass permits the achievement of high strength COD removal and the removal of nitrogen in an MABR.[14] Bioreactors are now becoming an integral part of testing biomaterials and pharmaceuticals. Bioreactors are generally preferred for priority tests because they are cost-effective, faster, and more controlled than multifactorial animal models. Specific hypotheses are tested in the bioreactors. Many parameters like flow rate, pressure, and pulsation amplitude are involved in predicting the cell's behaviour. But these parameters are required to be changed over time in the current promising models. Such an advanced bio reactor was developed to optimize some parameters, such as the pressure and flow rate (functions of time).[15] In the recent era, bacteria have been used for several applications. They provide one of the cost-effective and eco-friendly solutions to deal with the demand of modern industry. Biocatalysts help in the breakdown of waste products to produce some medically necessary materials like proteins and antibiotics; other products such as fuel, electricity *etc.* are also produced. Bacterial immobilization methods are versatile and economic processes that can be used in different industries to improve biological processes. The immobilization permits easier separation of the cells from the products and their reuse in subsequent steps,[16] making whole process efficient and more economically feasible.

The immobilization of bacterial cells on cryogenic materials has been considered a robust approach for the application of biotechnology. Cryogels possess high mechanical strength during twisting or elongation. This can reduce the damage to both the cryogel scaffold and its inherent microporous structure during its use in physically aggressive treatment. One of the novel technologies, *i.e.* aerobic granulation technology, is also gaining more interest among researchers because of its many advantages over conventional wastewater treatment methods. The aerobic granules are auto-immobilized microspheres of mixed microorganism species, produced while using an aerobic sequencing batch reactor.[17] These formed granules are more massive and denser than the flocs of the small microbes present in a conventional activated sludge process. This fact assists in easier separation of the sludge from the treated fraction of industrial wastewater.

### 9.1.3 Aim and Objectives of the Chapter

This chapter discusses the different designs of advanced bioreactors used for biological wastewater treatment such as sequencing batch, aerobic and anaerobic stirred tank, fixed and fluidized bed reactors. The chapter also discusses the use of membrane separation technology with bioreactor design and all possible integration approaches for improving the efficiency of the bioprocess.

## 9.2 Sequencing Batch Reactor for Effluent Treatment

The sequencing batch reactor is a widely employed configuration for wastewater treatment. The commercial application of the sequencing batch reactor has already been carried out in >1200 plants in North America, 700 plants in Japan, 100 plants in Australia, and ≈150 plants in Germany.[18] The sequencing batch reactor has also been studied *via* a wide-range of laboratory, pilot and full-scale applications for effluent treatment (municipal and industrial effluents), especially for reducing biochemical oxygen demand (BOD). Algal growth and the phenomenon of eutrophication in natural water resources result from the presence of nitrogen. The point sources of nitrogen to the natural water sources are majorly contributed by sewage discharge. The clean water act has imposed strict regulations for the discharge of nitrogen into sewage waste. Taking the example of the James River Basin in Virginia (USA), nitrogen discharge will be reduced by 43% by 2021. Sequencing batch reactor systems have been recognized to offer considerable benefits over the alternative traditional flow systems for the treatment of both industrial and domestic effluents. These systems can be designed with the use of single or multiple tanks in parallel.[19] Figure 9.1 shows a schematic representation of a sequencing batch reactor during one complete cycle.

The five distinctive phases of a single cycle in one of these tanks are denoted as fill, react, settle, draw, and idle. The designer can easily vary the time devoted to each phase. Different functions occur in each step as per the particular treatment objective. This flexibility of this system permits designers to use the sequencing batch reactor to study many research objectives. One objective is during construction (for reduction of organics and suspended solids),

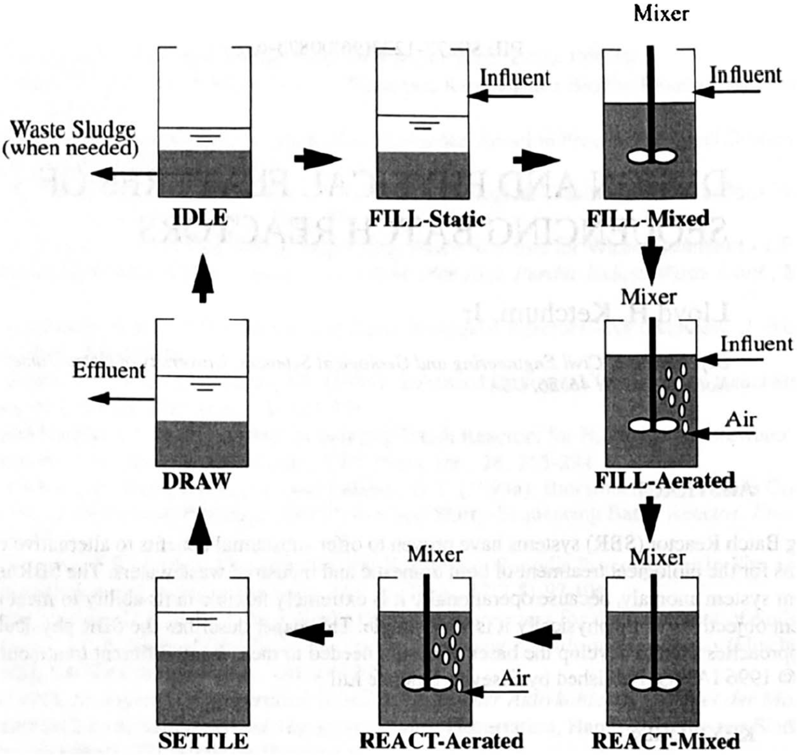

**Figure 9.1** Schematic representation of a sequencing batch reactor during one complete cycle. Reproduced from ref. 19 with permission from Elsevier, Copyright 1997.

and another objective is at a later stage (for removal of organics, suspended solids and nitrogen). The filling phase is for the addition of influent and may be static, mixed or aerated, depending on the study objectives. It results in the input of minimum energy and higher substrate concentration. The design of influent flow rates majorly determines the number of sequencing batch reactors. Multiple sequencing batch reactor systems are ubiquitous for many municipal and continuous industrial influents. In these systems, fill is not allowed to overlap with settle and draw. The sequencing batch reactor (SBR) method is possibly the most promising and is capable of working more successfully than the proposed activated sludge process for the removal of organics and nutrients.

One method for removing nitrogen during the treatment of wastewater is through the two-step oxidation of ammonia to nitrate with microbially mediated nitrification.[20] The oxidation of ammonia to nitrate was carried out in the first stage, with two chemolithotropic groups of bacteria, such as ammonia-oxidizing bacteria and nitrite-oxidizing bacteria. The process is sometimes integrated with denitrification, and is generally carried out by anoxic heterotrophic bacteria like Alcaligenes, Pseudomonas, Bacillus, and Methylobacterium. The biological removal of the phosphorous is dependent on the uptake of excessive phosphorous by phosphorous-accumulating organisms. This is done by alternating aerobic, anaerobic, and sometimes anoxic conditions. In recent times, research scholars have started to report the use artificial intelligence (AI) technologies. These technologies are widely implemented in different areas such as automation, chemical and biochemical processes, and some complicated nonlinear systems.[21] The most general AI controlling strategies are neural networks and fuzzy networks. These networks are integrated with proportional–integral–derivative (PID) control. The fuzzy method can prevent DO content in aeration. The fuzzy controller can save a significant amount of energy consumption compared to a standard on/off control. Zinc oxide nanoparticles could be used in wastewater treatment plants, but may have some adverse effects on functional microbes. These nanoparticles induced a moderate reduction in the COD, nitrogen and phosphorous removal after mid- to long-term exposure.[22] In this way, the sequencing batch reactor offers many attractive features for essential research applications.

## 9.3 Aerobic and Anaerobic Stirred-tank Bioreactors

Gola *et al.* studied the phenomenon of bioremediation for the removal of heavy metals like Cu, Cd, Zn, Cr, Pb and Ni from wastewater with the use of four continuous stirred tank reactors (CSTRs), in which two operated under aerobic conditions.[23] In contrast, the other two performed under anaerobic conditions. The system of four bioreactors (R1, R2, R3, and R4) was employed, with a working capacity of 4 L. These CSTRs were fabricated by using an acrylic cylinder of length 13 cm, with an inner diameter of 13 cm and an outer diameter of 15 cm. The stirred tank reactors were selected for the bioremediation because the concentration of contaminants and nutrients remains uniform in this type of bioreactor. It also assists in maintaining the consortium at a constant average growth rate. Bioreactors R1 and R2 functioned under aerobic conditions, while R3 and R4 operated under anaerobic conditions. The diffused air was supplied in the cylinder using an air pump to maintain the bioreactor's aerobic conditions. The diffuser was fixed to the bottom of the cylinder. Sparging was done for 10 min at a regular interval of 24 h to maintain the anaerobic conditions. Bioreactor R1 was fed with the real wastewater, while bioreactor R2 was fed with multi-metal spiked wastewater (30 mg $L^{-1}$ hexa-metal mixture). Likewise, bioreactor R3 was fed with actual effluent, while bioreactor R4 was fed with multi-metal spiked effluent. Figure 9.2 shows schematic diagrams of the continuously stirred tank bioreactors, *i.e.* R1, R2, R3, and R4 in parallel.

In the set stirred tank bioreactors fed with the real effluent, heavy metal removal of 30–100% was observed. The other group of bioreactors fed with spiked metal ion concentration showed heavy metal removal of 70–100%. The improvement in the heavy metal removal was observed because of the

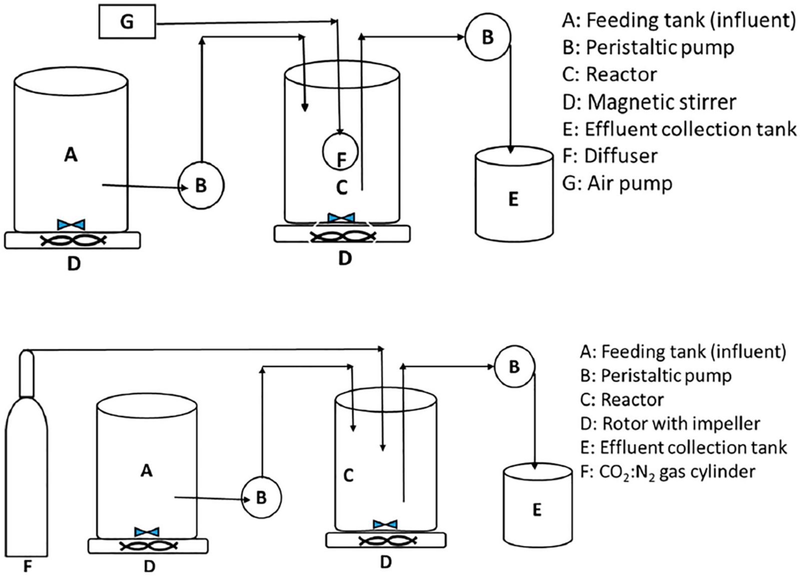

**Figure 9.2** Schematic diagrams of (top) aerobic bioreactors (R1 and R2), and (bottom) anaerobic bioreactors (R3 and R4). Reproduced from ref. 23 with permission from Elsevier, Copyright 2020.

acclimatization of the microbial consortia at a higher concentration of metals. Asato *et al.* investigated a two-stage anaerobic digestion system consisting of a CSTR and an up-flow anaerobic sludge blanket in series.[24] The system performance was evaluated for semi-continuous digestion of food waste and corrugated cardboard mixtures, comprising municipal solid wastes. The loading rate of organics to the CSTR was 8–32 g COD $L^{-1}$ with variable mixture ratios. In the CSTR, the yield obtained for volatile fatty acids reached 24%, using a mix of 65% food waste and 35% corrugated cardboard (calculated by taking a COD basis of 8 gm COD per litre).

A denitrification bioreactor (aerobic biofilm reactor cascade) was efficiently used to treat heavy oil refinery effluent.[25] Excellent results (for simultaneous removal of COD and nitrates) from this bioreactor system indicated that Rhodocyclaceae and Comamonadaceae were dominant denitrifiers in the nitrification reactor and Pseudomonas was the predominant microorganism in the aerobic biofilm reactor. Inglesby and Fisher used a semi-continuously fed CSTR and advanced flow-through anaerobic digestor in combination with a recirculation loop microbial fuel cell for methane generation using *Arthrospira maxima* (as a sole feedstock).[26] The methane yield was found to increase because of the use of recirculation loop microbial fuel cells. As a result, the energy efficiency of anaerobic digestion by *A. maxima* increases. Aerobic and anaerobic wastewater treatment systems could be assessed by conducting modelling studies, in which the energy requirements for both systems could be compared. The modelling studies require consideration of aeration for bioremediation in aerobic membrane reactors, the energy recovery from the production of methane in anaerobic membrane reactors and the energy demands of submerged and side-stream membrane configurations.[27]

## 9.4 Fixed- and Fluidized- Bed Bioreactor Designs

Ren *et al.* used a fixed-bed bioreactor to remove nitrate using $Fe^0$ and $Fe^0$ covered with $Cu^0$. It was a cost-effective, feasible and robust technology for reducing nitrate in an aqueous medium with chemical degradation.[28] Two parameters, including the pH of the solution and the mass ratio of $Fe^0$ and Fe/Cu, were optimized to study the system's performance, *i.e.* a fixed bed reactor. The developed method showed nitrate removal of >99% in a short hydraulic retention time of 16 min. The treatment of cassava starch wastewater was carried out in a horizontal shaped anaerobic fixed-bed reactor to remediate organics and biogas production. Two fixed-bed reactors were used with two different types of packing materials like bamboo rings, and flexible polyvinyl chloride (PVC) rings. PVC material of length 90 cm and diameter 15 cm was used. The reactor efficiency was tested in 13 assays (A1–A13) by using organic loading rates in the range 1.7–15 g $day^{-1}$ $L^{-1}$, and the hydraulic retention time varied from 4 to 0.8 days. The highest biogas productions of 1.4 and 1 per day were observed in assay A6 for an applied influent concentration of 15.1 g $L^{-1}$ and hydraulic retention time of 2.7 days. The COD removal efficiency was found to increase with an increase in the organic loading rates. Solids removal of ≈85% was achieved in both the bioreactor systems.[29] No changes were noticed in the packing materials composition and structure even after 450 days of treatment. It can be concluded that bamboo and PVC are the cheap and effective alternatives for biomass immobilization. Two pilot-scale membrane bioreactors (fixed-bed hybrid and conventional type) of the same volume, 1.8 $m^3$, a cross-sectional area of 0.36 $m^2$ and a height of 5.2 m were installed in parallel. Figure 9.3 shows the complete set-up of those membrane bioreactors. The set-up consists of two column-shaped reactors, which were made of stainless steel.[30] The effluent was pumped into both the bioreactors with the use of volumetric pumps. The flow rate was regulated with an electrode-type level switch. The aeration was fixed to the bottom side of the bioreactors and was also used for the cleaning of membranes. An airflow rate of 8 $m^3$ $h^{-1}$ was supplied, which also served the purpose of continuous stirring in the membrane zone. The rotameters measured the air coming from the blower and was used to maintain a constant flow rate.

Each bioreactor had a recirculation pump rate of 700 L $h^{-1}$. Hollow fibre membranes were used for both the bioreactors. Those membranes were made up of polyvinylidene fluoride having a nominal pore size of 2 $m^2$ per module. Six modules were fitted in each bioreactor to give a total filtering surface area 12 $m^2$. The only difference in the configuration of the reactors was that the hybrid membrane bioreactor consists of a support medium for the growth of the attached biomass. This pilot-scale study was performed to treat municipal

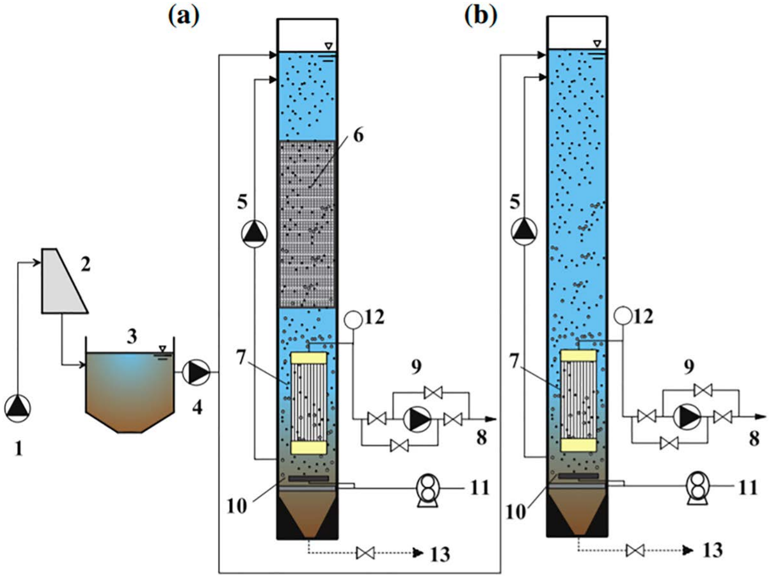

**Figure 9.3** Schematic diagrams of (a) a fixed-bed hybrid membrane bioreactor, and (b) a conventional membrane bioreactor.1 Municipal wastewater, 2 screen, 3 grit removal, 4 feed pump, 5 recirculation pump, 6 fixed-bed support, 7 membrane module, 8 permeate, 9 back-wash pipe, 10 air diffuser, 11 blower, 12 vacuum gauge, and 13 sludge purge. Reproduced from ref. 30 with permission from Elsevier, Copyright 1997.

wastewater and compare the performances of both bioreactor configurations. Long *et al.* reported heavy metals biosorption in industrial effluent using mushrooms in a small-sized pilot set-up using a packed-bed system.[31] Mushrooms were not used directly in the reactor; it was chemically-modified with sodium hydroxide (NaOH). Two types of mushrooms (*Agaricus bisporus* and *Pleurotus cornucopia*) were selected for the study. A removal efficiency of ≈95% was observed for all heavy metals with total feeding of 13.64 mg $g^{-1}$ in a treating volume 156 L. An anaerobic fixed-bed reactor from a lab-scale to a pilot-scale set-up was successfully employed to treat dairy effluent using a hybrid material composed of zeolite and tyre rubber.[32] The influence of hydraulic retention times ranging from 1 to 5.5 days, was studied in a fixed-bed reactor system. COD removal efficiencies of 28.3–82.1% were observed for the varying hydraulic retention times.

No clogging was noticed over 6 months. It means that one can use this reactor system to achieve a hydraulic retention time five times lower than with a conventional digestor. The produced biogas in the pilot set-up of packed-bed reactors was utilized for the farm's electricity generation. Around 63.6% of COD removal efficiency was achieved in a full-scale anaerobic plant for a hydraulic retention time of 3 days. Izadi *et al.* studied the performance of an integrated fixed-bed membrane bioreactor to remove contaminants in paper recycling effluent.[33] Such an integrated system for wastewater treatment is the most appropriate alternative to traditional methods. The removal efficiencies of COD, ammonium, nitrite, nitrate, and total nitrogen for permeate and supernatant were 92–99%, 59–97%, 78–97%, 59–98%, and 68–92%, respectively. This way, the integrated fixed-bed membrane bioreactor system can be employed effectively to remove water contaminants in paper recycling effluent. Like an anaerobic fixed-bed reactor, the anaerobic fluidized-bed bioreactor platform could also be used to treat wastewater. This platform uses a biofilm linked to a carrier medium, and hence the microorganisms used in such a process are anaerobic. As this reactor system only needs an anaerobic environment, a single, vertical column operated in a conventional fluidization regime can be used for the treatment. Figure 9.4 shows a schematic representation of an anaerobic fluidized-bed reactor system. For ideal operation, this type of fluidized-bed reactor system can be operated at a temperature of 37 °C and pH value in the range of 6.8–7.4.[34] An anaerobic fluidized-bed bioreactor can effectively treat low strength effluent with a COD of 100–200 mg $L^{-1}$. The use of coarse activated carbon particles fulfills the purpose of suspension in the fluidized-bed reactor system. This reactor system was developed to permit methane generation and the recirculation of effluent using air bubbles to suspend granular activated carbon particles.[35] The fluidized-bed reactor system can also be combined with the biological reactor of an activated sludge process and can be used to treat saline wastewater. 80% of COD removal efficiency was achieved for a salt concentration

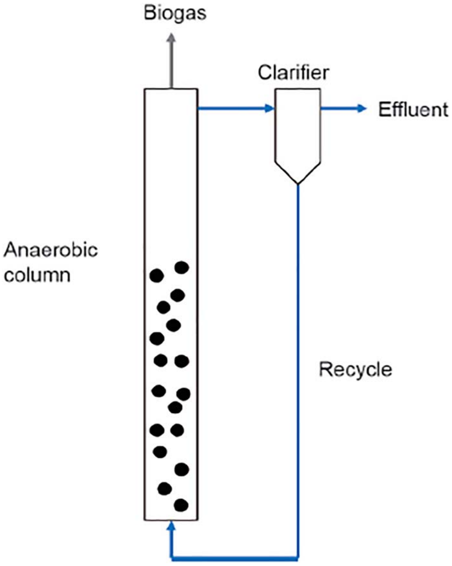

**Figure 9.4** Anaerobic fluidized-bed reactor set-up. Reproduced from ref. 34, https://doi.org/10.1016/J.ENG.2017.03.021, under the terms of a CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

of 0.5%, which was higher than a conventional reactor using an activated sludge process. The fluidized-bed reactor's hybrid system does not require sludge returning because of the uniform concentration of mixed liquor suspended solids (MLSS), one of the significant advantages of this system.[36] Moreover, the dissolved oxygen (DO) concentration in this hybrid system was observed to be higher.

Sulfur and nitrate contaminated effluent could be treated by using an anoxic sulfur oxidizing moving bed biofilm reactor. This treatment was continuously monitored for 306 days by feeding nitrogen to sulfur ratios of 0.5, 0.3 and 0.1, respectively.[37] The removal efficiency of thiosulfate reached >98% for the nitrogen to a sulphur ratio of 0.5, while nitrate ($NO_3^-$) was removed entirely for all nitrogen to sulfur ratios. Anaerobic and fluidized-bed membrane bioreactors have the full potential to treat domestic and other effluents effectively. There is only one limitation with this reactor system, *i.e.* membrane fouling. This fouling can be avoided if membranes are fixed directly in contact with granular activated carbon.[38] The polymer, low-density polypropylene, can also be effectively used as a bio carrier for effluent treatment in a fluidized-bed reactor system. This bio-carrier polymer was used with a surface area of 524 $mm^2$ and a density of 870 $kg\ m^{-3}$. COD removal efficiency of 97.5% was attained for an initial concentration of 2 $g\ L^{-1}$, superficial gas velocity 0.00212 $m\ s^{-1}$, and hydraulic retention time of 40 h.[39] It was found that the COD reduction was increased with an increase in the value of superficial gas velocity and *vice versa*. Three-phase fluidized-bed reactors have also gained substantial application in treating industrial effluent from chemical and biochemical industries. There are many reasons for its extensive use, such as simple construction, lower maintenance due to the lack of moving parts, higher functional interfacial surface areas and more mass and heat transfer per unit volume.[40]

## 9.5 Membrane-based Technology and Other Possible Integration Approaches

The effluent produced by different industries has a significant impact on the environment. The pulp and paper industry releases a large amount of wastewater and faces the challenges of meeting stringent regulations. The pulp and paper industry generates the third largest amount of effluent after primary chemical and metal industries. These water contaminants could be reduced by adopting membrane-based technology and specific integration approaches. Membrane bioreactor technology has been extensively used for different wastewater treatments because of its ability to treat wastewater as per the water quality regulations.[41] The major limitation in using a membrane bioreactor is membrane fouling, which can reduce effluent permeate flux. But the performance of the membrane bioreactor can be enhanced by effluent pretreatment methods and by the addition of a fouling reducer. Membrane-based technology has been found to be more effective than conventional wastewater treatments. In recent years, several methods like chemical (chemical oxidation and coagulation–flocculation), physical (adsorption and separation) and biological (sequencing batch and activated sludge) techniques have been employed for effluent treatment. Among various processes, membrane-based technology has immense potential for the efficient treatment of non-degradable effluent. This technology has the advantages of better effluent quality, higher volumetric loadings of organics, a lesser amount of sludge generation and a small footprint.

Further, the anaerobic membrane bioreactor offers the possibility of application in bioenergy production with microbial fermentation. It provides an entirely new method of integrating biological wastewater treatment with bioresource transformations.[42] Membrane bioreactor technology can also be combined with the activated sludge process with micro- and ultra-filtration.[43] It is widely regarded as an efficient tool for the treatment of industrial effluent. Submerged bioreactor systems are gaining more and more interest due to their robustness and flexibility of operation. This technology was commercially installed with a reverse osmosis (RO) system with a full-scale capacity of 200 $m^3$ $day^{-1}$ for water reuse in a German laundry. A small-scale of capacity 0.4 $m^3$ $day^{-1}$ has been successfully tested in a Chinese textile factory. Erkan *et al.* used an aerobic-type submerged membrane bioreactor to treat dairy effluent at a hydraulic retention time of 15 h and a sludge retention time of 14 days with constant permeate flux.[44] The removal efficiencies of COD, ammonia-nitrogen and orthophosphate were ≈98, 95, and 89%, respectively. These results show that the submerged aerobic bioreactor system is an effective treatment technique for removing organic matter and nutrients in dairy wastewater.

The integration of membrane bioreactors with RO is also a promising alternative for sewage treatment because of its low cost. Such types of bioreactor systems are also called osmotic bioreactor systems. This is also a potential solution for water reuse. The osmotic bioreactor's unique features, such as higher rejection of water contaminants and the absence of an RO brine system, support its full-scale installation in the industry.[45] Different media could be used as biofilm support, such as granulated activated carbon, sand, plastics, and several clay materials. Some critical surface characteristics of these media like surface area, porosity and especially surface roughness can influence biofilm generation during startup. Such bioreactors are popular and are described as expanded bed bioreactors. The biofilm is associated with a small inert medium, whose bed is augmented by the vertical velocity of incoming waste mixed with recycling.

Small-size particles (like catalysts) provide a larger surface area for the attachment of the biofilm, and become lighter and are fluidized at lower up-flow velocities, and hence reduce the recycle rate.[46] The phenomenon of anaerobic digestion can be integrated with photocatalytic treatment in a fluidized-bed reactor for the treatment of distillery wastewater. Anaerobic digestion is an efficient treatment for removing organic matter in industrial effluent, but it is ineffective for colour reduction. In addition, photodegradation can positively reduce the colour, but it requires a higher amount of energy.[47] The combination of both these processes improved colour reduction up to 85% compared with anaerobic digestion alone. Membrane bioreactor technology can also be integrated with advanced oxidation processes (AOPs), granulation technologies, and reverse and forward osmosis to enhance the efficiency of the effluent treatment process. The use of membrane bioreactors could be sustainably developed for biofuel production, electricity generation and the recovery of nutrients to benefit the environment and make money.[48] The combination of membrane bioreactors with other processes can be considered a multiple-barrier approach for effluent treatment. This integration's primary purpose is to improve the quality of permeate, reduce membrane fouling, and enhance the stability of the treatment process. Li *et al.* investigated a fluidized-bed membrane bio-electrochemical reactor using fluidized granular activated carbon as a means of membrane fouling control.[49] This technology can generate electricity with the removal of water contaminants from the wastewater. When this type of reactor was attached to a microbial fuel cell for treating the effluent in a cheese factory, the microbial fuel cell acted as a system for energy recovery and the removal of water pollutants. It can reduce the COD by >90% and remove >80% of suspended solids. Sathya *et al.* evaluated the performance of advanced oxidation processes combined with a membrane bioreactor to treat textile wastewater.[50] This study was conducted by using three reactors, including an ozonized membrane bioreactor, membrane bioreactor and photo catalysis process. A polyvinylidene difluoride hollow fibre membrane (pore size of 0.1 μm) was used as a filtration membrane. The visible photocatalyst, tungsten oxide, was utilized in spongy alginate beads in the photochemical reactor. A COD removal efficiency of ≈93% was observed for the optimum conditions of photocatalyst dose 500 mg $L^{-1}$, 10% membrane filterability and ozone dosage of 5 g $h^{-1}$. It can be concluded that membrane systems are suitable and well fitted for the treatment of textile industry effluent.

## 9.6 Conclusions and Future Perspectives

Advanced bioreactor technology can be efficiently applied in the treatment of industrial effluent to remediate organic matter and nutrients. The application of such a system is an emerging technology. Advanced bioreactors such as sequential batch, stirred tank, and different fixed-and fluidized-bed reactors are excellent alternatives to conventional biosystems. More research studies should be focused on using these bioreactors for the treatment of real wastewater. Some new modifications in this advanced technology are expected to yield better solutions for effluent treatment. The integration of bioreactor systems with other advanced processes can provide complete removal of colour and COD. Environmental researchers have developed various advanced bioreactors with attractive characteristics, and their industrial application is highly recommended. The many advantages of these advanced bioreactor systems make them more reliable and valuable for waste management than conventional processes. Future research in membrane bioreactor technology should be focused on the reduction of energy demand and membrane fouling. The continuing efforts of industry and academia can contribute to the emerging composite membrane bioreactor technology for effluent treatment and valorization.

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CHAPTER 10

# Membrane Bioreactors: An Advanced Technology to Treat Industrial Waste Water

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## 10.1 Introduction

Industrial development is a direct reflection of the progress of society. Through generation of employment, industrialization plays a pivotal role in controlling the socio-economic infrastructure of any country. However, besides societal development, industrialization may have a negative side effect, *i.e.* environmental pollution which imparts major damage to society. Industrial waste water is one of the most common by-products of any industrial/commercial activity. It is the water which has been used by the industry for its commercial production and once used it is considered as waste and needs to be treated before discharging to the environment, else it may pollute receiving water sources and cause a great threat to aquatic life and hence to the total life cycle.

Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

Industrial waste water includes contaminated storm water, cooling water, process waters and wash-down waters. It may be produced by any of the industries like chemical manufacturing, energy production, metal production and finishing, mineral processing, petrochemical works, fertilizer production, food processing, textile, leather, vehicle and plant processing, recycling works, water and waste water treatment *etc.* The nature of contaminants in industrial waste water vary depending upon their source. Depending on their nature, industrial water pollutants may be subdivided into organic, solid, toxic, oil, acid–base, biological, nutritional, aerobic, thermal, and sensory.[1]

One of the biggest sources of the industrial waste water is fossil fuel based power plants, specifically coal fired plants. The discharged waters from such plants contain a range of different metals, such as mercury, chromium, cadmium, lead, arsenic, selenium and also nitrogen compounds including different nitrates and nitrites.

The second most important source of waste water is oil and gas fracking. The water from shale gas drilling is highly salty containing ≈30 000–32 000 ppm of sodium. Moreover the water that is injected into the well to facilitate drilling contains sodium, magnesium, iron, barium, strontium, manganese, methanol, chloride, sulfate *etc.* in high concentrations. Water used for fracking may also contain toxic hydrocarbons like benzene, toluene, ethylbenzene and xylene.

In steel industries water is mostly used for cooling and by-product separation. It becomes contaminated with cyanide and ammonia. Cyanide is also available in the waste water stream of coal gas, coking, electroplating, acrylic, metal cleaning, gold and acrylonitrile refining industries. Waste water from steel industries contains benzene, naphthalene, anthracene, phenols and cresols. Water is used along with hydraulic oil in such industries as a lubricant and coolant during forming of iron and steel into sheet, wire or rods. Hence waste water is contaminated with hydraulic oil also. Oil is also present in the waste water stream of oil refining, food processing, natural gas processing and oil industries. Hydrochloric and sulfuric acids are used along with the water for steel galvanizing, hence the reject water contains waste acids. Similarly acid is available abundantly in the waste water stream of mining, chemical, steel, machinery and electroplating industries and non-ferrous metallurgy. The waste water from caustic soda, chemical, fibre, paper, leather, printing and dyeing, oil refineries, and electroplating industries contains alkali as a major contaminant.

The discharge from the heavy metal industries contains large amounts of metal-contaminated waste water. Industries handling heavy metal such as Cd, Cr, Cu, Ni, As, Pb and Zn are highly hazardous among the chemical-intensive industries. Similarly the waste water from smelting, metal mining, electroplating, batteries, metal processing and chemical industries is rich in Cd and its compounds. As is also found in the waste water from pharmaceutical, chemical, metallurgical, ore processing, pesticides, paint and fertilizer industries. The waste water stream of the specialty glass industry, smelting, mining, electroplating, chemical, metal processing, batteries, *etc.* contains a high concentration of Cr. The presence of Pb in high concentration has been identified in the waste water of pesticides, smelting, lead paint, gasoline explosion, chemicals and enamel industries. Hg is abundantly available in the waste water of explosives, mercury refining, chlor alkali, mercury pesticides, chemicals, instruments and electroplating industries. Because of their high solubility in the aquatic environment, heavy metals can be absorbed by living organisms and thus enter the food chain. The waste water discharged from metal plating, metal finishing and printed circuit board manufacturing operations contain metal hydroxides of iron, magnesium, nickel, zinc, copper and aluminium. Dealing with mine tailing is a challenge. It is a mixture of water and finely ground rock which is left over when the mineral concentrate is removed. Such tailing is an environmental liability and needs proper treatment.

Organic phosphorous, organic chloride, pesticides, insecticides, animal waste and fertilizer remain present in food and agricultural waste water. A large amount of particulate matters and soluble organic compounds are present in the water used to process food from raw materials.

One of the high water consumption sectors is the textile industry. Waste water from the textile industry is another important source of pollution as it contains a large amount of inorganic and organic chemicals such as salts, enzymes, surfactants, oxidizing and reducing agents and free chlorine and they are highly coloured because of the presence of dyestuffs. In fact textile industry waste water is of high pH and loaded with suspended particles, COD and BOD. Free chlorine is also present in the waste water of papermaking industries.

The waste water produced from nuclear and weapons production industries, hospitals and radioisotope laboratories is majorly contaminated with radioactive substances. The reject stream of the water treatment plant may contain different harmful compounds like trihalomethane, haloacetic acid, heavy metals, different synthetic organic compounds *etc.*

## 10.2 Conventional Techniques for the Treatment of Industrial Waste Water

One of the major hindrances to the sustainable development of society is the huge shortage of water, arising specifically due to rapid industrialization and population growth, and such water deficiency has enormous societal impact. Hence tremendous thrust has been given to the quest of proper solutions to solve this problem. It is critically important to treat such industrial waste water, not only to control environmental pollution but also to conserve today's most precious commodity on earth, *i.e.* water. Treatment of industrial waste water makes it suitable for agricultural and other miscellaneous purposes. Such efforts will not only recycle the water but will also control environmental pollution. The contaminants present in the water in quantities from $\mu g\ L^{-1}$ to $g\ L^{-1}$, known as micro-pollutants, are highly harmful to the environment and in turn to human health. Physical, mechanical, biological and chemical are the four fundamental techniques for the treatment of waste water.[2,3]

The three most important branches of physical methods are flotation, sedimentation and coagulation. Flotation is mostly used for solid–liquid separation where the density of the solid particles are lower, or is made lower, than the liquid in which they are found. This is basically a gravity separation method where rising gas bubbles act as a transport medium, attaching themselves to the solid particles and driving them from the body of the water to the surface. Sedimentation is a gravitational settling where insoluble and heavier particles like grit and particulate matter in suspension in water are settled out under the effect of gravity. Sedimentation is basically done prior to coagulation or filtration to reduce the load on the subsequent processes. Sedimentation is one type of clarification and there are several techniques for applying sedimentation, such as horizontal flow, radial flow, inclined plate, ballasted floc and floc blanket sedimentation. Sedimentation is done at the initial stage of the water treatment process. Coagulation is also applied for solid–liquid separation and is basically agglomeration of the finer particles by overcoming their interactive forces. Coagulation is done for particles which do not settle by standing. In a colloidal suspension the particles bear an electric charge and repel each other. A coagulant with the opposite charge is added to the water which overcomes the repulsive charge and destabilizes the suspension to form a micro-floc, and subsequently precipitation takes place.

Mechanical techniques for waste water treatment are screening and filtration. Screening is the first operation unit in a waste water treatment plant. It is the removal of the solid particles from waste water which may damage other process equipment and reduce the efficiency of the whole system. Different types of screens are available which are classified according to their openings and mechanism of removal. Filtration is basically removal of particles that are in suspension in water. Staining, sedimentation, flocculation and surface capture are the four different pathways through which removal might takes place in filtration. When particle removal takes place at the surface of the filter medium, it is known as straining, and when deposition takes place within the filter medium it is known as in-depth filtration.

Biological waste water treatment is basically a secondary waste water treatment which is done after removal of the larger contaminants either by settling or by filtration. It is basically the breaking down of the organic contaminants from highly organic laden waste water specifically produced from industries, such as food and beverage, oil and gas, chemical manufacturing *etc.* In this technique bacteria/some protozoa/other specialty microbes are used. These organisms break down the organic pollutants for their food, then stick together and generate a flocculation effect which results in the organic matter settling down out of solution. The generated sludge is dewatered and disposed of as solid waste. Biological waste water treatment may be aerobic, anaerobic or anoxic. In an aerobic process microorganisms need oxygen to break down the organic matter to $CO_2$ and microbial biomass. An anaerobic process is carried out without oxygen and products are mainly methane, $CO_2$ and excess bio-mass. In anoxic biological waste water treatment microorganisms use molecules other than oxygen specifically to remove nitrate, nitrite, sulfate, selenate, selenite *etc.*

In chemical waste water treatment the dissolved contaminants are removed by the addition of specific substances. The added reactant converts a previously dissolved substance into an insoluble substance that can be filtered out from the water. This process is comparatively unattractive compared with other techniques as it increases the net dissolved solids in the contaminated water. Chemical waste water treatment includes processes like adsorption, chemical precipitation, ion exchange, neutralization, disinfection *etc.*

Traditional waste water treatment processes involve three different steps, *i.e.* primary, secondary and tertiary.[4] Some applications need more advanced separation processes known as quaternary water treatment. This is needed when particles are present at ppm or ppb levels. This stage basically involves oxidation or very fine filtration. The nature and size of the solutes removed at each of these stages are different. Primary treatment is removal of particles that either float or settle by gravity. Screening, comminution, grit removal, and sedimentation are parts of the primary treatment. This is generally done in large settling tanks equipped with a mechanical scrapper. These scrappers hold back the settled material, *i.e.* sludge, and are fed to a digester, while the remaining liquid moves to the secondary water treatment. Secondary treatment is further purification of the waste water through biological degradation. The three primary steps for the secondary water treatment are bio-filtration, aeration and oxidation ponds. In bio-filtration three different filters, namely sand filters, contact filters or trickling filters, are used to remove any additional sediments from the waste water. Aeration is done by passing air for a long duration through the waste water mixed with a solution of microorganism. The process may last up to 30 h. It increases the oxygen saturation and degrades the soluble organics in the water. Oxidation ponds are generally used in warm climates where natural water bodies like lagoons are used. Waste water is passed through such bodies for a definite time period and then retained for 2–3 weeks. Secondary water treatment reduces the bio-degradable contaminants to a safer level which may be discharged to the environment. Tertiary water treatment is basically removal of dissolved nitrates and phosphates, which is done by using activated carbon. After tertiary treatment the quality of the water improves to the domestic or industrial level and sometimes it includes removal of pathogens, which upgrades the water to the drinking standard.

## 10.3 Advance Technologies for the Treatment of Industrial Waste Water

With the rapid and diversified growth of industries the nature of industrial waste water is becoming more and more complex. Although conventional water treatment processes remove most of the chemical and microbial contaminants, the effectiveness of these processes are facing challenges because of several stringent government-imposed environmental policies. A very strict regulation has been imposed over a much broader range of contaminants in discharged industrial waste water which specifically includes synthetic organic compounds and nutrients like nitrogen and phosphorous, as they are highly harmful to the human health. Because of the huge exploitation of water resources with ever increasing growth of population it is becoming a compulsory to recycle and reuse industrial waste water for domestic, agricultural and other purposes. Obviously this needs very precise removal of toxic contaminants. Such necessity has led to the development of advanced waste water treatment technologies which may remove potentially harmful contaminants in much efficient ways than the conventional water treatment processes. In some of the cases such newly developed advanced waste water treatment technologies have been found to be competent and cheaper than the conventional waste water treatment processes.[5] Hence advanced waste water treatment processes are those which reduce the level of impurities to a level that could not be attained through conventional secondary or biological treatment. Advanced waste water treatment is used for the removal of additional organic and suspended solids, nitrogenous oxygen demand, nutrients such as phosphorus and nitrogen, a high percentage of suspended solids and toxic material.[4]

To address such challenges, a variety of advanced waste water treatment technologies, such as advanced oxidation and photo oxidation processes (AOP), UV irradiation, automatic variable filtration (AVF), electrochemical processes, adsorption, photo-catalysis, membrane filtration *etc.* have not only been proposed but tested and applied to meet both present and future treatment requirements.

### 10.3.1 Advanced Oxidation Process (AOP)

In AOP a highly reactive radical, particularly the hydroxyl radical ($\cdot OH$), acts as primary oxidant, and reacts with pollutants to degrade them to simple, non-toxic molecules. Among the different free radical species, like superoxide anion radical ($O_2^{\cdot -}$), hydroperoxy radical ($HO_2^{\bullet}$) or alkoxy radical ($RO^{\bullet}$), the hydroxyl radical has attracted most of the attention because of its high reactivity, powerful oxidizing capability and non-selective nature. AOP is basically applied for the destruction of inorganic and organic contaminants from waste water. Radical addition, hydrogen abstraction, electron transfer and radical combination are the four basic pathways by which the hydroxyl radical attacks the organic pollutant. Hydroxyl radical generation is facilitated by combining ozone ($O_3$), hydrogen peroxide ($H_2O_2$), titanium dioxide ($TiO_2$), heterogeneous photo-catalysis, UV radiation, ultrasound and high electron-beam irradiation.[6] Among these $O_3$–$H_2O_2$, $O_3$–UV, $H_2O_2$–UV and heterogeneous photocatalytic processes have been found to be highly promising for the degradation of water pollutants. Apart from being ozone- and UV-based, AOP may be Fenton- and photo-Fenton-based also. In this case hydroxyl radicals are generated by the reaction of iron salts with $H_2O_2$ under mild acidic condition. Here the iron catalyst is regenerated. In the photo-Fenton process UV visible radiation is used to generate hydroxyl radicals.[7] The AOP concept has been extended to the oxidative process with sulfate radicals also. Ultrasound irradiation, *i.e.* sonolysis, has also been used for AOP.

### 10.3.2 UV Irradiation

UV radiation can be used effectively to reduce the micro-organism load in waste water. It basically reduces the concentration of pathogens, namely bacteria, viruses and protozoa. UV light, a form of electromagnetic radiation having wave length in the range 200–280 nm is able to inactive micro-organisms.[8] UV irradiation is absorbed by the protein, DNA and RNA of the micro-organism. At a higher UV dose the absorption by proteins leads to the disruption of the cell membrane and damage to the nucleic acid, which ultimately results in the death of the cell. This prevents the replication of micro-organisms. At a lower UV dose the absorption takes place by DNA or RNA and results in cell deactivation. The efficiency of UV light to inactivate the water-borne pathogens decreases in the order protozoa > bacteria > bacterial spores > viruses > bacteriophages. The performance of the UV radiation depends upon three different factors, namely intensity of the UV light, exposure time and characteristics of the water.[6] UV light intensity is controlled by nature of the UV lamp, reactor geometry and fouling characteristics of the materials present in the water. The characteristics of the water play a predominant role as many constituents of waste water can absorb UV light and thus reduce its average intensity. Suspended solid is one of the major culprits that reduces UV light intensity and also provides a shield to the micro-organisms, protecting them from UV light.

### 10.3.3 Automatic Variable Filtration

Automatic variable filtration (AVF) is a state-of-the-art tertiary water treatment technology used for removal of suspended matter, turbidity, BOD, reactive substances and phosphorous to make the waste water suitable for re-use. This process may effectively remove bacterial contamination and microorganisms like Giardia, Cryptosporidium and Cyclops, which generally need expensive membranes for their separation. In this process a proprietary medium is used which does not need regeneration. In the process upward flow of influent is cleaned by downward flow of filter medium. Most uniquely during the filtration process the filter medium is washed and cleaned by the filtered influent. Hence the process does not need any additional filter medium cleaning process or fresh water. The system works on the proprietary design of the continuously cleaned descending bed filters deployed in a variable array. The AVF process comprises two sets of media filters that can be operated in series or in parallel. Mostly the system operates in an in series configuration and this two-stage series configuration produces very high-quality filtrate. There are actuated valves, sensors and programmable logic controllers that automatically switch from serial mode to parallel mode depending on pre-set operating conditions. AVF has several advantages, such as higher solids capacity, low pressure drop, uniform flow distribution, continuous cleaning of the media filters, extremely low power consumption, no need of ancillary equipment, very low reject volume (5–15%), extremely low power consumption, low installation, operating and maintenance cost *etc.* The AVF process is user and operator friendly and can replace microfiltration membrane technology with the same quality of water produces at one-third of the operating cost.

### 10.3.4 Electrochemical Processes

The three major electrochemical techniques for the treatment of industrial waste water are electro-flotation, electro-deposition and electro-coagulation. In electro-flotation the pollutants are separated by floating them to the surface of the liquid phase. Electro-flotation is based on a combination of electrochemical and physicochemical phenomena. Electrochemical phenomena take place at the electrodes whereas physicochemical phenomena takes place in the liquid, *i.e.* waste water where a dispersed phase is present. It is a multistage process consisting of generation of gas bubbles during electrolysis, formation of a dispersed phase of particles, particles–gas bubbles flotocomplexation, buoying of the flotocomplexes and formation of a three phase froth consisting of particles–gas bubbles–water.[9] Of these five stages the most important one is the formation of the particle–gas bubble flotocomplex. During electrolysis of an aqueous solution different gases like hydrogen, oxygen, chlorine *etc.* are released and the size of the bubble depends on the composition, pH and temperature of the medium, the nature of the electrode, its shape and potential and the surface tension at the borderline of the electrode–surface interface. Particle flotation is basically controlled by the hydrogen bubble whose diameter (10–40 μm) is significantly smaller than that of the oxygen bubble (20–100 μm). Adhesion of the released gas bubbles and pollutant particles that occurs at the molecular level is the most important step in electro-flotation. External hydrodynamic forces are responsible for such convergence. When the distance between them reduces to 10 nm, molecular forces occur and the adhesion of particle to bubble is accompanied by a huge decrease in the surface energy of the bordering layers.

Electrodeposition is a technique for the removal of dissolved metal ions from water. By electrodeposition the dissolved metal ions are transformed into solid particles by deposition on an ionic conductor, *i.e.* cathode or anode. In general, in electrodeposition the organic pollutants in the waste water are degraded at the anode while the heavy metals are reduced and electroplated at the cathode. The advantages of the process are that it does not need any additional chemicals, no sludge is generated and almost all the metals can be removed. Disadvantages are high operation and maintenance costs.[1]

Electrocoagulation (EC) is the technique used to create conglomerates of the suspended, dissolved or emulsified particles in aqueous medium using electrical current. EC uses a low electrical current to remove not only the heavy metal ions but also suspended solids, dyes, tannins *etc.* Pollutants remain in the waste water either through the formation of hydrogen bonds or with the help of their surface electrical charge. In EC, when a low electrical current is applied reaction takes place at both the anode and cathode. The sacrificial anode (Al, Fe or other metals) immersed in the contaminated waste water dissolves and increases the ion content in the aqueous phase or forms complex species with $OH^-$. These species act as a destabilizing agent or coagulant by neutralizing the charge of the suspended or emulsified pollutant. As a result pollutants aggregate and coagulate as flocs. These coagulated contaminants are removed either by electro-flotation with the help of hydrogen, which generates at the cathode, or by sedimentation.[1,10]

Electrochemical methods are eco-friendly, easier to handle, cheap and fast in nature, with comparatively lower sludge generation. The product water is colourless, odourless and potable.

### 10.3.5 Adsorption

Sorption, which is a mass transfer process of ions from solution to the solid phase, includes a group of processes of which adsorption is the most important. Adsorption is used to treat industrial waste water enriched with heavy metal ions. In adsorption the substance that is transferred from liquid to solid phase is bound to the solid phase by physical or chemical interaction. Adsorbents may be derived from natural material, agricultural waste, industrial by-products, modified bio-polymers *etc.* The three main steps involved in the adsorption of pollutants on the solid sorbent are: (1) transport of the pollutant from the bulk solution to the outer surface of the adsorbent, (2) pore diffusional mass transfer from the outer surface to the inner surface of the adsorbent, and (3) adsorption of adsorbate onto the active sites of the pores of the adsorbent.[11] Among these three steps the last step is very fast, hence steps 1 and 2 control the kinetics of the adsorption process. Different types of adsorbents exist. Natural materials, specifically natural zeolite, have gained lot of interest in this area because of their ion-exchange capability. Among natural zeolites, clinoptilolite is an important adsorbent because of its selectivity for different metal ions. Clay-polymer composites and different types of phosphates also act as good adsorbents. The metal removal efficiency of industrial by-products like hydrous titanium dioxide, waste iron, fly ash, iron slag *etc.* may be improved by chemical modification and these modified materials act as good adsorbents. Chemical modifications of different agricultural by-products like rice husk, pecan shell, maize cob or husk *etc.* to activated carbon, converts them to good adsorbents for heavy metal ions. Biopolymers like polysaccharide-based materials possess different functional groups like amine, hydroxyl *etc.* Such materials may act as good adsorbents for metal ions. Hydrogels, *i.e.* crosslinked hydrophilic polymers, are also used for the treatment of waste water. These 3D network compounds are very useful for the removal of heavy metal ions.

## 10.3.6 Membrane Filtration

One of the most important and advanced technologies for the treatment of industrial waste water is membrane technology. A membrane is a thin selective barrier which separates the components in a fluid by a combination of sieving and sorption diffusion mechanisms. Inlet (feed) stream fed to a membrane is divided into two components, *i.e.* permeate and retentate. Permeate contains the materials that have passed through the membrane whereas the retentate has the materials rejected by the membranes. Membranes can separate versatile components, from suspended materials and pathogens to dissolved inorganics and organics. High product flux, efficient rejection of contaminants, good durability and chemical resistance as well as low cost are the characteristics of a good membrane. Membrane-based water clarification and purification processes have replaced many of the conventional unit operations because of several advantages, such as low energy consumption (no phase change in such separations), ease of operation (follows a simple flow sheet rather than complex control schemes), minimum maintenance, high selectivity, involvement of versatile polymers and inorganic materials as membrane material (providing huge control over separation selectivity), ability to recover valuable minor component from major less useful components *etc.* Membrane filtration processes are categorized in different sub-sections depending on different factors like driving force, membrane structure and composition, membrane pore size, rejection mechanism and geometry of construction. Among different membrane processes the most important are pressure-driven processes which are differentiated depending on the pore size of the membranes and their operating pressure. Over time, several membrane-based separation processes have been evolved, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) *etc.* MF is applied for water clarification and mostly removes particles having molecular weight >400 kDa. Membranes operate at a pressure of <2 bar and the pore size of the membranes varies between 0.05 and 10 μm. MF is basically applied for the removal of turbidity and flocculants from waste water, additionally it also remove pathogens and bacteria. The pore size of UF membranes varies between 2 and 200 nm and the membranes operate at a pressure of 1–10 bar. Apart from removal of dissolved and colloidal materials UF has versatile applications in the treatment of industrial waste water specifically for the food and pharmaceutical industries. It is also used for the treatment of whey in dairy industries, concentration of textile sizing, concentration of biological molecules *etc.* NF membranes lie between UF and RO membranes in terms of their properties. These are charged porous membranes; their pore size varies between 0.5 and 5 nm and their operating pressure varies from 5 to 15 bars. These membranes produce higher flux at an operating pressure lower than that of RO membranes. The rejection behaviour of these membranes is controlled by two different phenomena, namely sieving and Donnan exclusion. The rejection of neutral components is governed by the sieving mechanism whereas Donnan exclusion is the charge exclusion where electrostatic interaction of the solute molecules with the membrane surface charge is responsible for the specific rejection of different inorganic and organic salts. NF has versatile applications in the treatment of effluents from textile, dye, leather and pharmaceutical industries. Among all the pressure-driven process the most refined one is RO; the molecular weight cut-off of RO membranes varies between 100 and 200 Daltons and the operating pressure range is 15–50 bar. RO membranes work by a diffusion mechanism and they are mostly applied for brackish and sea water desalination. These membranes have tighter pore morphology than NF membranes and permit water molecules to pass through while prohibiting the salts. RO is the most widely accepted commercial desalination technology because of its consistency, reliability and low specific energy. Apart from desalination RO may also be used for waste water treatment.[12] Both MF and UF are two-layer composite membranes where the bottom layer, having thickness 100–120 μm, is made up of non-woven polyester fabric. This bottom layer imparts the mechanical strength to the membrane. The upper layer, made of different polymers like polysulfone (PSF), polyether sulfone (PES), poly acrylonitrile (PAN), poly vinylidene fluoride (PVDF) *etc.*, is porous and asymmetric in nature. The thickness of this layer varies between 30 and 40 μm and it is made by a phase inversion process. This upper layer acts as the rejection layer of these membranes. NF and RO membranes are tri-layer membranes where in addition to the above two layers there is a third layer of thickness 100–150 nm which is basically a polyamide layer and made by interfacial polymerization reaction between difunctional aliphatic/aromatic amines with trifunctional acid chloride. This nano-layer acts as the rejection layer of NF and RO membranes. In practical applications membranes are applied in two different module configurations, *i.e.* hollow fibre module and spiral wound configuration. Hollow fibre module is applied for MF and UF and has a high surface area to volume ratio and easy backwash facilities. However in NF and RO, spiral wound modules are used which generate turbulence and thus reduce concentration polarization and fouling. Presently, efforts are ongoing to reduce fouling by upgrading the membrane properties and module geometry.

Both ultra- and micro-filtration are very effective, energy efficient membrane separation processes for solid–liquid separation. Fundamentally they are used for the separation of suspended particles and large molecules. Recent developments indicate that the combination of these membrane processes with other conventional treatment processes can separate small dissolved species. The membrane bioreactor is one of such hybrid process which has been found to be immensely successful and highly promising in water and waste water treatment.

## 10.4 Membrane Bioreactor

Membrane bioreactor (MBR) technology is a combination of a biological degradation process by activated sludge with direct solid–liquid separation by membrane filtration. Presently MBR technology is widely used for the treatment of industrial waste water and municipal water. Micro- or ultra-filtration membranes with pore sizes varying between 0.05 and 0.4 μm, which completely retain bacterial flocs and virtually all the suspended solids, are used in MBR.[13] These porous membranes separate the bio-mass from the treated effluent by retaining a significant portion of the suspended solids. Instead of using a secondary clarifier MBR utilizes a suspended growth activated sludge system along with MF/UF membranes for solid–liquid separation.

The history of MBR goes back to late 1960s when the first commercial MF/UF membranes appeared in the market. The original MBR process was introduced by Dorr–Olivier Inc. and was a combination of an activated sludge bioreactor with a crossflow membrane-filtration loop.[14] A polymeric flat sheet membrane having pore size 0.003–0.01 μm was used in the process. The basic idea behind the introduction of MBR technology was to replace the settling tank of the conventional activated sludge process. However it was initially difficult to justify the introduction of MBR for several reasons like high membrane cost, huge membrane fouling and low-value product. Hence people tried to justify the introduction of the first generation MBR by attaining very high product flux which could be achieved by pumping the mixed liquor suspended solids (MLSS) at a high crossflow velocity to abate the membrane fouling. However it was an energy intensive process. For these reasons, for a long time the use of MBR was restricted to very few selected areas. In these first-generation MBRs the whole filtration system including membrane modules were kept outside of the reactor and hence filtration was possible only at a high *trans*-membrane pressure. Researchers tried continuously to improve the MBR design and a unique development came in the 1989 when Yamamoto *et al.* proposed a design where the membrane module was submerged in the bioreactor.[15] At the same time two-phase bubbly flow was introduced to control membrane fouling, and modest product flux (25% less than that of first generation MBR) was accepted. These improvizations reduced the operation cost of MBR and at the same time, due to research in membrane development, membrane costs also decreased. Both these factors played a pivotal role in the popularization of MBR technology since the mid-1990s. Since then a lot of improvization has been made in MBR design and processes, *e.g.* the present solid retention time (SRT) is ≈10–20 days with MLSS concentration of 10–15 g $L^{-1}$, which previously used to be 100 days and 30 g $L^{-1}$. This has made the process easily manageable and it require less frequent membrane cleaning. Today, although most of the commercial MBRs use submerged membranes some still also use externally fixed modules.

Generally bioreactors are cylindrical stainless steel vessels that supports a biologically active environment. Bioreactors contain organisms. Such organisms, or biochemically active compounds derived from such organisms, help to carry out the chemical reactions, which may be aerobic or anaerobic. In MBR, both the chemical reaction (catalysed by enzymes or cells) and separation takes place simultaneously. The basic idea behind the introduction of MBRs in place of an activated sludge process was to replace the settling tank.

### 10.4.1 Working Principles of MBRs

The membrane is at the heart of the MBR. In MBR processes a membrane separates the MLSS into two streams. One is the particle-free permeate/filtrate/effluent stream and the other is the concentrate stream (biomass/return sludge/MLSS) which remains in the reactor. The working principles of an MBR are shown in Figure 10.1.

MBRs connect a biological process with perm-selective membranes. It is an advanced technology for the removal of organics and suspended solids. It is a combination of a suspended-growth biological treatment, specifically a conventional activated sludge (CAS) process, with membrane filtration, specifically filtration through micro- or ultra-filtration membranes. In general the CAS process needs secondary and tertiary clarifiers along with tertiary filtration, which are eliminated in an MBR. The MBR allows a very refined level of filtration to produce high-quality effluent and eliminates the sedimentation and filtration processes which are commonly used in waste water treatment. As the sedimentation process is eliminated, in an MBR system the biological process may be performed at a reasonably higher mixed liquor concentration, which is generally kept in the 1.0–1.2% solid range, four times higher than in a conventional plant.

MBRs may be vacuum or pressure driven. In a vacuum driven MBR the hollow fibre or flat sheet membranes are immersed either in the bioreactor or in a subsequent membrane tank whereas the pressure-driven systems are in a pipe cartridge system which is placed externally to the bioreactor. An MBR is comprised of different zones, such as a fine screening (headwork) zone, membrane zone and in most cases a post-disinfection zone. Fine screening is an essential pre-treatment to avoid the entry of unwanted solids into the membrane tank. This protects the membrane from damage, increases membrane life, reduces operating cost, helps to ensure a higher sludge quality

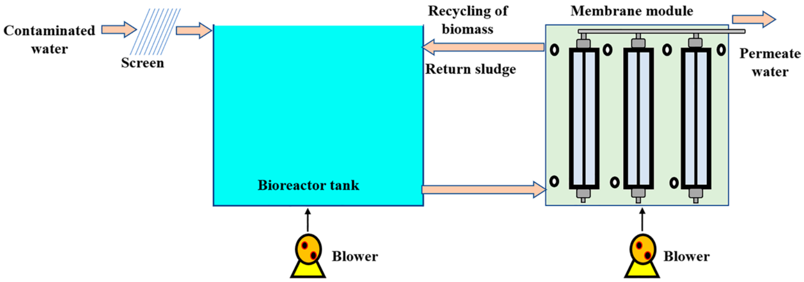

**Figure 10.1** Working principles of a membrane bioreactor.

and guarantees trouble-free operation. After initial screening of the waste water, microbes are used to degrade pollutants which are then filtered by a series of submerged membranes (or membrane elements) in the membrane zone. A number of membranes housed in units are known as a module, cassettes or racks, and combinations of these modules in series or parallel are known as working membrane elements. Diffusers are used to purge air continuously for multiple purposes, such as scrubbing the membrane surface to avoid membrane fouling, to supply oxygen to the biological process and also to facilitate mixing in some cases.

### 10.4.2 Choice of Membranes and Membrane Elements for MBRs

The basic characteristics of the membranes needed for MBR are good chemical and mechanical strength, narrow pore-size distribution, high throughput and reduced fouling tendency. Membranes should be porous so that suspended solids can be removed by a sieving mechanism. Both ceramic and polymeric membranes may be used in an MBR. Although ceramic membranes are unique from the viewpoint of their chemical resistance, thermal stability, mechanical strength and anti-fouling behaviour, these membranes are too expensive for waste water treatment applications. In this context polymeric membranes are widely accepted in waste water treatment. Although the above-mentioned properties are slightly inferior for polymeric membranes compared with ceramic membranes they are much cheaper and have wide flexibility with respect to membrane configuration and module design. Polymers that are currently used for membrane applications are polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), polyethersulfone (PES), polyvinylidenefluoride (PVDF) *etc.* All these polymers have excellent chemical resistance.

For application in an MBR membranes should be configured in the form of elements known as membrane modules. For biomass separation ideally the membrane modules should have the following properties.[16]

- The modules should have adequate chemical, mechanical and thermal stability.
- There should be low pressure drop.
- Modules should not have any dead zone where sludge may accumulate.
- Membranes should have high packing density ($m^2$ membrane area to $m^3$ bulk volume of the module) in the module.
- Feed side should have a high degree of turbulence which will help to reduce fouling and enhance the mass transfer.
- Module geometry should be favourable for low energy requirement per unit volume of treated water.
- Module should be easy to clean.
- Easy to install and facile membrane replacement.

Three different membrane module designs are suitable for MBR applications. These are hollow fibre (HF), plate and frame, and tubular.

In the HF module a bunch of hollow fibre membranes are potted on fixed support. Support may be provided either on both sides or on one side of the membranes depending on the cartridge design. The bundle of fibres are aligned in the casings either vertically or horizontally. The modules having high packing density are submerged in the bioreactor either vertically or horizontally. Continuous aeration is done by passing gas bubbles which act as a scrubber on the membrane surface. Membranes are mostly work in the "out to in" mode and their operation includes periodic relaxation (pressure release) and back flushing to remove the fouled layer from the membrane surface.

In the plate and frame configuration flat sheet membranes supported by rectangular plates are arranged in parallel. In such case membranes arranged in rectangular plates may be submerged vertically. Membranes may also be arranged in rotating plate modules. Sometimes the flat membrane modules may be kept outside the aeration tank. As with HF modules, here also fouling is controlled by coarse bubble aeration. Most of the systems are relaxed periodically and can be back pulsed at a very low pressure.

Unlike HF membrane modules tubular modules are operated in "in to out" mode. The installation length of such tubular modules may be up to 6 m. Arrangement of such tubular modules may be either horizontal or vertical. Efforts are made to maintain high packing density by reducing the tube diameter. To control fouling, aeration systems are maintained in some of the tubular modules. Low operating velocity (1–4 m $s^{-1}$) is maintained for side stream modules. Hydrodynamic control is found to be better for tubular modules in comparison with plate and frame. The modules are sometimes back pulsed or flushed to control fouling, *i.e.* to clean the membrane surface.[16]

## 10.4.3 Types of MBR

MBRs may be classified in two different categories depending on the location of the membrane module in the MBR system. These are submerged membrane bioreactor (SMBR) and side stream membrane bioreactor (SSMBR).

### *10.4.3.1 (SMBR)*

In this system two processes, *i.e.* chemical reaction and separation, take place simultaneously in the reactor tank resulting in a synergistic effect. The design of an SMBR is shown in Figure 10.2.

In such systems, membranes in flat sheet or hollow fibre configuration are immersed vertically in the reactor tank, *i.e.* feed chamber. Permeate, *i.e.* product water, is collected either under hydrostatic pressure or slight vacuum with the help of collectors which are placed outside the reactor. The net effect of the simultaneous reaction and separation is acceleration of the

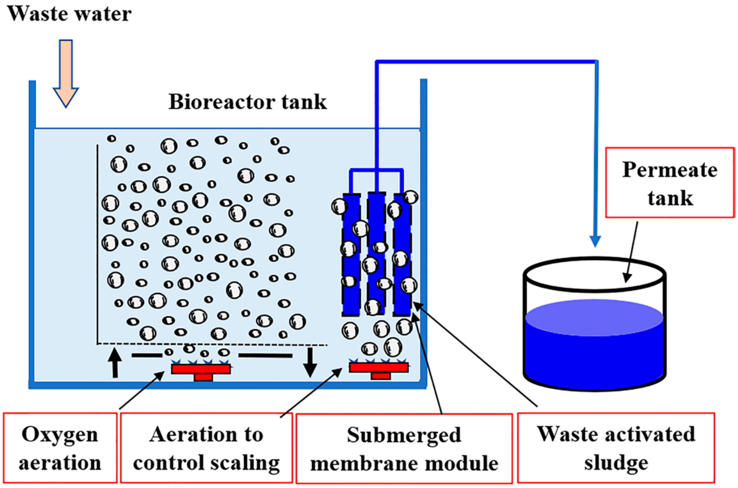

**Figure 10.2** Submerged membrane bioreactor.

kinetics of the process. Continuous removal of the product shifts the reaction equilibrium towards right, *i.e.* towards product and the efficiency of the process increases. SMBR is always accompanied with gas purging. The gas supplied from the bottom of the reactor tank flows over the membrane surface and creates turbulence. Such gas purging helps to remove the filter cake from the membrane surface, which in turn reduces concentration polarization and enhances membrane flux. Air is purged in the case of an aerobic reactor and inert gases are used for an anaerobic reactor.

A CAS process depends on gravity settling for the separation of biomass from the treated water. Hence for CAS process design, the primary emphasis is on choosing those parameters which will ensure effective flocculent settling. This puts a limitation on the maximum amount of biomass that can be retained in the aeration tank. This limit is again interrelated to sludge retention time (SRT) and hydraulic retention time (HRT). Considering large organic molecules, integration of these parameters often leads to an oversized biological reactor. A conventionally designed CAS process reactor sometimes may be unable to secure a settleable microbial community, and under unfavourable condition it may create a severe bulking and foaming problem which may results in total collapse of the system.[17]

In comparison with the conventional activated sludge bioreactor (ASB), SMBR has several advantages.[18]

- Easy access for the microorganisms to the substrate (thickness a few micron) and results into faster bioconversion in comparison with an ASB where activated sludge is a few hundred microns thickness
- Because of the continuous separation through membranes the kinetics of bioconversion and mass transport in an SMBR is much faster than that in an ASB

- An SMBR can be operated at a low COD value even below the threshold value for an ASB.
- An SMBR uses a very simple and cheap technique, *i.e.* gas purging to remove the filter cake from the membrane surface, which in turn reduces operating expenses.
- SMBR design is compact, consisting of closely packed membranes immersed in the bioreactor, and it does not require any settler, hence capital cost is low.
- Because of the compact design the space requirement (foot print) is less for an SMBR
- Because of the facile kinetics of the chemical reaction an SMBR has better flexibility and versatility for bio-conversion.
- In comparison with an ASB, an SMBR has high-performance density, ease of design and scale-up, easy disposal of waste and ease of automation. Hence such a system is easier to control and operate.

### *10.4.3.2 Side Stream Membrane Bioreactor (SSMBR)*

When the membrane unit is located external to the bioreactor it is known as side stream MBR (Figure 10.3).

In The MBR arena this configuration has the longest history as originally the MBR was developed in this configuration in the 1960s. It is mostly used for industrial waste water treatment.[19] This configuration is simple and compact, with easy membrane maintenance, and can provide direct hydrodynamic control over fouling. The major advantage of an SSMBR is the high permeate flux, which is 3–4 times higher than what could be achieved with an SMBR (24–44 L $m^{-2}$ $h^{-1}$).[20] Moreover such systems have the ability to treat waste water of extremely high fouling potential. However such systems require high energy to generate sufficient sludge velocity, provided by a recirculation pump across the membrane surface, to minimize fouling.

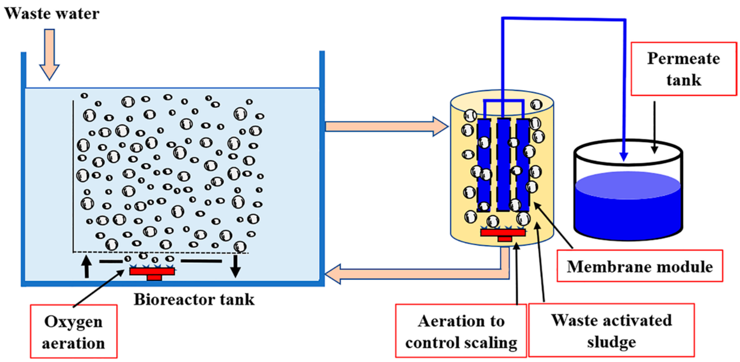

**Figure 10.3** Side stream membrane bioreactor.

The shear velocity of the sludge inside the membrane surface plays a dominant role in the performance of an SSMBR. It can be operated in two different modes, *i.e.* bio-flow mode and bio-pulse mode. In the bio-flow mode high sludge velocity in the range 3.5–4.5 m $s^{-1}$ is maintained inside the membrane. In this mode SSMBRs can treat waste water of extremely high fouling potential, like oily waste water, and a high permeate flux (75–150 LMH) could be achieved. In the bio-pulse mode comparatively lower sludge velocity of 1–2 m $s^{-1}$ is maintained inside the membrane, which is accompanied by an intermittent water back pulse from permeate side to mixed liquor side. In the bio-pulse mode an SSMBR can treat waste water with moderate fouling potential and the permeate flux varies in the range 40–70 LMH.[21]

### *10.4.3.3 Batch, Fed Batch and Continuous Reactor*

Depending on the mode of operation MBRs may be of three different types namely batch, fed batch and continuous.

The batch MBR is a closed system where all the nutrients are provided in the beginning of the process and no additional nutrients are added during the entire process except control elements like gases, acids and bases. The bioprocess continues until the nutrients are totally consumed. In this process, as the carbon source and the oxygen transfer are the limiting factors, microorganisms are not in exponential growth for a long time. The advantages are short duration, ease of management and less chance of contamination as no nutrient is added. As it is a batch process, from the bio-reactor point of view the process is repeatedly interrupted by cleaning and sterilization and there is an increased rate of substrate inhibition, which is an interference with enzyme activity and might induce metabolic feedback and reduce the yield.

A fed batch reactor is a partly open semi-continuous system where nutrients are being fed intermittently during cultivation. The advantage of intermittent feeding is that it allows the achievement of overall higher product quantity. Under certain growth conditions the microorganisms follow an exponential growth pattern. That is why the feed rate needs to be increased exponentially. In this mode it is also possible to fix the feed rate as needed, *e.g.* linear, exponential, pulse wise *etc.* The advantages are: it extends a culture's productive duration, can be operated for maximum productivity using different feeding strategies and can also be used to switch genes on or off by changing substrates. However it allows the accumulation of toxins and may produce higher cell density numbers and product yield which are difficult to handle in the downstream.

Once equilibrium with respect to particular components is established in a batch growth process, a steady state is achieved. At this stage whatever amount of fresh culture medium is added the same is removed. This bioprocess is refer to as continuous culture. This is advantageous when excess nutrients result is inhibition due to toxin build-up. Reduced product inhibition and better space time yield are the other advantages of continuous culture. In such reactors the inflow and outflow rates should be lesser than the doubling time of the microorganism. Continuous cultures are of three different types as follows. Chemostat: the rate of addition of a single growth-limiting substrate controls cell multiplication. Turbidostat: it indirectly measures the cell numbers through turbidity or optical density. It controls the addition and removal of liquid. It has an additional sensor and is driven by real-time feedback. Perfusion: this is continuous bioprocessing mode. It is based on either retaining the cells in the bioreactor or recycling the cells back to the bioreactor. Fresh medium is provided and cell-free supernatant is removed at the same rate.

The advantages of continuous culture are maximum productivity, reduced time for cleaning, easy sterilization and handling of the vessels and it is possible to have a steady state metabolic study. The disadvantages are increased risk of contamination, difficult to keep a constant population density over prolonged periods and the products cannot be neatly separated into batches for traceability.

### 10.4.4 Membrane Fouling and Its Control in an MBR

Fouling is a derogatory phenomenon which reduces membrane performance. It is the precipitation or deposition of molecules or particulates (bio-solids, colloidal species, scalants or macromolecular species) on the membrane surface as well as within the membrane pores, resulting in an increase in membrane separation resistance, reducing membrane productivity and/or altering membrane selectivity. Due to an increase in membrane resistance the transmembrane pressure need to be enhanced to keep the performance of the membranes at a steady level. As a consequence maintenance and operation costs of the membrane increase.

Membrane fouling may be of two different types, *i.e.* reversible and irreversible. Fouling on the membrane surface that can be removed by physical washing is known as reversible fouling. However when fouling takes place internally, *i.e.* within the membrane pores and can be removed (mostly partially) by chemical cleaning only, is known as irreversible fouling.

In the case of an MBR three main factors are responsible for membrane fouling, *i.e.* biomass characteristics, membrane properties and operating conditions.[22]

Biomass characteristics:

- nature and concentration of MLSS
- particle size distribution of bio-solids
- the extent of the dissolved portion of extracellular polymeric substances (EPS)
- viscosity and hydrophobicity of the biomass

Membrane properties:

- shape of the membrane and its porosity and pore-size distribution
- dimensions and geometry of the membrane modules
- membrane surface morphology and properties like polarity and hydrophilicity/hydrophobicity

Operating conditions:

- membrane hydraulics, specifically flow rates
- system hydrodynamics, such as crossflow velocity, aeration rate, flow rate, pulse rate, relaxation time *etc.*
- cleaning, such as cleaning intervals, back flush, physical or chemical cleaning

**Fouling remediation**

Fouling may be controlled by[21]:

- flux reduction
- enhancement of shear
- back flushing
- modifying mix-liquor composition
- physical and chemical cleaning
- appropriate pre-treatment

Fouling may be reduced by reducing the membrane flux. However in such cases to maintain the productivity of the MBR, the surface area of the membranes needs to be increased. This results in lower fouling at the cost of higher energy demand.

Fouling may also be decreased by increasing the air flow rate. High flow rate increase the shear velocity which scrubs the submerged modules vigorously. However higher aeration results in higher energy cost. For SSMBRs having tubular membrane modules, fouling is controlled by applying high sludge velocity at the membrane surface. This will help to remove accumulated particles. In some SSMBRs air flushing or intermittent back-pulsing are also applied to reduce fouling. However higher flow velocity results in increased pressure drop, which ultimately results in higher energy demand, *i.e.* higher operational cost.

Membrane fouling could be slowed down by cyclical back-flushing with permeate and/or relaxation, which may be automatically initiated. Relaxation cycles may range from a few minutes to several hours. It has been observed that less frequent, longer back-flushing (*e.g.*, 600 s filtration, 45 s backflush) are more efficient than more frequent but shorter back-flushes (*e.g.*, 200 s filtration, 15 s back-flush).[21] As the net flux decreases at higher back-flush, in order to compensate the system requires a large membrane surface area with a final impact in cost.

Mixed liquor can be changed by adjusting the sludge retention time or by addition of chemicals. Membrane hydraulic performance can be improved by the addition of coagulants/flocculants like ferric chloride or aluminium sulfate. Addition of adsorbents like powdered activated carbon (PAC) reduces the EPS and affects the filtration performance.

Apart from the precautionary steps to be followed to control membrane fouling, membranes also need regular cleaning to keep permeability loss at a constant reasonable value. There are two different cleaning methods, *i.e.* mechanical cleaning and chemical cleaning. Physical removal of solids from the membrane surface is known as mechanical cleaning. Chemical cleaning can be done in two different ways. The first one is *in situ* chemically enhanced back-flush with chemicals like acids or oxidizing agents, which may be done daily or weekly depending on the fouling intensity. This is *in situ* cleaning where the membranes are cleaned inside the tank (submerged) or chemicals are pumped through the pipes (side stream module). The important parameters are duration, frequency and the back-flush flux. The second one is vigorous cleaning outside the MBR (*ex situ*). Here submerged membranes are removed from the aeration tank and cleaned outside. This needs high chemical concentrations (1000 ppm of citric acid and NaOCl) and is done once or twice a year.

Pre-treatment includes screening, oil and grease removal, treatment in an equalization tank and removal of inorganic chemicals. Multiple-stage screening is done with small-mesh sieves (mesh size <0.5 mm) to remove fibres, hair or sharp-edged materials. The highest amount of screening could be achieved when the screen is cleaned in a discontinuous mode. No hair was observed in a discontinuously cleaned drum filter screen. Pre-treatment system should be provided with oil and grease traps as they reduce membrane flux. Such traps can remove only 50% of the mineral oil present. It is necessary to level off the hydraulic peaks in the bioreactor so that the membrane surface area may be designed for maximum flow. An equalization tank operates with alternate water levels and this phenomenon should be considered in the design phase. At municipal plants, the maximum storm water flow at low temperatures has to be taken in account. Continuous aeration also has a negative effect. High aeration on the membrane surface stripped off $CO_2$, which will increase the pH of the solution, as a result $CaCO_3$ may precipitate on the membrane surface. Such scaling may be removed by weak acid treatment.

### 10.4.5 MBR *vs* CAS

The MBR has been introduced as a partial replacement of the conventional CAS process by eliminating the necessity for secondary and tertiary clarifier but using a suspended growth activated sludge system. The nature of this activated sludge differs in an MBR and CAS. In CAS, biomass capable of forming flocs that are big enough to settle down is used. In the case of an MBR, the sedimentation question does not arise, hence sludge having single bacteria may be used. In this case microbial floc size is much smaller with the presence of free suspended cells.[23] Membrane operation is a pressure-driven process, hence in an MBR there is a chance of pressure variation. Such pressure variation may hamper biocenosis which may be aggravated by high flow rate. Because of this stressed condition EPS may be generated from the cells.[23] As the reactor volume in an MBR is smaller than that of CAS, EPS under a high aeration rate may create foaming problems in the reactor. This may be eliminated by modifying the reactor design.

The activated sludge process is applied in the treatment of waste water. The concentration of suspended solids in an aeration tank during the activated sludge process is known as mixed liquor suspended solids (MLSS) concentration. MLSS is basically a combination of microorganisms and non-biodegradable suspended matter. In a MBR, biomass separated by the membranes is retained, independent of sludge sedimentation properties. As a result, high biomass concentration and low food to microorganism ratio (F/M) could be maintained in an MBR. In CAS the biomass concentration is restricted to 3–5 g MLSS $L^{-1}$, whereas in an SMBR the MLSS concentration typically remains 10–15 MLSS $L^{-1}$ and in an SSMBR the MLSS may be up to 30 g $L^{-1}$. Sludge viscosity also plays an important role in the operation of an MBR.[24] An increase in viscosity results in a decrease in mass transport through membranes, which in turn results in less efficient oxygen supply and reduced oxygen capacity. With an increase in viscosity the energy requirement for pumping and mixing the sludge also increases.

Excess sludge or surplus activated sludge results from the degradation processes occurring in the mass of active bacteria, due to different reasons like the presence of inert suspended solids in the raw water, different chemical reactions for the removal of phosphorous *etc.* and inorganic residuals from the biological degradation processes. Hence the mass of the activated sludge grows with time both in an MBR and CAS. This will disturb the equilibrium in the reactor. Moreover the yield will also decrease with a decrease in the F/M ratio, *i.e.* with increase in sludge retention time. Hence some of the sludge, known as surplus sludge, should be discharged. The mass of discharged surplus sludge is one of the parameters to determine the sludge retention time (SRT) in the activated sludge system. It has been observed that at high to very high sludge ages (calculated value of several hundred days) it is possible to achieve low or zero sludge production. It has been concluded that at similar SRT (in the normal range of 30 days) the yields of CAS and MBR are comparable. Design of an MBR may be done in such a way that it works between two extremes: (1) extremely long sludge age, low F/M ratio, very low sludge production, high biochemical oxidation and (2) small aeration tank but with the same F/M ratio and similar surplus sludge production as in the CAS process.

### 10.4.6 Application of MBRs

Worldwide the major application of MBRs is for municipal waste water treatment. This is because the total flow of sewage is greater than that of industrial effluent. Municipal waste water are generally treated to meet the legal requirements for discharge into the environment. However because of the ever increasing demand for water, a lot of emphasis is being given these days to the reuse of treated waste water. The major contaminants that need to be removed from municipal waste water are suspended solids, organic matter, ammonia, nitrates, phosphates, pathogenic bacteria and micro-pollutants. In order to discharge the treated waste water into bathing areas or reuse it, *e.g.* in irrigation, it is necessary to remove the pathogenic bacteria. An MBR provides a very high level of disinfection and also clarifies the water to such a level that disinfection by UV radiation in the downstream becomes highly effective.

One of the rapidly expanding applications of MBRs is in water reclamation. The advantages of MBRs are their easy operation and small footprint. Hence, instead of putting in a large central plant, small MBR plants may be put at the point of reuse. MBR effluent may be further treated with RO. After RO treatment the water obtained satisfies all the specification of drinking water and sometimes it is of higher quality than the virgin water. However irrespective of being of very high quality, such water is not acceptable by the public for drinking. Hence, such water may be used for forest irrigation, crop irrigation, park and garden irrigation, livestock watering, cooling, industrial cleaning, industrial processes, fishery use, public grey water *etc.*

MBR is an excellent technology to treat industrial waste water. Industrial waste water is of high strength and is nutrient limited. This results in the poor settling of biomass. Hence, as an alternative to conventional systems, membrane-based processes are now widely accepted in this arena. As industry consumes a huge amount of water per day, reuse of MBR-treated water in industry results in a reduction in water consumption. If this happens in all industries, it will contribute hugely to water conservation. These days waste water of different industries is being treated by MBR technology, as described in the following sections.

#### *10.4.6.1 Textile Industry*

Among several industries the textile processing industry is one of the largest consumers of water. Here water is mainly used as one of the major media for removing impurities and applying dyes and finishing agents. In such industries water consumption varies from 20–350 $m^3$ per ton of fabric produced. The wide range actually depends on the variety of processes and process sequences adopted from case to case. Waste water from such industries is an important source of pollution as it contains high concentrations of inorganic and organic chemicals, specifically high-coloured residual dyestuff; 50% of the dye produced annually is used in the textile industry. Apart from dyes such effluents generally contains surfactants, salts, enzymes and different oxidizing and reducing agents. In other words the water contains a high level of suspended solids, COD, BOD, high pH and strong colour. Hence from the viewpoint of volume and composition of the waste water generated, the textile industry may be considered as one of the most polluting industries, specifically the dyes and their breakdown products are highly carcinogenic to humans.

It is common practice to treat textile industry waste water either by chemical precipitation, activated carbon adsorption, biological treatment, evaporation or by membrane filtration, specifically nanofiltration. Chemical oxidation using chlorine and its derivatives and $H_2O_2$ has been found to be quite effective for de-colourization. Similarly, physical adsorption using activated carbon or low-cost adsorbents like peat, fly ash *etc.*, coagulation, flocculation or electrocoagulation are also adequately effective. However technological innovations have led to more reliable and feasible alternatives, such as MBRs. Both anaerobic and aerobic MBRs are efficient for colour removal, however aerobic MBRs are popularly used in several pilot plants because of the very high quality of the treated water.

Badani *et al.* used a tangential flow side stream MBR pilot system to treat real textile waste water.[25] A PVDF UF tubular membrane module with membrane pore size of 25 nm was used in the process. The waste water was pumped from an equalizing tank into a bioreactor of capacity 500 L which was filled with activated sludge of concentration 5–15 g MLSS $L^{-1}$. Dissolved oxygen concentration was maintained at 1–3 mg $L^{-1}$ in the aeration tank. The mixed liquor was pumped from the bioreactor to the membrane through a centrifugal pump at a transmembrane pressure of 0.5–1.5 bar and the pilot plant was operated at a constant velocity of 2 $ms^{-1}$. It was observed that the average reduction of the COD was 97% and the rate of elimination of the ammoniac nitrogen was 70%, regardless of the age of the sludge. The average removal of colour was 70%. The author suggested post-treatment of the treated water with nanofiltration to achieve high-quality water.

Yutrsever *et al.* studied the performance of sequential anaerobic (sulfate reducing) and aerobic MBRs (sulfide oxidizing) in the treatment of synthetic textile waste water under various operating conditions by varying COD (1000–2000 mg $L^{-1}$), NaCl (500–1000 mg $L^{-1}$) and sulfate (500–1500 mg $L^{-1}$) while keeping the dye (Remazol Brilliant Violet 5R) concentration constant at 200 mg $L^{-1}$.[26] A membrane module with an effective membrane area of 0.01 $m^2$ containing a flat sheet polyether sulfone MF membrane with pore size 0.45 μm was used in the process. The same gas (biogas for anaerobic and air for aerobic MBRs respectively) flow rate of 1 $m^3(m^2$ membrane area $h)^{-1}$ was maintained in both the reactors to scrub the cake layer. Oxygen concentration was maintained above 3 mg $L^{-1}$ in the aerobic MBR. An intermittent filtration cycle, *i.e.* 5 min suction followed by 1 min relaxation (non-suction) was adopted in both MBRs to alleviate cake formation on the membrane surface. Complete removal of dye was achieved in an anaerobic MBR (AnMBR) where COD removal efficiency was 80–85% and sulfate reduction efficiency was 55 and 95% at COD : sulfate ratios of 0.67 and 2.0, respectively. In an aerobic MBR (AeMBR), sulfide was completely oxidized to sulfate. High molecular weight soluble organics, proteins and polysaccharides were found in the cake layer of both the MBRs. It was observed that AnMBR sludge has less filterability. It was also observed that the resistance of a chemically cleaned membrane (NaOCl and acid cleaning) was almost the same as that of a new membrane.

It may not be always possible to achieve water of the desired standard for direct reuse using MBR alone. Hence a combination of MBR along with other membrane technologies has been tried. It was observed that MBR with post-treatment by nanofiltration is the best choice to achieve water for direct use. However this approach needs high technological accuracy and involves high cost.[27]

### *10.4.6.2 Pharmaceutical Industry*

Pharmaceutical industries use both inorganic and organic raw materials and produce a wide variety of products. The organic raw materials may be of synthetic, vegetable or animal origin. With the proliferation in the production of pharmaceuticals new materials are being continuously released into the environment along with industrial waste water. This pharmaceutical waste water is a major, complex and toxic industrial waste and if not properly treated it mixes with the water bodies and cause huge contamination. Such environmental contamination by partially metabolized pharmaceuticals has become a matter of great concern from the viewpoint of human health and aquatic life. The low molecular weight micro-pollutants which are categorized as pharmaceutically active (PhACs) are able to contaminate the environment at very low concentrations and they may be considered as a major source of pollution. Among the PhACs non-steroidal anti-inflammatory drugs and antibiotics are extensively used worldwide. Almost two-thirds of these drug are excreted into the sewer system, their main route of emission. They have severe adverse effects, such as aquatic toxicity and genotoxicity, and increase resistance to pathogenic bacteria and endocrine disruption. Contamination of drinking water sources by such pollutants is a matter of great worry as very little is known about the chronic health effects associated with long-term ingestion of these compounds. Hence removal of these PhACs from contaminated industrial waste water is essential. However as pharmaceutical waste waters contain solvents and organics that are often non-biodegradable and toxic for microorganisms, their treatment is quite complex. Some of the pharmaceuticals are highly hydrophilic which limits their adsorption onto sludge. As a result the degradation of such compounds by bacteria is considerably inhibited. Additionally the structure of some of these compounds protect them against attack from the biocoenosis. As a result the treatment of such water by conventional activated sludge processes becomes non-effective. Hence an alternative has been thought of and the most advanced membrane bioreactor technology has been introduced.

Tambosi *et al.* prepared a synthetic effluent solution containing six pharmaceutical compounds that are widely used worldwide.[28] Three of them are non-steroidal anti-inflammatory drugs (NSAIDs), acetaminophen, ketoprofen and naproxen, and the other three are antibiotics, like roxithromycin, sulfamethoxazole and trimethoprim. Two different MBR systems, *i.e.* MBR-15 and MBR-30 were chosen for the study. The SRT, sludge concentration (SC) and HRT of the pilot-plants were 15 days, 12 g $L^{-1}$ and 9 h for MBR-15, and 30 days, 12 g $L^{-1}$ and 13 h for MBR-30, respectively. Submerged poly ether sulfone-based hollow-fibre UF membranes having pore size 0.04 μm and membrane area 1.43 $m^2$ under continuous aeration were used in both MBR systems. The mechanism by which the pharmaceuticals were removed in the MBR was a combination of sludge sorption, biodegradation and membrane retention. Out of these three, biodegradation was found to a play major role as higher removal efficiency could be achieved for higher SRTs. It was observed for both MBRs that the NSAIDs were removed with higher efficiency than the antibiotics, and MBR-30 provided higher removal efficiencies than the MBR-15 for all compounds studied. However the removal by an MBR was only partially successful as biological transformation products of NSAIDs produced by waste water biocoenosis were identified in permeates from both the MBRs. However such discharge could be reduced by the combination of some additional process like activated carbon adsorption, advanced oxidation process, nanofiltration or RO along with the MBR.

A submerged MBR (SMBR) system has also been used by Kimura *et al.* to study the removal efficiency of some acidic pharmaceutically active compounds (PhACs) like clofibrie acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid, naproxen and one acidic herbicide dichloprop.[29] Two pilot-scale SMBRs were used in the process. The MBRs were equipped with a hollow fibre microfiltration membrane module containing a PVDF membrane of pore size 0.4 μm and total membrane area 1.3 $m^2$. Of the two MBRs one was directly fed with the contaminated water, while the other one was a hybrid MBR (HMBR) where the raw water was pre-treated by coagulation/sedimentation and then fed to the MBR. The hybrid MBR helped to mitigate fouling. Aeration was carried out in both the MBRs. The MBRs used a CAS process. The HRT in this plant was ≈13 h and MLSS concentration in the aeration tank was maintained around 1700 mg $L^{-1}$. It was observed that in comparison with a conventional activated sludge process the MBR exhibited better removal efficiency specifically for ketoprofen and naproxen. It was also observed that PhACs with complicated structures can be removed by an MBR which cannot be done efficiently a by CAS process. For other PhACs having simple structures, like ibuprofen, both CAS and the MBR exhibited equal removal efficiency. The HMBR acted in a better way than the MBR for the removal of naproxen.

Kaya *et al.* carried out systematic studies on the performance of an SMBR in the removal of the PhAC etodolac.[30] The experiments were carried out at three different SRTs [15 days, 30 days and without sludge wasting (WSW)] under constant pressure. The SMBR tank was aerated at the bottom to supply oxygen for the microorganism to grow and to rub the membrane surface. Four different flat-sheet membrane modules of total area 84 $cm^2$ were used. Four different MF membranes (MP005 pore size 0.05 mm, MV02 pore size 0.2 mm, CA cellulose acetate pore size 0.45 mm, MCE nitrocellulose mixed ester pore size 0.22 mm) were used in the modules separately. In the first phase the continuous bioreactor was operated at SRTs of 15 and 30 days and WSW, and after reaching steady state the MBR operation started in the second phase. With increase in SRT, permeate volume and steady-state flux increased. For both the SMBR and bioreactor the best removal of etodolac (86.6%) was achieved in the case of WSWat. The COD removal efficiency of bioreactor and SMBR was 80.72 and 86.72%, respectively at all SRTs.

Synthetic pharmaceutical waste water containing acetaminophen was treated with an external loop airlift membrane bioreactor (ELAMBR).[31] A polyether sulfone-based 50 kDa UF membrane module was used in the process. Experiments were carried out in semi-batch mode under continuous air purging. The performance of the ELAMBR was monitored for almost a month to study the consistency of the system as well as the effects of SRT on the removal efficiency of acetaminophen. It was observed that the removal efficiency of ELAMBR was higher than that of a conventional activated sludge process. Complete removal of acetaminophen was possible by running the system for 2 days. Removal of acetaminophen is mainly dependent on the primary concentration of acetaminophen, COD and MLSS.

Pharmaceutical waste water containing organic solvents, nutrients (ammonia, phosphorous) and corticosteroids [levonogestrel (levo), bethametasone valerate (betha-V), bethametasone dipropionate (betha D) and medroxyprogesterone acetate (medro)] was treated with an SMBR system.[32] The MBR contained a hollow fibre membrane module with a PVDF UF membrane having average pore size 0.04 µm. The system could be operated for 20 weeks without substantial fouling. The module produce an average flux of 2.87 LMH. In such a system 0.99% of ammonia and total organic matter were removed while phosphorous elimination was 40%. The removal efficiency of all the four corticosteroids was >93%.

MBRs have also been made by using ceramic NF multi tubular membranes having a 600 Da cut-off with an effective membrane area of 0.16 $m^2$. An SSMBR system was applied for the removal of two pharmaceutical antibiotic compounds namely cyclophosphamide and ciprofloxacine. During the experiment the supernatant COD in the tank increased to a steady value of 100–200 mg $L^{-1}$ and the MBR exhibited high COD removal. At the same time total suspended solid and colour were effectively removed. The two antibiotics were weakly degraded even with acclimated sludge, and only a small fraction of these compounds was retained when fouling of the membrane increased.[33]

### *10.4.6.3 Tannery Industry*

Among different industries the tannery industry is one of the major creators of environmental pollution. High organic loading in tannery effluent is the major polluter. Many complex stages are involved in the conversion of animal hide into leather. This includes different types of chemical treatments using large number of chemicals like surfactants, acids, metalorganic dyes, natural or synthetic tanning agents, sulfonated oils, huge concentration of salts *etc.* Different stages of the tanning process consume large quantities of fresh water. As a result tannery industry effluents are enriched with high COD, BOD, sulfides, chloride, chromium, ammonium salts and suspended solids. Of this degradable fraction 19% is readily bio-degradable organic matter whereas 60% is classified as slowly biodegradable organic matter. Moreover, tannery industries are not really up to date with waste water management.

Conventionally tannery industry waste water goes through primary and secondary treatment. In the primary treatment suspended solids are removed whereas in the secondary treatment, which is basically a biological treatment, colloidal organic matter, COD and colours are removed. A combination of both physical and chemical methods has been tried to remove nitrogenous compounds and organic pollutants. In addition coagulation and flocculation may also be applied to remove suspended solids and to reduce COD. However these processes are expensive, consume chemicals and produce secondary sludge. Hence it is necessary to develop simple, economic and technically viable processes to treat such waste water. Advanced processes should effectively remove the organics and reduce sludge production and consumption of chemicals. The MBR has been found to be a good alternative to conventional processes. With an MBR it is possible to increase the SRT and less reactor volume is needed for BOD and nitrogen removal.

A MBR containing a Zenon ZW-10 reactor with a volume of 220 L equipped with a hollow fibre UF membrane module was used to treat the waste water from the beam house stream of a tannery.[34] The membrane pore size was 0.04 μm and surface area was 0.9 $m^2$. The MBR was operated for a period of 51–120 days with an OLR (organic loading rate, kg COD $m^{-3}$ $day^{-1}$) of the waste water of 0.5–1.5, *trans*-membrane pressure of 5–40 kPa, permeate flow of 5–10 L $h^{-1}$ and under an air flow of 70–133 L $h^{-1}$. The membrane module was operated in cycles of 15 min of permeation and 45 s backwashing with permeate. 86% removal of COD could be achieved from the tannery effluent. COD concentration in permeate was always <100 mg $L^{-1}$. An increase in the biomass concentration in the reactor did not affect the COD of permeate.

To achieve better performance a HMBR containing electrocoagulation, an activated sludge process and a membrane has been proposed by some researchers.[35] Electrocoagulation is not only a better option to remove the organics and metal ions from the waste water but it also increases the biodegradability index of the effluent above 0.4 which is necessary for an effective degradation process. Tannery waste water was collected from a common effluent treatment plant. Electrocoagulation was performed on the tannery waste water for a period of 15 min to bring the bio-degradability index to 0.4. This was followed by activated sludge treatment at an MLSS concentration of 8 g $L^{-1}$ for 6 h. Oxygen was provided continuously to the biomass. This was followed by dead-end membrane filtration using a PVDF MF membrane having pore size of 0.22 μm. The COD and colour removal by the HMBR were found to be 90.2 and 92.75%, respectively. In the HMBR prior electrocoagulation helped to reduce membrane fouling by 11% more than in the MBR.

Tannery effluent water was also treated with a combination of MBR and powdered activated carbon (PAC).[36] PAC has the ability to absorb tannin and other inhibiting compounds and it is effective at protecting biomass (autotrophic and 4-heterotrophic microorganism) from load peaks. Additionally, nitrifier micro-organisms may also grow on a PAC surface. Use of PAC in MBRs increases the sludge filterability and decreases the membrane fouling rate. This in turn results in lower energy and chemical consumption in the MBR. An SMBR has been used in the present process. The membrane system contained four submerged HF modules containing polyethylene HF membranes having membrane area for each module of 1.5 $m^2$ with a molecular weight cut-off of 0.4 μm. Membrane fouling was controlled by air-blowing and maintaining a cycle of alternate filtration and relaxation. Use of PAC with the MBR resulted in higher process stabilization and decreased the variability in the effluent quality. It imparted better control of fouling rate, which decreased with an increase in PAC concentration. It also facilitated fouling reversibility and membrane life cycle.

### *10.4.6.4 Food and Beverage Industries*

Dairy and milk processing farms account for a major area of food industries. Being unware of the consequences, such industries often discharge their waste water to their close surroundings, which creates huge environmental pollution. The waste water generated from milk production can be divided into two groups. The primary one is dairy industry waste water which is produced in large volumes, and the second one is named "punctual pollution" *i.e.* the effluent produced in the breeding farm, *e.g.* milk transformation units for cheese production *etc.*, which is comparatively of lesser volume. Apart from these another water stream known as "white water" is also produced by washing of the milking or cheese production device. This white water is generated only once or twice a day when production units are cleaned. This white water usually contains some milk, whey and acidic or basic washing products. As multiple activities like pasteurization, cleaning and disinfection of milking sheds and other facilities are done during the processing of dairy products, dairy waste water contains organic matter in high concentration, different solids and nutrients and some dissolved inorganic pollutants.

In general dairy industry waste water is treated in conventional activated sludge plants by gathering the waste water into a tank where by adopting mechanical/chemical means the medium is kept homogeneous. However the disadvantages of using such tanks is that they occupy space and unexpected microbial transformations may occur. As an alternative a compact bio-reactor has been thought of. As the effluents are recovered once or twice a day the waste water produced during cheese production can be handled by a sequential batch reactor. However the sludge used in such a reactor should have good settling properties. Such settling properties depend upon the operating conditions like load, flow rate *etc.* as well as microbial population and variation of its composition with time. As the composition of the dairy waste water and its flow rate and microbial concentration may vary, sludge settling can vary and may be insufficient to guarantee sludge separation. To avoid this drawback membrane filtration units have been used in conjunction with sequential batch reactors. In such systems the membrane filtration unit was immersed in the reactor and sludge settling was replaced by membrane filtration.

Castillo *et al.* proposed a new bio-reactor to carry out in-line biological treatment of the white water produced from a dairy breeding farm.[37] The reactor was a sequential batch reactor where the settlement phase was replaced by a membrane filtration unit. The filtration unit was a polysulfone HF based module of length 10 cm, fibre inner diameter of 1.44 mm and cut-off 0.1 µm with a total filtration area 0.22 $m^2$. After each run the membrane was chemically regenerated with sodium hydroxide (4 g $L^{-1}$, 45 °C, and 2 hours) and oxalic acid (5 g $L^{-1}$, 20 °C, 0.5 h). Effluent was sequentially (every 12 h) fed to the reactor where biological degradation of the organic pollutants took place. Before the next filling stage, mixed liquid sludge was filtered and the permeate was drawn off. The cycle, "effluent supply–batch step–permeate removal", was carried out twice a day in order to simulate the in-line treatment of real white waters. By this system efficient treatment of white water could be achieved with total retention of the suspended solids and the COD value of the permeate was <125 mg $L^{-1}$. There was no need of an initial mixing tank and post-treatment process.

Am immersed MBR (IMBR) was used to treat combined dairy and domestic waste water collected from a farm in Israel.[38] The IMBR was equipped with an Ultrafiltration ZeeWeed ZW-10 hollow fibre membrane module, with a surface area of 0.93 $m^2$ and a nominal pore size of 0.04 µm. During the operation of the MBR a constant product flow of 7 L $h^{-1}$ was maintained. The transmembrane pressure increased from 0.05 to 0.13 bar, temperature was maintained between 30 and 37 °C, pH ranged between 4 and 9, total suspended solids from 353 to 1000 mg $L^{-1}$ and COD ranged between 900 and 12 800 mg $L^{-1}$. Fouling was found to be a major problem for the membranes which could be managed by introducing air and mixed liquor at the bottom of the membrane module through air-lift effects. By applying a face analysis model the correlation among different parameters of the IMBR was derived.

An MBR has also been used to treat the waste water of beverage industries.[39] In beverage industries the spent process water is generated from different operations like juice production, bottle washing, cleaning of tanks and pipes *etc.* All these waters are mixed and treated. Initially physical pre-treatment is done to remove the suspended solids, followed by biological treatment which may be either aerobic or anaerobic. Because of several disadvantages of the activated sludge process (ASP), like poor settling characteristics, MBR has been successfully applied along with conventional processes for the treatment of such water. Experiments were carried out in a pilot plant MBR. It contains a HF module (Zenon ZeeWeeTM-10, 0.4 µm pore size, 0.92 $m^2$ surface area) which was vertically submerged in the bioreactor. The membrane was bubbled with air to avoid fouling and oxygen concentration was maintained at 6 mg $L^{-1}$ in the bioreactor. The bioreactor was inoculated with activated sludge from a full-size municipal waste water treatment plant with there was an initial 10 g $L^{-1}$ of MLSS in the bioreactor. It was observed that the MBR could successfully remove all the pollutants in terms of COD, BOD and TOC with an efficiency >90%. The MBR effluent was suitable for discharge. The MLSS and HRT are the two factors which influenced the performance of an MBR and these were reasonably high in highly polluted water. Frequent backwash and intensive aeration was allowed to avoid membrane fouling and with this continuous MBR operation of 30 days could be achieved.

Katayon *et al.* applied MBR for treating food industry waste water.[40] The MBR used was a combination of an activated sludge reactor along with an MF HF membrane. They mainly emphasised studying the effect of MLSS concentration on the performance of an MBR. Waste water and activated sludge samples were collected from a Nestle factory in Malaysia. A bio reactor having a working volume of 20 L was filled with activated sludge and the HF membrane module was submerged horizontally and vertically. The pore size of the membrane was 0.4 µm. It was observed that low MLSS value favoured the removal of suspended solids and turbidity which were 99.2 and 99.73%, respectively. Moreover comparatively higher flux (5.03 LMH) was achieved at low MLSS than that achieved at high MLSS (2.27 LMH). The effectiveness of MLSS also depend on the positioning of the membrane module.

### *10.4.6.5 Refinery Waste Water*

Water which remains present in the reservoirs along with the hydrocarbons and is produced with crude oil and natural gas is known as produced water (PW). Such water is a major source of pollution in oil and gas fields as it contains different substances like oils, salts, heavy metals, organic acids, radionuclides *etc.* Hence there are problems associated with such water is its disposal. Surface discharge of PW is not advisable as it has many drawbacks like salt deposition, harm to natural vegetation, stream bank erosion *etc.* Two options have been recommended for the management of PW. The first one is re-injection to the discharged well and the second one is reclamation of such water for its reuse in the oil producing arid regions where there is water scarcity. More than 60% of PW is re-injected into the well. Reclamation is also becoming equally important due to the ever-increasing demand for water. The two most important components that need to be removed from PW are oil and salt and the removal should be done in economic and environmentally friendly ways. The conventional methods applied for the treatment of PW are gravity separation and skimming, air flotation, de-emulsification, coagulation and flocculation *etc.*[41] However such processes have many disadvantages like high footprint, high chemical consumption, lower effluent quality, high operation cost *etc.* Hence there is a great need to develop an economical and advance treatment process. In this context an MBR has been applied to treat PW. It has been found to have several advantages in comparison with conventional processes, such as better effluent quality, low sludge production, higher loading rate, no chemical additives, compactness and low energy cost.[41]

PW was treated with an SMBR system.[41] PW is a very complex mixture of dissolved and dispersed oil compounds, production chemical compounds, dissolved formation minerals, production solids (including bacteria, asphaltenes, waxes, formation solids, corrosion and scale products) and dissolved gases. A laboratory scale, continuous-flow SMBR was used in the process. The vertically mounted HF membranes used in the study were supplied by Zena Membranes and had a total area of 0.188 $m^2$ and nominal pore size of 0.1 μm. The aeration rate was 6–8 L $min^{-1}$ in order to meet the dissolved oxygen concentration requirement. The seed sludge used in the MBR system was obtained from a laboratory-scale MBR treating leachate. The COD removal efficiency of the MBR process was 80–85% which was independent of SRT. Almost all the light hydrocarbons from n-C9 to n-C13 were removed by the MBR. Additionally appreciable reduction of hydrocarbons in the range C13 to C40 could also be achieved. On average the hydrocarbon removal efficiency of the MBR was 99%. Oil and grease removal efficiency improved dramatically from 60% to 85% with increase in sludge age. Physical cleaning could restore the permeability of the membrane module to 60% whereas with subsequent chemical cleaning 95% of the permeability could be restored.

Rahman *et al.* studied the application of a crossflow MBR in the treatment of petroleum refinery waste water.[42] The performance of the crossflow MBR was studied at two different MLSS concentrations, namely 5000 and 3000 mg $L^{-1}$. The performance of the whole process was evaluated in terms of COD removal efficiency and hydraulic efficiency. The effect of HRT on process performance was also evaluated. Alumina-based HF membranes having pore size 0.2 μm, with inner and outer diameters of 7 and 10 mm, respectively, with effective surface area 0.09 $m^2$ were used in the MBR system. The system contained an activated sludge bioreactor and a crossflow membrane separation unit. The oil content and COD of oily waste water were found to be $160 \times 10^3$ mg $L^{-1}$ and $370 \times 10^3$ to $2300 \times 10^3$ mg $L^{-1}$, respectively. It was observed that COD removal efficiency was >93% at both MLSS values. The study also showed that HRT did not have a significant effect on the system's performance.

### *10.4.6.6 Pulp and Paper Industry*

Among different industries the pulp and paper industry is one of the huge consumers of water. Process streams in the pulp and paper industry can even be up to cubic meters per second. In fact the pulp and paper industry is responsible for 50% of all the wastes dumped into rivers. As a massive amount of water is consumed in pulp and paper industries, water reclamation is essential. Because of stringent environmental regulations from an anti-pollution viewpoint, a lot of attention is being paid to the treatment of waste water from such industries. Such waste waters form a heterogeneous group, their natures vary widely depending upon the process stage from which they have originated. The temperature and pH of such waters also vary widely. Thousands of different compounds can be identified in such waste water which contains different amounts of wood-based compounds like lignin, polysaccharides, wood extractives *etc.* In addition it also contains degradation products of the wood components depending not only on their origin but also on the nature of the chemicals and additives used in the processing of raw materials or the manufacturing processes adopted. The waste water of pulp and paper industries may be categorized as black liquor, pulp bleaching effluent, white water and so on. Bleaching-stage effluent, having a temperature of >70 °C with acidic or alkaline pH, contains strong colour, high COD and BOD and adsorbable organic halogens. Paper mill white water of temperature 40–60 °C and neutral or faintly acidic or alkaline pH contains suspended solids, microorganisms and colour. Coating colour effluents contain strong colour and pigments. Biologically treated effluents of neutral pH contain strong colour, microorganisms, inorganics, recalcitrant organics and eco-toxic compounds.[43]

In general pulp and paper industry waste water is treated by coagulation followed by an activated sludge process. However in many cases the effluent quality achieved by conventional processes does not satisfy the strict environmental regulations. In this context membrane technology is becoming more popular day by day in treating pulp and paper industry waste water because of its several advantages, such as operation simplicity, reduced foot print, energy economy *etc.* However because of the erratic and extreme nature of waste water the membranes should be thermal, chemical and microbiallt resistant. Although conventional membrane processes like UF, NF, RO or their combination have already been established as quite competent for treating such waste water, the MBR system has been found to be more beneficial. This is because adaptation of the MBR to the variation in the quality of the effluent is much better and the characteristics of the waste water produced from the pulp and paper industry vary widely depending on the changes in the quality of the raw material and conditions employed in the pulp and paper making process.

Zhang *et al.* treated the waste water of a Chinese paper mill through an integrated membrane process consisting of an MBR, a continuous membrane filtration unit (CMF) and RO.[44] The water discharged from the first sedimentation tank was treated with an anoxic/aerobic MBR system. The MBR system of capacity 10 $m^3$ contained a biological treatment system and a submerged HF microfiltration membrane module. Aeration was done to supply oxygen to the aerobic biomass and also to create turbulence to minimize concentration polarization and fouling of the MBR membranes. Dissolved oxygen concentration was maintained above 2 mg $L^{-1}$. In an MBR, $NH_3$–N and dissolved or undissolved organic compounds are eliminated. Permeate from the MBR was then passed through the CMF which is used as a safeguard for the RO system. Although the quality of the permeate of the MBR is quite good, however it is not suitable for reuse in the papermaking process directly. Hence RO is used to produce high-quality paper-making water. The conductivity of RO permeate was <200 μS $cm^{-1}$, COD <15 mg $L^{-1}$, turbidity <0.1 NTU, the chroma of the RO permeate was <15 PCU and the recovery was >65%. Such water could be used in the paper manufacturing process.

Galil and Levinsky studied the application of an MBR to treat waste water from a paper mill.[45] They upgraded the activated sludge process by adopting an MBR. The membrane unit of the MBR contained a hollow fibre membrane module (ZEE WEED 10) with a working capacity of 500 L $day^{-1}$. A flux of 15 LMH was enabled for good operation of the MBR. Anaerobic treatment was carried out. COD, BOD and ammonia reductions of 86, 98 and 90%, respectively were achieved. The TSS (total suspended solid) in the effluent was always <5 mg $L^{-1}$ with an average of 2.5 mg $L^{-1}$. The bioreactor could maintain high levels of MLVSS (mixed liquor volatile suspended solid) (11 000 mg $L^{-1}$ on average) resulting in cell residence times in the range of 20–25 days.

### *10.4.6.7 Metal Industry*

The modification of the surface of any object to enhance its durability and appearance is defined as metal finishing. It is generally done by electroplating where a thin metal coating is electrodeposited on another metal surface. The process yields a considerable amount of metal finishing effluent. Metal plating as well as electrical and electronic component processing industries discharge large volume of water containing heavy metals, such as chromium, zinc, copper, lead, arsenic, nickel and cyanides in reasonably high concentrations. Since these metals cannot be degraded they remain in the environment. Some of these metals, like manganese, zinc, iron, copper and chromium, are important for physiological function and are ingested at low concentration. But if these metals are ingested beyond a threshold limit they can cause acute or chronic toxicity in higher organisms, microorganisms and plants. Metals like cadmium, lead, mercury and nickel are potentially hazardous to the aquatic environment whereas copper, chromium and zinc are classified as the potential pollutants. Contaminated water from the metal industry affects the food chain of bio-organisms including human beings. These metals can damage or reduce mental health and central nervous system functions, lower energy levels, and damage blood composition, lungs, kidneys, liver and other vital organs. Long-term exposure may result in slowly progressing physical, muscular and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy and multiple sclerosis.[46]

The conditions to be met for the disposal of such contaminated water into the water bodies has become highly restricted due to environmental protection laws. Hence it is imperative to treat such water to make it environmentally friendly before discharge or reuse. The conventional processes used to treat such contaminated water are cementation, solvent extraction, ion exchange, chemical precipitation, evaporation *etc.* In addition membrane technology like NF and RO may also be used to treat such water. However membrane processes are expensive and the concentrate stream generated in the membrane filtration process is of huge volume and itself has disposal issues. Such concentrates are more toxic than the feed water. Hence use of membrane processes in conjunction with biological treatment has attracted huge attention. Here membrane treatment acts as a secondary treatment after various types of pre-treatment. Thus, MBRs have been introduced in the area of waste water treatment containing heavy metal ions. The main advantage of an MBR is its uncoupled HRT and SRT. It can be operated at long SRT with a smaller footprint and high MLSS concentration. Hence the impact of MLSS on metals removal is thus a key consideration for MBRs. As, basically, the membranes in an MBR (MF or UF) function using size-exclusion phenomena, all particulate matter <0.1 mm is expected to be rejected.[47] In such cases removal of metals associated with suspended solids are expected to be quantitative. By using an MBR >95% metal removal has been observed for metals such as Cd, Cr, CU, Pb and Hg.[46] Exceptions are Ni and Zn. This indicates that metals mostly remain in suspended form or they precipitate reasonably well in the treatment process. It has also been observed that metals present even at low concentrations are removed efficiently by an MBR. An MBR can remove 77–85% of Cu when its influent concentration is 2.6 mg $L^{-1}$.[48]

SRT has a great influence on the removal of metal ions. For Co, Cr, Cu, Ni, Pb and Zn longer SRTs facilitate their improved retention in an MBR. An increase in SRT from 10 to 30 days increased Cr removal from 56% to 85%.[49] Similarly the removal efficiency of Ni and Pb increased from 40% to 89% and 50 to >98%, respectively, on increasing the SRT from 11 to >1000 days.[48,50] The removal of Zn, the most abundant transition metal, increases from 51% to 94% on increasing the SRT from 10 to >300 days.[48,49] In general it has been observed that an increase in SRT and/or MLSS concentration increases the removal efficiency of most metal ions by 12–66%.[46] SRT does not have any effect on the separation of metal ions when they are present at very low concentration, *e.g.* As concentration <4 μg $L^{-1}$[49,50] and also on those metal ions which have great affinity for biomass or biomass-bound ligands like cadmium, silver and vanadium.[48,49,51]

Moslehi *et al.* studied the removal of Cr, Zn and Pb by using an MBR containing tubular ceramic microfiltration membranes having a pore size of 0.1 μm.[52] The membranes were hydrophilic with external and internal diameters of 10 and 7 mm, respectively, and an internal membrane area of 50.5 $cm^2$. It was observed that by using an MBR under all experimental conditions the COD removal efficiency was much better than what could be achieved in an activated sludge process. For concentrations of Cr, Zn and Pb <50 mg $L^{-1}$ the removal efficiencies were 95, 76 and >60%, respectively. In all the three cases the performance of an MBR was much better than the CAS process.

A combination of an MBR with RO was tried by Malamis *et al.* to study the removal of heavy metal ions.[53] Municipal waste water was spiked with Cu, Pb, Ni and Zn. The MBR contained PVDF membranes with pore size 0.04 μm. The MBR was operated at an SRT of 15 days and at a HRT of 11.2 h.

The removal efficiency of MBR was in the order of Pb (96%) > Cu (85%) > Zn (78%) > Ni (48%). The variability in metal removal efficiencies was attributed to fluctuations in influent metal concentrations, metal competition, changes in pH and MLSS concentration. When RO was combined with the MBR the heavy metal ion removal efficiency increased to Cu (98.1%), Pb (99.3%), Ni (97.1%) and Zn (97.5%).

### *10.4.6.8 Chemical Industry*

Phenol is a common contaminant in the effluent of different industries, such as chemical, pharmaceutical, petrochemical, oil refineries, paint production, phenol resin *etc.* Even at a very low concentration phenol is very harmful to human health and the ecosystem because of its toxicity. Phenol absorption may result in different fatal diseases like skin cancer, cardiac arrhythmias, renal diseases *etc.* Because of such harmful effects on human health and the ecosystem removal of phenol from waste water is of high priority. In general phenol is removed by traditional techniques, such as, adsorption, steam distillation, wet air oxidation, liquid–liquid extraction and bio degradation. It is also treated by some advanced techniques like photo oxidation, electrochemical oxidation, membrane extraction *etc.* Among all these processes, biodegradation has some advantages because of its low cost. However at a high concentration of phenol, microorganisms are inhibited because of the high toxicity of phenol and at the same time the floating bio-degradative population becomes dominant and is washed out with time, making the CAS process ineffective. To prohibit the washout of the floating population an MBR has been introduced.

Ahn *et al.* applied an MBR to remove high-loading phenol contamination.[54] The MBR contained a HF MF module with a PVDF membrane having pore size of 0.4 µm and effective area of 14 cm$^2$. The reactor was inoculated with activated sludge (≈2000 mg VSS L$^{-1}$). The pH and dissolved oxygen level (1.5 mg DO L$^{-1}$) of the reactor was monitored. The mineral medium contained 2.13 g $Na_2HPO_4$, 2.04 g $KH_2PO_4$, 1 g $(NH_4)_2SO_4$, 0.067 g $CaCl_2{\cdot}2H_2O$, 0.248 g $MgCl_2$ $6H_2O$, 0.5 mg $FeSO_4{\cdot}7H_2O$, 0.4 mg $ZnSO_4{\cdot}7H_2O$, 0.002 mg $MnCl_2{\cdot}4H_2O$, 0.05 mg $CoCl_2{\cdot}6H_2O$, 0.01 mg $NiCl_2{\cdot}6H_2O$, 0.015 mg $H_3BO_3$ and 0.25 mg EDTA per litre It was observed that when phenol was loaded at a low concentration, *i.e.* ≈100 mg L$^{-1}$, it was efficiently removed under a stable and steady performance of the MBR. However at high loading of phenol, *i.e.* at a toxic level (≈1000 kg L$^{-1}$) a microbial community shift was observed. A milky loading population appeared in the bio-reactor after an acclimation period of 3 days. These non-settling floating fungal populations (*Fusarium oxysporum* and/or *Symbiodinium* sp.) were able to tolerate phenol-mediated stress and degraded phenol five times more efficiently than settling microbes at this high concentration.

An extractive membrane bioreactor (EMBR) was used by Loh *et al.* for the removal of phenol.[55] The EMBR is a novel waste water treatment process which is a combination of an aqueous–aqueous extractive membrane process and bio-degradation. In this process the organic pollutant is transported from feed solution to receiving solution through a non-porous membrane by a solution diffusion mechanism driven by the concentration gradient across the membrane. At the receiving side the organic pollutant is degraded by microorganisms. Contaminated water in very harsh conditions like extreme pH and high salt concentration can be treated by an EMBR very easily as the membrane separates the bioreactor from the feed solution. Additionally as continuous biodegradation of the organics is happening in the receiving side, the organic concentration gradient, *i.e.* the driving force, can be maintained easily. However the membrane should have high organic flux and it should be impermeable to inorganics and water. In this study composite HF membranes were prepared by coating a layer of polydimethylsiloxane (PDMS) on poly etherimide (PEI). It was observed that the overall mass transfer coefficient of phenol depends upon the degree of intrusion of PDMS into PEI. Sample analysis from the bioreactor at regular intervals showed that the phenol concentration in the bioreactor remained at zero, indicating that acclimated sludge was able to degrade all the phenol that diffused from the feed chamber to the receiving chamber.

An EMBR has also been used by Liao *et al.* for the removal of phenol.[56] For this work a nanofibrous composite membrane with a four-tiered structure, consisting of a dense PDMS selective layer, a PVDF nanofibrous sublayer, a non-woven mechanical support and a rough micro/nano-beaded layer, was developed by electrospinning and spray-coating. They carried out both cross-flow and submerged-membrane operations. The composite membranes exhibited a very high mass transfer coefficient of phenol even at a high feed concentration of 1000 mg $L^{-1}$.

## 10.5 Conclusion and Future Prospects

One of the most advanced technologies in the area of separation and purification is MBR technology. Today MBR technology is applied commercially around the world for municipal and industrial waste water treatment. This is because of several advantages of MBRs, such as higher efficiency, smaller footprint and lower sludge production compared with conventional activated sludge processes. Presently several large-scale MBR plants with capacity 0.100 MLD are in operation in different parts of China, Singapore, South Korea, Oman, Hong Kong, Sweden, France, Belgium, Italy and the USA. These plants are mostly for domestic and municipal waste water treatment and their capacities vary from 40 to 800 MLD.

In addition to the treatment of municipal waste water MBR technology is gradually becoming popular to treat the waste water of different industries like pharmaceutical, textile, petrochemical, food *etc.* The selection of the type and design of MBR depends upon the characteristics of the waste water, namely its turbidity, BOD, COD, suspended solids, colour, pH, concentration of heavy metals, oil and grease content *etc.* However, besides the many advantages of MBRs they have a few disadvantages which need to be removed for their widespread commercial application. The most important one is the avoidance of membrane fouling. Fouling is an unavoidable problem associated with membrane applications. It imposes a genuine limitation on the application of MBRs. Mixed liquor suspended solid concentration and soluble microbial products are majorly responsible for membrane fouling. In addition factors like inherent membrane properties, operating conditions and design of the total MBR system are also contributing factors to fouling. An enormous amount of research is being undertaken to develop antifouling membranes, and at the same time a proper antifouling strategy equally applicable to all MBR systems needs to be developed to mitigate fouling. Moreover optimization of the basic characteristics of the sludge, such as F/M ratio, SRT, HRT, dissolved oxygen *etc.* may also help to reduce fouling.

High-energy consumption and high transmembrane pressure are also the limitations to the broader application of MBRs. Of the total energy consumed 50% goes to aeration. Hence membrane aeration time makes a vital contribution to the total cost. Reduction of aeration time and SRT are vital for an economic MBR. Proper care should be taken to maintain the carbon to nitrogen ratio and EPS concentration in the reactor as decrease in C/N and increase in EPS concentration results in a fall in MBR performance. Efforts are ongoing to make MBRs an economic waste water treatment process through imposition of proper pre-treatment, fouling mitigation systems, reduction of aeration and pumping costs and maintenance of optimum sludge properties. With such scientific and technical improvisation taking place, MBRs are one of the most promising commercial waste water treatment technologies of the future.

## List of Abbreviations

| | |
|---|---|
| AeMBR | Aerobic membrane bioreactor |
| AnMBR | Anaerobic membrane bioreactor |
| AOP | Advanced oxidation process |
| ASB | Activated sludge bioreactor |
| ASP | Activated sludge process |
| AVP | Automatic variation filtration |
| BOD | Biochemical oxygen demand |
| CAS | Conventional activated sludge |
| CMF | Continuous membrane filtration |
| COD | Chemical oxygen demand |
| EC | Electrocoagulation |
| ELAMBR | External loop airlift membrane bioreactor |
| EMBR | Extractive membrane bioreactor |
| EPS | Extracellular polymeric substances |
| F/M | Food to microorganism ratio |
| HF | Hollow fibre |
| HMBR | Hybrid membrane bioreactor |
| HRT | Hydraulic retention time |

| | |
|---|---|
| IMBR | Immersed membrane bioreactor |
| LMH | Litre $m^{-2}$ $h^{-1}$ |
| MBR | Membrane bioreactor |
| MF | Microfiltration |
| MLD | Million litres per day |
| MLSS | Mixed liquor suspended solid |
| MLVSS | Mixed liquor volatile suspended solids |
| NF | Nanofiltration |
| NSAID | Non-steroidal anti-inflammatory drugs |
| PAC | Powdered activated carbon |
| PAN | Polyacrylonitrile |
| PDMS | Polydimethylsiloxane |
| PE | Polyethylene |
| PEI | Polyetherimide |
| PES | Polyether sulfone |
| PhACs | Pharmaceutically active compounds |
| PP | Polypropylene |
| PSF | Polysulfone |
| PTFE | Polytetrafluoroethylene |
| PVDF | Polyvinylidene fluoride |
| PW | Produced water |
| RO | Reverse osmosis |
| SC | Sludge concentration |
| SMBR | Submerged membrane bioreactor |
| SRT | Sludge retention time |
| SSMBR | Side stream membrane bioreactor |
| TOC | Total organic carbon |
| UF | Ultrafiltration |

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CHAPTER 11

# *Membrane Bioreactors for Industrial Wastewater Treatment*

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## 11.1 Introduction

A membrane bioreactor (MBR) is a technology used to treat wastewater that combines a bioreactor and membrane separation process. A bioreactor in an MBR system has the same function as the aerated tank of any activated sludge process in which wastewater is treated by the activity of microorganisms. In an MBR process, instead of separating treated water and microorganisms by gravity, porous membranes with 0.05–0.1 mm pore diameters are used to separate treated water and microorganisms. The membranes appropriate for MBR application will be small enough to reject activated sludge flocs, free-living bacteria, and even large size viruses or particles. Hence, the MBR produces very high-quality treated water containing almost no detectable suspended solids. The treated water quality obtained in an MBR process is equivalent to tertiary wastewater treatment. Membrane filtration in an MBR process generated a smaller footprint than an activated sludge process. Both the activated sludge process and MBR processes utilise the metabolic power

Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

of microorganisms in bioreactors for the treatment of wastewater. Therefore, the rate of wastewater treatment is basically proportional to the concentration of active biomass in the bioreactor, however in an activated sludge process it is impossible to increase the concentration of activated sludge greater than a certain level due to the limitations of secondary clarifiers. About 5000 mg $L^{-1}$ of mixed liquor suspended solid (MLSS) in a bioreactor is regarded as the maximum concentration of activated sludge for operating a secondary clarifier while in an MBR process a maximum MLSS of 8000–12 000 mg $L^{-1}$ is regarded as optimum. Higher MLSS concentration during MRB operations results in a smaller bioreactor foot print and higher quality treated water with an equivalent amount of wastewater as compared to a conventional activated sludge process (CAS). Higher MLSS concentration in an MBR reduces waste sludge production (due to endogenous decay of microorganisms), hence reducing the cost associated with waste activated sludge. Another characteristics feature of MBR operation is the long 'solid retention time', typically >20–25 days compared with a conventional activated sludge process which is typically 5–15 days, resulting in high-quality effluent. In an MBR process with MLSS concentration equal to waste activated sludge concentration, 'solid retention time' can be modulated in a simple and precise way.[1] Some of the negative aspects of the MBR process have also been cited by several researchers and are presented in Table 11.1.

High COD (chemical oxygen demand) loading and lower F/M (food to microorganism ratio) ratio favour growing of nitrifying bacteria and more compact design. The longer solid retention rate in an MBR compared to a conventional activated sludge process also favours consistent nitrification efficiency and better removal of persistent organic matter. An attempt has been made over the last few decades to resolve the limitations of membrane

**Table 11.1** Comparison of the MBR process with the conventional activated sludge process.

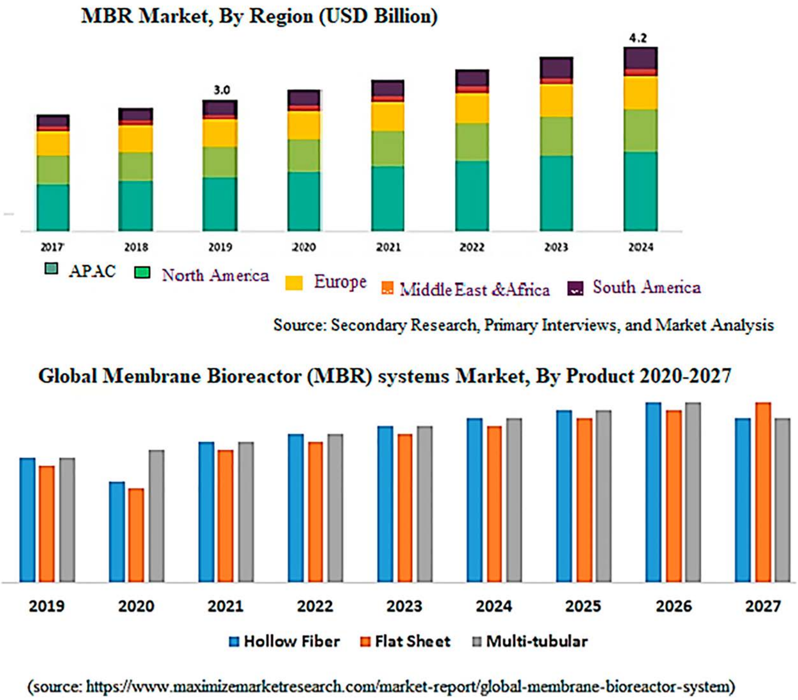
| Advantages | Disadvantages |
|---|---|
| Potable grade high quality treated water free of pathogens | Fouling tendency of membrane involves high maintenance cost operational complexities |
| Low foot print and smaller, compact design | Higher installation and operational cost to adopt antifouling strategies, anti-foaming strategies |
| Higher chemical oxygen demand (COD) loading results compact bioreactor | |
| Reduced waste activated sludge production | |
| Easy tuning of the solid retention time in the bioreactor | |

fouling and the operational complexities that result in the high expenditure associated with the MBR process by integrating it with cutting edge technologies like nanotechnology and molecular biology. Incorporation of carbon nano tubes with the membrane have been reported to retard growth of microorganisms in the pores and on the surface of the membrane.[2] Various smart aeration designs have been adopted to make the MBR process commercially viable and reducing aeration energy consumption during MBR processing is still a crucial area of research and development for the industries concerned. The direct addition of chemicals and enzymes as a fouling reduction strategy has also been attempted.[3] Another technique, as reported by several groups of researchers, is the application of quorum sensing as a method of fouling amelioration using quorum-quenching bacteria encapsulated in a microporous membrane or using externally entrapped quenching bacteria.[4,5] The future direction of MBR technology for wastewater treatment will involve the design and application of hybrid processes like MBR coupled with reverse osmosis and MBR coupled with an advanced oxidation process, as potential water reuse practices. MBR technology has been studied since 1969 and full-scale commercial MBR technology has been reported since 1991, while the largest MBR plant reported so far is in France: Aval municipal WWTP by GE designed to treat 224 000 $m^3$ $day^{-1}$ of wastewater.[2] The application of MBRs has been attempted to treat effluent from various industrial sectors, such as food and beverages, petroleum, pharmaceutical, pulp and paper industries, textile, and ship industries. Industrial applications differ from municipal application based on issues like, (i) higher concentrations of organic matter, more bio refractory and less biodegradable than municipal effluent, (ii) more variation in the concentrations of pollutants, both seasonally and diurnally, (iii) very significant variations across the different industrial sectors, with the least bio refractory effluents from the food and beverage industry and the most bio refractory from landfill leachate applications, and (iv) no requirement for the removal of pathogenic micro-organisms, unless the effluent is combined with a sewage stream. This article covers the basics of MBRs with various operational features, configurations and applications in various industrial sectors. Significant results of scientific publications are highlighted along with the associated advantages and drawbacks of MBR adoption in industry.

## 11.2 Basics of a Membrane Bioreactor

An MBR is an advanced integrated recycle and reuse solution. The MBR operation principle is based on the inherent principle of the membrane separation process specifically using perm-selective membranes, like ultrafiltration/microfiltration. The MBR integrates the concept of membrane separation with a biological treatment process either as a separate unit operation downstream of the biological step (polishing unit), or integrated into a biological process. An MBR integrates the function of a biological reactor with an advanced membrane separation process. Commercial MBR processes utilize the membrane as a filter medium for rejection of solid materials produced during biological treatment of wastewater to obtain clarified and disinfected effluent. In wastewater treatment, an MBR functions as a tertiary treatment to reject sludge flocs and free living bacteria with membrane 0.05–0.1 μm. MBR application has got attention as a promising wastewater treatment option where space is limited and high-quality effluent is required for reuse application. Increasingly stringent environmental legislation coupled with decreasing capital (specifically membrane) and operating (primarily energy) costs has promoted MBR installations and implementation, which has driven substantial growth in the number of MBR plants with >100 mega litres per day (MLD) in peak daily flow (PDF) capacity. The global MBR systems market was valued at US$ 2.53 bn in 2019 and is expected to reach US$ 5.62 bn by 2027, at a compound annual growth rate (CAGR) of 15.55% during a forecast period (including lockdown impact) (Figure 11.1)

The key MBR market players profiled in MBR market statistics involve SUEZ Water Technologies & Solutions (France), Kubota (Japan), Evoqua Water Technologies (USA), Mitsubishi Chemical Aqua Solutions (Japan),


MBR Market, By Region (USD Billion)

Source: Secondary Research, Primary Interviews, and Market Analysis

Global Membrane Bioreactor (MBR) systems Market, By Product 2020-2027

(source: https://www.maximizemarketresearch.com/market-report/global-membrane-bioreactor-system)

**Figure 11.1** Global membrane bioreactor market scenario.

Toray Industries (Japan), CITIC Envirotech Ltd. (Singapore), Koch Membrane Systems (USA), Alfa Laval (Sweden), Veolia (France), and Newterra (Canada). These companies have adopted various organic as well as inorganic growth strategies between 2014 and 2019 to enhance their regional presence and meet the growing demand for MBRs from emerging economies. MBRs have been implemented in various industrial sectors with emphasis on treatment of high organic carbon containing biodegradable pollutants. The design of a membrane bioreactor system depends on three basic units, namely, configuration of the membrane (geometry of the membrane, *e.g.* hollow fibre, flat sheet or tubular, and the flow pattern), membrane separation process (placement of the membrane module in the overall MBR process, *i.e.* either inside or outside the tank), and associated bio-treatment process (types of pollutant load and types of products formed). The biotreatment component may be 'aerobic treatment' (using oxygen) and leading to carbon dioxide as the main carbon-based product or 'anaerobic treatment' in the absence of air with methane as the major product. Figure 11.2 represents most of general characteristic features of an MRB and probable designs adopted in various industries.

When considering configurations, there is a trade-off between the perceived robustness and simplicity of the sidestream configuration and the generally lower cost of the immersed configuration. This cost difference, which is associated with the higher energy and membrane cost (cost per $m^2$ of membrane area) of the side stream configuration, becomes less significant (in terms of the cost per unit time) for small installations. So for small flows of difficult-to-treat (or 'biorefractory') effluents, the side stream

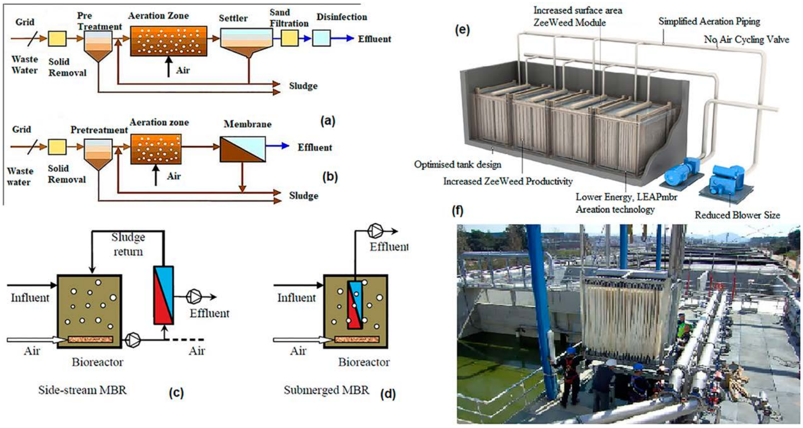


**Figure 11.2** Operational schematics of waste water treatment methods. (a) Conventional activated sludge process, (b) membrane bioreactor process technique, (c) side stream MBR operation, (d) submerged MBR operation, (e) submerged MBR operation adopted in industry, and (f) side stream MBR adopted in industry.

configuration is often selected because it is simpler in operation, is smaller in footprint, and simpler to service, especially with reference to membrane replacement. For very large plants, the immersed process configuration is always selected and nearly always the hollow fibre membrane configuration since the operating (or running) expenditure (opex) is usually lower than for flat sheet membranes.

The MBR process was introduced in 1969, as part of the Dorr–Oliver research programme, combining the use of an activated sludge bioreactor with a crossflow membrane filtration loop (side stream configuration) and the set-up was maintained with crossflow velocity of 1.2–1.8 m $s^{-1}$, 150–185 kPa with flux 13–23 L $m^{-2}$ $h^{-1}$, with biological oxygen demand (BOD) < 5 mg $L^{-1}$ in processed water and 100% removal of coliform bacteria. The breakthrough for the MBR came in 1989 with submerging the membranes in the bioreactor (direct solid–liquid separation using hollow fibre (HF) in activated sludge tank) using a 0.1 μm polyethylene HF membrane, suction pressure 13 kPa, and hydraulic retention time (HRT) 4 h. A generalized process schematic for an MBR is shown in Figure 11.3.

The selection of an MBR process for wastewater treatment is based on efficacy and cost factors. 'Efficacy' relates to the throughput and treated wastewater quality. Efficacy also embraces robustness of the system, its ability to consistently meet the treated water quality, and its susceptibility to process failure or breakdown. The cost factor is usually divided into the capital (or investment) expenditure ('capex') and the operating (or running) expenditure ('opex') involving the membrane and energy costs.

Typical MBR operational process conditions and effluent quality and MBR effluent quality are been presented in Table 11.2.

MBR components are basically categorized into two types (1) biological treatment, and (2) membrane separation unit. Biological treatment involves removal of microbiological floc, aggregated bacterial matrix (EPS),

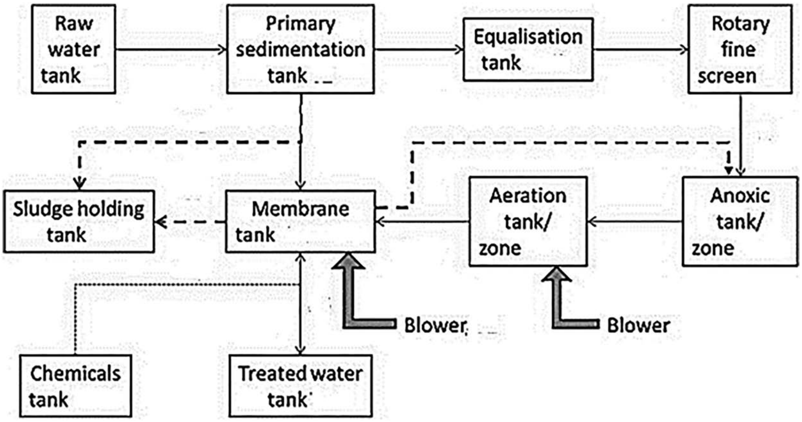


**Figure 11.3** Process schematic of the membrane bioreactor.

**Table 11.2** Operational features of the MBR process and MBR effluent quality.

| Classification | Unit | Typical value | Range |
|---|---|---|---|
| *Operational condition* | | | |
| COD loading | kg $m^{-3}$ $day^{-1}$ | 0.5 | 1–3.2 |
| MLSS | mg $L^{-1}$ | 10 000 | 5000–20 000 |
| MLVSS | mg $L^{-1}$ | 8500 | 4000–16 000 |
| F/M ratio | g COD/g MLSS per day | 0.15 | 0.05–4.0 |
| SRT | day | 20 | 5–30 |
| HRT | h | 6 | 4–9 |
| Flux | L $m^{-2}$ $h^{-1}$ | 20 | 15–45 |
| Suction pressure | | 10 | 4–35 |
| Dissolved oxygen (DO) | mg $L^{-1}$ | 2.0 | 0.5–1.0 |

*Typical MBR effluent quality*

| BOD mg $L^{-1}$ | TSS mg $L^{-1}$ | $NH_3$–N mg $L^{-1}$ | Total P mg $L^{-1}$ | Total N mg $L^{-1}$ | SDI (silt density index ) | Turbidity NTU | Total coliforms cfu/100 mL | Faecal coliforms cfu/100 mL | Coliform reduction log removal | Virus reduction log removal |
|---|---|---|---|---|---|---|---|---|---|---|
| <2.0 | <2.0 | <1.0 | <0.1 | <3–10 | <3.0 | <0.5 | <100 | <10 | >5–6 | <4 |

and various types of microorganisms (both eukaryotic and prokaryotic) of diverse species in an open system. The membrane separation unit is further categorized with regard to types of membranes, types of modules, and membrane cassettes. Types of membrane may be either ceramic or polymeric on the basis of composition; the membrane may be an RO, NF, UF, MF ion-exchange membrane, charged membrane or composite type based on selectivity and pore-size distribution, and modules may be flat sheet (FS), HF and multitube (MT) type based on configuration and MBR performance requirement. Table 11.3 presents a brief summary of membrane and module configurations adopted in various industries for wastewater treatment purposes.

A recent advance in MBR technology is moving bed biofilm reactor (MBBR) technology which employs thousands of polyethylene biofilm carriers operating in mixed motion within an aerated wastewater treatment basin.[6] Each individual biocarrier increases productivity through providing a protected surface area to support the growth of heterotrophic and autotrophic bacteria within its cells. It is this high-density population of bacteria that achieves a high-rate biodegradation within the system, while also offering process reliability and ease of operation. Some of the specific features of the MBBRs are the presence of suspended or fixed biocarriers (or media) to the aeration tank to promote growth of biofilm on the surface of biocarriers, use of strainers to prevent suspended biocarriers from being carried over to the membrane tank and damaging the membrane, improved membrane performance due to the lower MLSS (a great portion of microorganisms are attached, not suspended), improved oxygen transfer efficiency (OTE) due to the lower MLSS, increased contact time of bubbles with liquid since biocarriers hinder bubbles from rising, increased effective microorganisms population in the aeration tank including suspended and fixed microorganisms, and the volumetric organic, volume to food mass ratio (V/F), can increase while tank size shrinks.[7] Some specific process benefits involve (1) reduced and compact design, (2) easily expandable nature (capacity can be easily upgraded by simply increasing the fill fraction of biofilm carriers), (3) single-pass process, *i.e.* no return of activated sludge stream is required, (4) highly load-responsive in nature (actively sloughed biofilm automatically responds to load fluctuations), and (v) minimal maintenance, no specific range of F/M ratios or MLSS levels are required to be maintained during operation. As reported in several publications, during industrial wastewater treatment BOD level is reduced to <250 mg $L^{-1}$. Moving bed biofilm reactors have been reported to be ideally suited for nitrification applications because the process enables the proliferation of nitrifying bacteria within the protected surface area of thousands of plastic pieces, which helps to achieve highly reliable, complete nitrification within compact tank volumes. MBBR technology also enables the biological process to sustain a high-density population of nitrifying bacteria without relying on increased solids retention time (SRT) or MLSS, addressing current wastewater requirements and expandability to meet future loads or more stringent discharge requirements within a compact design.

**Table 11.3** Commercial membrane and module configuration.

| Membrane configuration | Module configuration or operating method | Driving force | Pore size | Common applications[a] | Example |
|---|---|---|---|---|---|
| FS | Plate and frame (PF) | Pressure | MF/UF | WWT, EDI | Pall DT™, Electrocell (EC) |
| | Immersed membranes | Vacuum | MF/UF | iMBR | Kubota, Toray Membray, Mycrodyne Bio-Cel®, Pure Envitech SBM |
| | Spiral wound (SW) | Pressure | UF/RO | DS, PR | Dow Filmtec, Hydranautics, Toray Romembra, Woongjin CSM® |
| HF | Contained in pressure vessels | Pressure | MF/UF/RO | WT, PR, *etc.* | Asahi Microza®, Toyobo Hollowsep®, GE ZW1500 |
| | Immersed module without pressure vessels | Vacuum | MF/UF | WT, iMBR | GE ZW500, Asahi Microza®, Mitsubishi Sterapore™, Econity |
| TB | Pressure filtration | Pressure | MF/UF | WWT, PR, sMBR | Koch Abcor®, ITT PCI, |
| | Vacuum filtration with bubbling | Vacuum | MF/UF | sMBR | Norit Airlift™ |

[a] DS, Desalination; ED, electrodialysis; PR, process recovery; WT, water Treatment; WWT, wastewater treatment.

A technological advancement of the MBBR is the membrane aeration biofilm reactor (MABR), which is the extension of the aerobic biological treatment process to MBRs.[8] The MABR has been commercialized since 2015, although the term 'MABR' was first introduced in the 1990s when the process, originally based on a pure oxygen-fed technology, was originally studied.[9,10] Its operation is fixed-film based, like a trickling filter, avoiding a purely suspended growth process like activated sludge, as is the case for the MBR. In an MABR, usually HF membranes are used as an alternative aerator, rather than for biomass separation, hence requiring an additional membrane separation stage to obtain highly-clarified effluent. The biofilm is usually formed on the membrane itself, and the oxygen is delivered directly into the biomass. The usual mass transfer limitations of a conventional fine bubble diffuser aerator (FBDA), limiting the standard oxygen transfer efficiency (SOTE) to somewhere between 10 and 40%, therefore no longer apply. The membrane provides greatly increased aeration efficiency, and significantly reduced aeration energy costs, but the high cost associated with the membrane limits its application. Biofilm growth on the HF membrane with higher membrane clogging enhances operational complexity. Several others technological advancements that have been reported are a bubbleless aeration MBR and extractive membrane bioreactors (EMBR).

## 11.3 Limitations and Trouble-shooting of MBR Operation

In an MBR process, the operational limitations basically involve a decline in permeate flux which is the consequence of membrane fouling, membrane clogging, and cleaning. Membrane fouling refers to the accumulation of solute molecules on the membrane surface or the plugging of the membrane pores with dissolved, colloidal, and fine solutes, which are normally removed by physical and chemical cleaning cycles. Clogging (sludging) involves the agglomeration of gross solids within or at the entrance to the membrane channels. The only solution to overcome the limitations of the membrane separation process is basically the tuning of the membrane cleaning operation according to the process feed nature with optimization of the process economy. Both physical and chemical routes of membrane cleaning may be employed in MBR operation and maintenance. Physical cleaning is usually done by reversing the flow back through the membrane (back flushing), or by scouring the membrane with air bubbles (relaxation). A combination of these two techniques is sometimes also used to enhance the cleaning performance. In a chemical cleaning process, oxidative chemicals are often used in industry in combination with mineral acids/organic acids/weak bases. Some industries with severe fouling problems have reported a combination of physical and chemical cleaning protocols, described as 'chemically-enhanced backflush' (CEB). Although chemical cleaning is effective in overcoming irreversible/permanent fouling, neither physical nor chemical cleaning protocols have been reported effective in countering clogging of the membrane. Foam (chemical/biological) creation has been practiced in MBR systems to enhance the performance of the membrane. Anthropogenic surfactants (detergents)/ biosurfactants (formed from micro-organisms/filamentous bacteria) have been used in MBR systems for foam generation.

Though no standard protocol has been suggested by researchers to control foaming in an MBR, some techniques practiced by industries are the proper identification of the reason for foaming, identification of organisms, and optimization of the operational principle, and the strategies involve the reduction of SRT. Some other techniques are the washing out of filamentous bacteria and surfactant substrates, the introduction of selectors before aeration tanks, control of filamentous bacterial growth by the addition of various oxidizing agents.[11] The exploration of antifoaming agents has become a growing research and development area associated with MBRs. Research and development involving exploration of antifoaming agents has become a growing research area associated with MBRs.

## 11.4 Commercial MBR Plants and MBR Application in Industrial Sectors

A summary of the industrial MBR plants commercially implemented worldwide is presented in Table 11.4.

## 11.5 Industrial Application of Membrane Bioreactors

Application of MBRs has already been practiced for full-scale municipal wastewater treatment worldwide and utilization of the MBR system in industrial sectors is the most important recent technological advance in the waste effluent treatment sector. The MBR system, represents a decisive step in the production of high effluent quality and hygienically pure effluent with high operational consistency. Advanced MBR wastewater treatment technology has already been successfully applied at an ever-increasing number of locations around the world as presented in Table 11.3. The industrial waste stream differs from the municipal waste stream because of the presence of high organic loading and persistent organics, which necessitates the application of the MBR.[12] Some of the notable industrial sectors utilizing the MBR system for recycling and reuse purposes are (1) food and beverage sectors; (2) pharmaceutical industries; (3) petrochemical industries; (4) tannery and winery industries; (5) textile industries; and (6) paper and pulp industries, but the potential is not limited to these industries only and researchers are developing advanced MBR technologies suitable for broad spectrum of application irrespective of the nature of the pollutants in the waste stream. This technology has also been reported suitable for toxic effluents such as textile wastewaters (dos Santos *et al.*, 2007),[13] solvent-containing pharmaceutical

**Table 11.4** Summary of the industrial MBR plants commercially implemented worldwide.

| Installation | Location | Technology supplier | PDF (MLD) | ADF (MLD) |
|---|---|---|---|---|
| Tuas Water Reclamation Plant | Singapore | Total bacterial count (TBC) | 1200 | 800 |
| Beihu WWTP | Hubei, China | Beijing Origin Water Technology Co., Ltd (BOW) | 1040 | 800 |
| Henriksdal, Sweden | Near Stockholm, Sweden | SUEZ – Water Technologies & Solutions | 864 | 536 |
| Huaifang Water Recycling Project | Beijing, China | Memstar | 780 | 600 |
| Water Affairs Integrative EPC | Xingyi, Guizhou, China | Beijing Origin Water Technology Co., Ltd (BOW) | 399 | 307 |
| Seine Aval | Acheres, France | SUEZ – Water Technologies & Solutions | 357 | 224 |
| Canton WWTP | OH, USA | Ovivo (GLV Group) | 333 | 159 |
| 9th and 10th WWTP | Kunming, Yunnan, China | Beijing Origin Water Technology Co., Ltd (BOW) | 325 | 250 |
| Wuhan Sanjintan WWTP | Hubei Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 260 | 200 |
| Jilin WWTP (Phase 1, upgrade) | Jilin Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 260 | 200 |
| Caotan WWTP PPP project | Xi'an, Shanxi, China | Beijing Origin Water Technology Co., Ltd (BOW) | 260 | 200 |
| Huhehaote Xinxinban WWTP | Inner Mongolia, China | Beijing Origin Water Technology Co., Ltd (BOW) | 260 | 200 |
| Weibei Industrial Park Wanzi WWTP | Xi'an, China | Beijing Origin Water Technology Co., Ltd (BOW) | 260 | 200 |
| Liaoyang City Centre WWTP Phase 2 | Liaoyang, China | Memstar | 260 | 200 |
| Fuzhou Yangli WWTP Phase 4 | Fuzhou, China | Memstar | 260 | 200 |
| Chengdu Xingrong Project (Plant 8) | Chengdu, China | Memstar | 260 | 200 |
| Chengdu Xingrong Project (Plant 3) | Chengdu, China | Memstar | 260 | 200 |
| Chengdu Xingrong Project (Plant 5) | Chengdu, China | Memstar | 260 | 200 |
| Gaoyang Textile Industrial Park WWTP Phase 1 & 2 & 3 | Gaoyong, China | Memstar | 260 | 260 |
| Euclid | OH, USA | SUEZ – Water Technologies & Solutions | 250 | 83 |
| Shunyi | Beijing, China | SUEZ – Water Technologies & Solutions | 234 | 180 |

| | | | | |
|---|---|---|---|---|
| Qinghe WRP (Phase 2) | Beijing, China | Beijing Origin Water Technology Co., Ltd (BOW) | 195 | 150 |
| Nanjing East WWTP (Phase 3) | Jiangsu Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 195 | 150 |
| Yantai TaoziWan WWTP (Phase 2) | Shandong Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 195 | 150 |
| Jilin WWTP (Phase 2) | Jilin Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 195 | 150 |
| Chengdu Xingrong Project (Plant 4) | Chengdu, China | | 195 | 150 |
| Jiaxin Project | Jiaxin, China | Memstar | 195 | 150 |
| Brussels Sud | Brussels, Belgium | SUEZ – Water Technologies & Solutions | 190 | 86 |
| Riverside | CA, USA | SUEZ – Water Technologies & Solutions | 186 | 124 |
| Changsha 2nd WWTP | Hunan Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 182 | 140 |
| Nanyang High-tech Zone Optoelectronics Industry Park WWTP | Henan, China | Beijing Origin Water Technology Co., Ltd (BOW) | 182 | 140 |
| Brightwater | WA, USA | SUEZ – Water Technologies & Solutions | 175 | 122 |
| Visalia | CA, USA | SUEZ – Water Technologies & Solutions | 171 | 85 |
| Zhangzhou dongdun WWTP Phase I | Fujian, China | Beijing Origin Water Technology Co., Ltd (BOW) | 169 | 130 |
| Guangzhou Jingxi Underground MBR Project | Guangzhou, China | Memstar | 169 | 130 |
| Daxing Huangcun WRP | Beijing, China | Beijing Origin Water Technology Co., Ltd (BOW) | 156 | 120 |
| Jinyang WWTP (Phase 1) | Shanxi Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 156 | 120 |
| Huhehaote Zhanggaiying WWTP | Inner Mongolia, China | Beijing Origin Water Technology Co., Ltd (BOW) | 156 | 120 |
| Santa Giustina | Rimini, Italy | MEMCOR – Evoqua Water Technologies LLC | 152 | 76 |
| Changi Train 5 | Changi, Singapore | MEMCOR – Evoqua Water Technologies LLC | 150 | 108 |
| Carré de Reunion | Versailles region, France | Koch Membrane Systems Inc. | 144 | 42 |
| Shiyan Shendinghe | China | Beijing Origin Water Technology Co., Ltd (BOW) | 143 | 110 |
| Urumqi Ganquanpu WRP | Xinjiang Uygur Autonomous Region, China | Beijing Origin Water Technology Co., Ltd (BOW) | 137 | 105 |
| North Las Vegas | NV, USA | SUEZ – Water Technologies & Solutions | 136 | 97 |

(*continued*)

**Table 11.4** (*continued*)

| Installation | Location | Technology supplier | PDF (MLD) | ADF (MLD) |
|---|---|---|---|---|
| Ballenger McKinney ENR WWTP | MD, USA | SUEZ – Water Technologies & Solutions | 135 | 58 |
| Wenyuhe River Water Treatment (Phase 2) | Beijing, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| Hebei Zhengding WWTP | Hebei Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| ZhuHai Qianshan WWTP | Guangdong Province, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| Beijiao WWTP renovation project | Ordos, Inner Mongolia | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| Xianlin WWTP PPP project | Nanjing, Jiangsu, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| Chengxiang WWTP Phase I | Haiyan, Zhejiang, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| Urumchi hexi WWTP (Phase 2) | Xinjiang, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 120 |
| Urumchi hedong WWTP | Xinjiang, China | Beijing Origin Water Technology Co., Ltd (BOW) | 130 | 100 |
| Al Ansab | Muscat, Oman | Kubota | 125 | 96 |
| Assago | Milan, Italy | SUEZ – Water Technologies & Solutions | 125 | 55 |
| Hwaseong-Dongtan STP | Hwaseong City, Gyeonggi Province, South Korea | MCAS/Hyundai | 122 | 122 |
| Cox Creek WRF | MD, USA | SUEZ – Water Technologies & Solutions | 116 | 58 |
| Yellow River | GA, USA | SUEZ – Water Technologies & Solutions | 114 | 71 |
| Aquaviva | Cannes, France | SUEZ – Water Technologies & Solutions | 108 | 60 |
| Busan City | Korea | SUEZ – Water Technologies & Solutions | 102 | 102 |
| Guangzhou | China | Memstar | 100 | — |
| Shek Wui He | Hong Kong | MEMCOR – Evoqua Water Technologies LLC | 80 | 40 |

wastewaters (Enright *et al.*,2005),[14] polymer synthesis effluents (Araya *et al.*, 1999),[15] and pulp and paper industry wastewaters enriched with organic halides and phenolic effluents (Savant *et al.*, 2006).[16] Industrial MBR systems are specifically used to achieve either zero liquid discharge (ZLD) or eco-friendly effluent for better environmental practice.

### 11.5.1 Application of the Membrane Bioreactor in Food and Beverage Industries

The food and beverage sectors have extensively utilized MBR technologies. Both side stream MBR systems and immersed MBR configurations have already been implemented on site. Since long retention time is attainable in an MBR, it allows more effective biological treatment of recalcitrant compounds in comparison with conventional biological processes. The waste stream generated by food and beverage sectors may involve diverse organic chemicals and may cover a broad range of subsections like, dairy, maltings, breweries, distilleries, wineries, soft drinks, cereals, potato chips, salads and produce, coffee, confectionery, edible oils, meat and poultry processing and various other prepared foods. The general characteristic of the food and beverage industries are high BOD and COD concentrations which are reportedly about 5–100 times higher than for domestic waste. Substantial amounts of total suspended solid (TSS) and fat, oil and grease (FOG) with high levels of ammonia and phosphorus have also been reported. Effluents are readily biodegradable with COD/BOD ratios ranging from ≈0.4–0.5 for bakery products to >0.8 for poultry processing. Typical effluent composition of industrial effluent is presented in Table 11.5. Dereli *et al.* (2012)[17] described the potential of anaerobic MBRs to overcome treatment limitations induced by industrial wastewaters. This group of authors have presented a comprehensive review on applications of anaerobic MBR technology for industrial wastewater treatment, indicating its appropriateness for effluents with extreme compositional features like high salinity, high temperature, high suspended solids concentrations, and toxicity. As reported by this group this type of MBR may be used to retain targeted microbial communities responsible for degradation of specific pollutants in the wastewater. They explain in details the advantages and disadvantages of anaerobic MBRs under extreme conditions of suspended solid, FOG content, toxicity and calcium scaling. For industrial wastewaters under extreme conditions, an MBR is the best choice for production of cleaner effluents, with water recovery and reuse benefits. A summary of the performance of an anaerobic MBR for COD removal from various industrial effluents like palm oil mill, craft pulp mill, and slaughter house waste has also been reported by same group of authors.[17] Full-scale anaerobic installations with flat-sheet membranes, which treat a wide spectrum of substrates such as alcohol production stillage, organic wastes, wastewater treatment sludge, and food processing residues (dairy, potato, confectionary) have also been reported.[17] Another full-scale unit for treatment of effluent from the food

**Table 11.5** Characteristics of some typical industrial waste effluents.

| Parameters of waste water | Food and beverage sector[a] | Pharmaceutical Industry[b] | Tannery effluent[c] | Textile[d] | Paper and pulp[e] | Petrochemical |
|---|---|---|---|---|---|---|
| COD mg L$^{-1}$ | 468 | 15 000–16 000 | 3980 | 150–12 000 | 800–1500 | |
| BOD mg L$^{-1}$ | 210 | | 920 | 80–6000 | 200–300 | |
| FOG mg L$^{-1}$ | 240 | — | | 10–30 | | |
| Chloride mg L$^{-1}$ | 136 | — | 1300 | 1000–6000 | | |
| Alkalinity mg L$^{-1}$ | 462 | 412–540 | 950 | | | |
| pH | 7.34–7.38 | 7.5–10 | 7.5 | 6–10 | 6.5–7.1 | |
| TSS mg L$^{-1}$ | 942 | 432–565 | 6800 | 15–8000 | 450–500 | |
| TDS mg L$^{-1}$ | 680 | | 14 000 | | 900–950 | |
| Conductivity mS cm$^{-1}$ | 1200 | | 18.65 | | 1.4–3.0 | |
| Nitrogen (organic) mg L$^{-1}$ | — | 33–34 | | <10 | | |
| Phosphorus (total) mg L$^{-1}$ | — | 0.9–0.95 | | <10 | 1.3–1.5 | |
| Sulfate mg L$^{-1}$ | | | 4000 | 600–1000 | 600 | |
| Sodium mg L$^{-1}$ | | | | 7000 | | |

[a] Dairy effluents.[13]
[b] Pharmaceutical effluents.[14]
[c] Tannery effluent.[15]
[d] Textile industry.[16]
[e] Paper and pulp industry.[37]

industry dealing with salad dressings and barbeque sauces (COD: 34 g $L^{-1}$, total solid (TS): 1.1%) has reported COD removal efficiency of 99.4% and a flux rate ranging between 2.5 and 4.2 L $m^{-2}$ $h^{-1}$ during the first 2 years of operation.[17] A full-scale tubular crossflow membrane for the treatment of acid cheese whey with COD removals efficiency of 99%, an MBR for treatment of potato processing wastewater (COD: 56.9 g $L^{-1}$, TSS: 14.8 g $L^{-1}$) with 95% COD removal efficiency, and a pilot-scale MBR with FS membranes for treatment of ethanol stillage with 98% COD removal efficiency have also been reported.[17] An MBR with HF membranes, for snacks factory wastewater treatment with FOG content up to 6000 mg $L^{-1}$ and COD removal efficiency of 97% was reported in same review.[17] Citrus fruit processing makes a significant contribution to the food and processing industries, requiring a heavy water load (10 million L per day for processing of 25 t $h^{-1}$ lemon) for washing machinery and fruits; for extraction of juice and essential oils (EO) from the fruits/fruits peels, cooling purposes, enriched high organic matter, SS and EO. A study by Trapani *et al.* (2019)[18] reported treatment of citrus processing effluent with an MBRs for water reuse purposes and amalgamation of the MBR system with aerobic granulation sludge (AGS) as a strategy of to enhance metabolic activity in the MBR. This group of researchers conducted studies to explore the feasibility of the MBR using two different schemes. In Scheme 1, a conventional HF MBR was employed for the treatment of the raw process water, while scheme 2 involved a combination of in series reactors (AGS+MBR). In both the schemes, very high COD removal (99%) was been reported with higher metabolic activity of the biomass in the AGS+MBR, but with higher resistance to filtration and higher irremovable resistance which may cause reduced service life for membranes. Long-term ultrafiltration-based MBR systems with polymeric membranes experience severe fouling, which necessitates upgrading of existing MBR technology in new directions. Vergine *et al.* (2020)[19] have reported the self-forming dynamic MBR (SFD-MBR) as a suitable technology for agro-industrial wastewater treatment. The SFD-MBR technique involves the replacement of ultrafiltration membranes with synthetic microfiltration nets made of polyethylene terephthalate (PET) or nylon, to provide physical support for biological cake layer formation, which may act as the real filter medium; the cake-forming bacterial groups contribute to the biodegradation of targeted pollutants. As per the published report, the effluent quality from a vegetable canning process and winery process was found to be similar to that obtained using a conventional MBR system, with the advantage of high filtration flux and very low *trans*-membrane pressure (TMP). In the F and B industry MBRs are specifically used for the treatment of process waters rather than for effluent treatment in order to achieve ZLD for better environmental practice. As reported, implementation of MBR technology for F and B process water treatment has been carried out since the late 1990s, coinciding with declining MBR costs, increasing freshwater supply costs, increasingly stringent legislation, improved technology design and reliability, and spatial restrictions.

### 11.5.2 Application of the Membrane Bioreactors in Pharmaceutical Industries

The pharmaceutical industry usually generates large amounts of effluent enriched in various types of persistent organic chemicals, endocrine disrupting chemicals, various antibiotics with signification ionic components and salinity. In the present context, release and accumulation of pharmaceuticals and personal care products is a global concern with regard to environmental protection and awareness. In pharmaceutical waste treatment, MBRs enhance the enrichment of drug-resistant microorganism and are able to effectively retain sludge floc and dispersed microorganism, promote the development of rich microbial communities, and improve the biodegradation of target pollutants. MBR systems may experience problems associated with accumulation of organic and inorganic compounds that are difficult to biodegrade in the bioreactor. An MBR has the potential to remove residual antibiotics in the waste stream and alleviate the possible effects on the environment. Zhou *et al.* (2020)[20] reported in detail the membrane fouling characteristics observed while treating penicillin wastewater enriched with sulfate ions. The effect of the characteristic pollutant salts in pharmaceutical wastewater on MBRs performance is also been worthy of attention. From a phenomenological point of view, salinity will affect the physicochemical parameters and biological activity of activated sludge, thus affecting the pollutants removal efficiency of an MBR. The characteristics of antibiotics, including their salinity and concentration have an immense effect on MBR functioning. Some research publications have reported the adverse effect of salinity on the physicochemical parameters and biological activity of activated sludge, thus affecting the pollutants removal efficiency of an MBR.[20] It has also been reported that increasing the sodium chloride concentration had a negative impact on the performance of an anaerobic MBR in wastewater treatment and the fouling characteristics of the MBR. Chen *et al.* (2020)[21] have cited the performance of a novel multiple draft tubes airlift loop membrane bioreactor for the treatment of ampicillin-rich waste streams with a detailed study of temperature effect on the operational features. About 98% COD removal was achieved in an MBR at 36 °C while similar separation characteristics were achieved at 7 °C for membrane separation. The effect of the coagulant ferric hydroxide during the treatment of pharmaceutical effluent has been reported by Huang *et al.*,[22] with the major finding that membrane fouling was reduced by 35%. Coagulant addition has also been reported to enhance floc size and reduce bacterial activity at high molecular organic concentrations (carbohydrate, biopolymer) in mixed liquor, with a lower abundance of bacterial association and biofilm formation. Pharmaceutical waste stream enriched with different toxic solvents (methanol and ethanol being 80–90% of the total organic load with the rest a mixture of tetrahydrofuran, dichloromethane, acetone, ethyl acetate, tripropylamine, acetonitrile, toluene, isopropanol, acetone, and dimethylacetamide) has been reported by Svojitka *et al.* (2017).[23] COD removal efficiency was up to 97% with addition of excess methanol as a carbon source, in comparison to lower COD removal efficiency (around 78%) when the anaerobic MBR was operated with incoming pharmaceutical wastewater as the sole carbon source. Lindroos *et al.* (2019)[24] have described a study on MBR use for continuous removal of chloroquine from a pharmaceutical waste stream using melanin-covered *Escherichia coli*. A continuous-flow membrane bioreactor containing melanized *E. coli* cells was utilized for removal of chloroquine from the influent until saturation and subsequent regeneration, with maximum observed chloroquine capacity about 3-fold higher than that previously observed for the same strain in batch conditions. Asif *et al.*, (2018)[25] have reported a detailed study of pharmaceutical industry effluent treatment involving pharmaceutical drugs, personal care product, steroids, pesticides, and hormones in an MBR using laccase catalyst, focusing on carbamazepine, sulfamethoxazole, diclofenac, atrazine and oxybenzone. The permeate toxicity was reported to be below the detection limit, (rTU (relative toxic unit) < 1), illustrating the effectiveness of laccase in reducing bacterial toxicity. Hu *et al.* (2020)[26] described a sustainable anti-infective pharmaceutical wastewater treatment technology based on a variable diameter MBR with online control of dissolved oxygen for ceftriaxone sodium. COD and $BOD_5$ ($BOD_5$ indicates how much dissolved oxygen (mg/L) is needed in a given time for the biological degradation of the organic wastewater constituents) removal were 87.3 and 95.3%, for the corresponding effluent COD and $BOD_5$ values of 189 and 24 mg $L^{-1}$, respectively. Hence it may be concluded that a MBR system with appropriate modification and updated design, as per specification of the pharmaceutical effluent, can act as suitable technique to meet the demand of water treatment and reuse facilities for pharma-industrial effluent.

### 11.5.3 Application of the Membrane Bioreactor in Petrochemical Industries

Petroleum refineries one of the largest waste stream producing industries. In all petroleum refining sites, the produced waste stream typically contains dissolved and suspended oil substances, dissolved minerals, heavy metals, chemical ingredients, and dissolved gases. The salt, oil and grease concentration varies considerably with plants. Petrochemical wastewater treatment is challenging due to its recalcitrant and toxic nature.[27] Since a large amount of fresh water is also consumed during processing, reuse of the waste stream is an important feature of water economy for the petroleum industry. Membrane filtration has already been employed for treatment of greasy/salty wastewater for decades because of the reduced chemical requirement to break (oil in water) O–W emulsions and the high COD treatment capability. MBR techniques permit the physical maintenance of bacterial flocs and almost all suspended solids within the bioreactor. It has been reported that MBR permeate from the treatment of various petrochemical wastewaters could meet the strict discharge requirements (Huang *et al.*, 2020).[27] Hence, the MBR method has now become an interesting choice for the treatment and reutilization of industrial and urban wastewaters. Razavi and Miri[28] used a HF-based immersed MBR for treatment of real petroleum refinery wastewater under various HRTs, fluxes and temperatures. The removal rate of COD, $BOD_5$, TSS, volatile suspended solids (VSS), and turbidity were significant and reported as 82, 89, 98, 99, and 98%, respectively. Huang *et al.* (2020),[27] studied in detail the performance and process simulation of MBRs for treating petrochemical wastewater. In brief, COD, nitrate and MLSS concentration reductions were reported as 75–80, 77–82, and 80–90%, respectively. Lebron *et al.*, (2021)[29] developed an osmotic membrane bioreactor (OMBR) for refinery wastewater treatment. The OMBR is a newer version of the conventional MBR which combines physical and biological processes for wastewater treatment aimed at producing a high quality permeate with advantages of reduced membrane fouling, enhanced process productivity, and reduced energy and operational cost. In an OMBR, the water permeates from the mixed liquor (ML) to the draw solution (DS) due to an osmotic pressure gradient across the membrane interface. Incorporation of forward osmosis (FO) membranes in OMBR systems improves the rejection rate of dissolved species and causes minor fouling potential. Significantly, high rejection rates in OMBRs allows the permeate to be suitable for applications requiring water with high physicochemical quality. In an OMBR operation, salinity build-up may impede the efficiency of the biological process. The complex nature of refinery wastewater, due to presence of high recalcitrant compound content and salinity development during operation, induce process complexities in the operation of OMBRs. Wiszniowski *et al.* (2011)[30] ave studied removal of petroleum pollutants and the nature of the bacterial community structure in an MBR. Their study was based on the vacuum distillate of a crude oil fraction (emulsified state) as a model of petroleum pollutants, with the aim of monitoring long-term operational stability in removing organics and ammonia from the waste stream. The operation was carried out with plug-flow MBRs (with a submerged A4 Kubota membrane) under aerobic conditions with >90% COD and total organic carbon (TOC) removal along with nearly complete removal of petroleum originated non-polar micropollutants. Removal percentages of BOD, COD and TOC were reported to be 99%, 93% and 96%, respectively, irrespective of feed concentration, and the observation was also validated with chromatographic analyses of the complete reduction of oily hydrocarbons in synthetic wastewater. Moser *et al.*, (2019)[31] presented a comparative study of hybrid ultrafiltration–OMBR (namely UAnSFB), and a conventional MBR for oil refinery effluent treatment, focussing on overall performance. Moussavi and Ghorbanian (2015)[32] studied the biodegradation potential of total petrochemical hydrocarbon (TPH) in a hybrid MBR. The hybrid MBR system was effective in removing of 99% TPH at an HRT of 24 h by a nitrate-reducing mechanism. TPH biodegradation in the hybrid MBR system was unaffected by salinity build-up. The bacterial colony responsible for biodegradation of hydrocarbons produced biosurfactant under nitrate-reducing conditions, adding extra importance to the production of value added compounds as a process byproduct. Hence, with respect to petroleum refinery waste treatment, MBR technology, with all the necessary amendments and tuning, has become a reliable technology for biological wastewater treatment for waste streams with high recalcitrant compound concentrations.

### 11.5.4 Application of the Membrane Bioreactor in Textile Industries

The textile industry is another industry involving utilization of huge amounts of water with large effluent containing various dyes, textile auxiliaries and some other toxic compounds associated with dyeing processes. Because of the variation in effluent quality depending on the contaminating sources, textile effluent varies in terms of flow rate, chemical oxygen demand (COD), colour, pH, salinity and toxicity, and it is therefore very difficult to suggest or standardize any sole technology for the treatment of textile effluents. Textile effluent techniques involve a combination of both biological and physicochemical treatments to meet effluent discharge standards. Application of an MBR system for dye treatment has been presented by several authors, highlighting the type of dye components.[33] Studies have also compared the performances of anaerobic MBRs (AnMBR) and aerobic MBRs (AeMBR) for the treatment of azo dye containing synthetic textile wastewater. An AnMBR was found to be more effective for textile wastewater treatment, but with severe fouling compared with AeMBRs. Anaerobic dynamic MBR (AnDMBR) processes were found to be advantageous for removing highly coloured pollutants, with reduced fouling effect. In the dynamic MBR, the developed cake layer on the support system acts as secondary filter and offers higher flux, low fouling tendency, an easy cleaning. In MBR operation biofilm growth was found to be a problem in presence of sulfate ions which affect COD removal efficiency. In all MBR operations dealing with textile effluent decreases in COD removal efficiency may be due to toxic effect of produced sulfides.[33] An integrated fungal membrane bioreactor and photocatalytic membrane reactor for the treatment of industrial textile wastewater has been reported by Deveci *et al.* (2016).[34] The study involved the combination of a fungal membrane bioreactor (FMBR) and semiconductor photocatalytic membrane reactor (PMR) for treatment of the dye component in a textiles waste stream. As reported, colour removal and COD reduction efficiencies were 88 and 53% for photocatalytic degradation, respectively, while corresponding values were ≈56 and 60% for fungal biodegradation using *Phanerochaete chrysosporium*, respectively. The scheme as presented by the group of authors involves photocatalytic degradation as a post-treatment step after the fungal biodegradation process with colour and COD removal efficiency of 93 and 99%, respectively. The fungal biodegradation process was found to have satisfactory performance with regard to COD reduction but colour removal performance was poor, while in the integrated FMBR–PMR system better performance was reported than with the two processes applied separately. Treatment of anthraquinone dye rich textile wastewater using an

AnDMBR has been reported by Berkess *et al.* (2020),[35] with specific focus on the performance and microbial community structure. The assembled reactor set-up showed excellent soluble COD and colour removal of 98.5 and >97.5%, respectively, with Remazol Brilliant Blue R containing simulated textile effluent. Treatment of textile effluent enriched with methyl orange was investigated in a high-rate anaerobic decolourization membrane reactor based on a HF membrane by Bai *et al.* (2020),[36] with a MO decolourization efficiency of nearly 100%, for HRT of 2–1.5 days and a maximum decolourization rate of 883 mg $L^{-1}$ $day^{-1}$. Based on all the technical data on MBR operations for textile industry effluent treatment, with specific emphasis on the nature of the components, small- and medium-scale textile industries are also trying to implement MBR-based technologies on site for water reuse and to maintain safe discharge protocols.

### 11.5.5 Application of the Membrane Bioreactor in Paper-pulp and Tannery Industry

As per research and publications pulp and paper plants have been reported as a significant source of aquatic pollution and the third most water intensive industry after metals and chemicals industries. This water intensive industry is also reported as a substantial source of more than 250 chemicals which also contaminate water bodies, creating serious ecological problems. Since conventional treatment technologies could not meet stringent environmental discharge standards, and effluents with significant organic content and low biodegradability have been detected, advanced technologies like MBRs have been applied to treat wastewater from paper mills. The presence of high organic matter require either aerobic or anaerobic biological treatment processes to be applied for paper and pulp industry effluent. In aerobic treatment, activated sludge is usually used for effective lowering of BOD of the lignin and tannin contained in pulp mill bleaching effluent, but the presence of aromatic and complex compounds makes it difficult to biodegrade. Application of an MBR for treatment of paper and pulp effluent makes the removal of persistent organics from effluent easier. The optimal HRT reported for COD removal from pulp and paper wastewater was 1.1 ± 0.1 days with significant cake layer formation. In some other reports MBR operation with a HRT of 19 h was shown to be technically feasible even at high temperatures for industrial applications (50–60 °C).[37] It has been claimed that the treated water of MBR operation fulfills all the standards required for process water of paper mills and could be reused in the paper manufacturing process. Athermophilic submerged anaerobic MBR for kraft evaporator condensate treatment t has been investigated, suggesting a feasible method of biogas production and organic matter removal. In general, integrated bioreactors that combine aerobic and anaerobic degradation pathways in a single reactor have been reported as cost-effective and efficient techniques with smaller footprints as compared to sequential anaerobic–aerobic systems. Use of a hybrid MBR, combining a granular activated carbon-sponge fluidized-bed bioreactor with a nano-filtration MBR unit, has been attempted in several industries. Fixed-bed biofilm reactors combined with an MBR has also been attempted *in lieu* of conventional technologies for real paper effluents to obtain recyclable wastewater with a COD removal percentage of 92–99%, suggesting the efficiency of fixed-bed MBRs for the removal of pollutants from real paper-industry wastewater. Dias *et al.* (2005)[38] reported biological treatment of kraft pulp mill foul condensates at high temperatures using an MBR for a condensate with very high COD, total reduced sulfur (TRS) and methanol removal in the mesophilic temperature range. Xia *et al.* (2016)[39] have n reported the use of an anaerobic MBR for the treatment of bamboo industry wastewater. In operation, average COD removal efficiencies of 94.5 and 89.1% were achieved with aerobic and anaerobic MBRs, respectively. Poojamnong *et al.* (2020)[40] described the performance of an MBR-based pilot plant for pulp and paper mill wastewater treatment using a submerged polyvinylidene fluoride (PVDF) MBR.

Attempts have also been made to treat a tannery waste stream, which is characterized by high BOD, high total dissolved solids, chromium, phenolics, and a variety of toxic organic and inorganic toxic chemicals, with MBR systems. As conventional technologies to treat tannery wastewater involve high cost, generation of environmentally destructive components, and creation of secondary pollution, emerging green technologies with water recycling and reuse facilities have been designed and implemented in some industrial sectors. Artiga *et al.* (2005)[41] reported treatment of tannery and winery wastewaters in a submerged membrane bioreactor. A hybrid-type membrane bioreactor (HMBR) with an electrocoagulation unit has been used for the removal of 90% of COD and 93% of colour from tannery wastewater. A study by Umaiyakunjaram *et al.* (2016)[42] reported the efficient treatment of raw tannery wastewater (with high concentrations of suspended solids) using a flat-sheet submerged anaerobic membrane reactor (SAMBR), used for treating hypersaline anaerobic seed sludge to recover biogas. SAMBR treatment achieved high COD removal efficiency (90%) and significant biogas yield of 0.160 L $g^{-1}$ of COD. As a unique feature of membrane fouling control, the acidification of hypersaline influent wastewater by biogas mixing with high $CO_2$ achieved multiple benefits, including of gas–liquid and solid separation, *in situ* pH and $NH_3$ control, *in situ* $CH_4$ enrichment, and prevention of membrane fouling, suggesting the suitability of SAMBR for high suspended solids tannery wastewater. In a comparative study of a pilot-scale MBR and a conventional activated sludge plant (CASP), involving treatment of the same tannery wastewaters under the same operating conditions in the presence of Gram negative nitrifying bacteria, results showed higher COD removal with stable and complete nitrification with higher abundance of α- and γ-*Proteobacteria* in the MBR bioreactor and the presence of AOB aggregates only on the surfaces of MBR flocs. MBR application in the treatment of complex tannery waste water has been studied to achieve maximized water recovery, emphasising the importance of biological and chemical–physical process modelling while treating industrial wastewater.[43]

## 11.6 Future Prospects for Membrane Bioreactor Technology

Though several studies have demonstrated the potential of MBRs for treatment of industrial effluents, with targeted fouling reduction and desired throughput quality, specific pollutant-specific amendments of MBRs have already been carried out. Research and developments are still underway for newer modifications of MBR technology like extractive MBR (EMBR), which is still in its infancy, but with interesting prospects for biological treatment with the removal of specific targeted compounds from liquid waste streams as well as waste gas streams. The removal efficiency as reported was 99% of hydrocarbon, and 90% of $Zn^{2+}$ and nitrate. Separation of the feed stream and bio-medium in the EMBR avoids effluent contamination. The future of the MBR system involves not only the design of hybrid or integrated membrane modules but also of more selective membranes. In EMBR, use of highly selective membranes helps to achieve maximum separation efficiency but with low permeation flux. Hence, syntheses of pollutant-specific, highly permeable and low cost membranes are the future aims of MBR research.

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CHAPTER 12

# Investigation and Treatment of Industrial Wastewater by Membrane Bioreactors: An Innovative Approach

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## 12.1 Introduction

The membrane bioreactor (MBR) involves the integration of the membrane module with the biological stage[1] and has been effectively used for the treatment of pollutants. It has been studied intensively and has its utility in applications worldwide.[2–9] The research area of MBR technology has extended in numerous sectors since the early 1990s and since then has seen tremendous upgrading with respect to its application at laboratory scale and large scale. Super-large scale MBRs have been studied globally and their progress can be observed from the papers being published yearly in highly reputable journals.[10–20]

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

In case of the MBR the membrane can either be placed outside or inside the system/bioreactor. In an MBR with an external membrane the mixed liquor is filtered under pressure in a precise membrane module whereas in the case of a submerged membrane the filtration is performed in the aeration basin by suction removal of the pollutant effluent (Figure 12.1). Among the membrane systems the submerged membrane is more suitable because it is much more economically feasible and no recycle pump is required as aeration allows tangential flow of liquid around the membrane.[21] In addition,

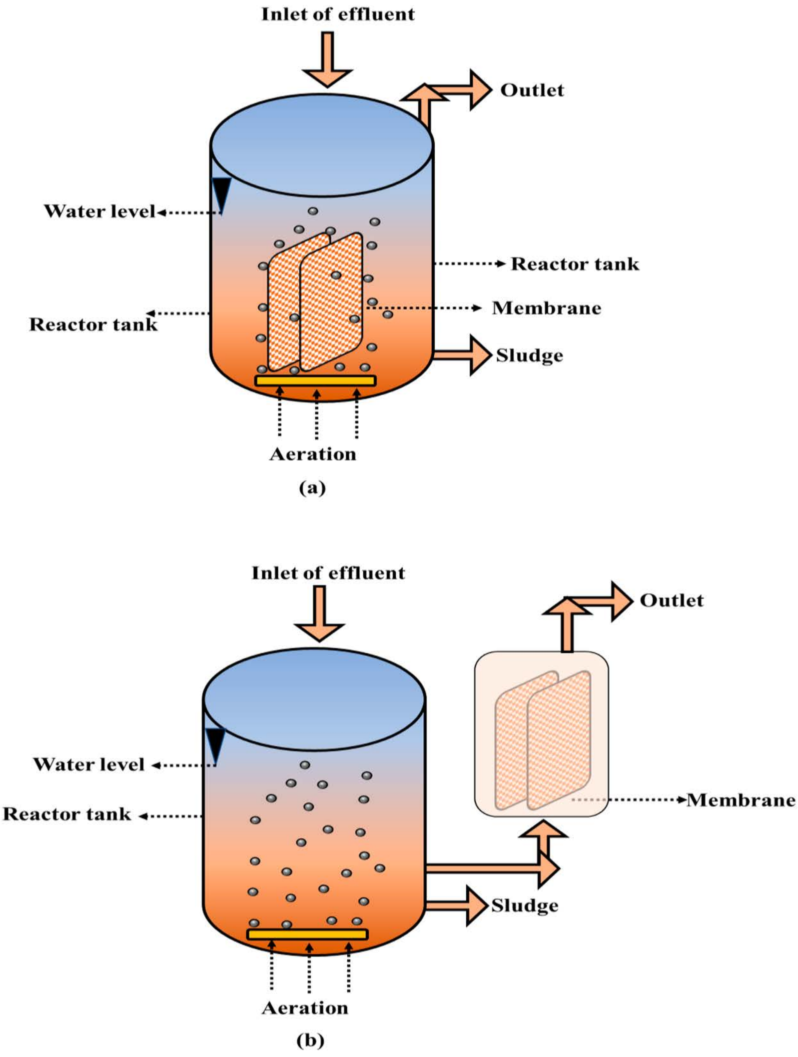

**Figure 12.1** Schematic representation of the (a) submerged and (b) external membrane bioreactor.

MBR technology offers several advantages such as the membrane module being compact and as the sludge settling velocity does not impact the quality of rejected water, the biomass concentration can be higher as compared to traditional treatment plants.[22]

Membrane separation in case of MBRs allows the bioreactor to retain the biomass and enhances the sludge retention time independently of the hydraulic retention time, thereby allowing the concentration of sludge in the bioreactor to increase and also enhancing the pollutant degradation efficiency of the bioreactor.[21]

This chapter includes process description and configuration, effect of MBRs on microorganism, quality of water after treatment along with the cost associated with MBR technology. Further, the limitations, advantages and technological advances are also elaborated in the chapter.

## 12.2 Process Description and Configuration of MBR

Two types of configuration exist for MBRs, *i.e.* extractive and diffusive. In the extractive system the membrane is used for the extraction of a required component, either for its treatment or for the treatment of effluent.[23,24] In the diffusive system, gas in molecular form is added to the bioreactor to improve the biotreatment process. The MBR has numerous applications and has been used for the biotreatment of effluent at high load under aerobic conditions,[25] treatment of hospital wastewater,[26] removal of micropollutants[19] *etc.* However, despite numerous applications the commercialization of MBRs has been an issue and much troubleshooting and research is required for its effective implementation.

The MBR configuration depends upon the cylindrical/planar structure of the system and presently there are five types of MBR: hollow fibre, spiral wound, plate and frame, pleated filter cartridge and tubular. Among the above-mentioned MBRs, hollow fibre, spiral wound and plate and frame are the most commonly used. In a hollow fibre MBR many membranes are grouped into bundles and the ends of the fibres are sealed *via* epoxy block and connected to the outside section of the housing that enables in-flow and out-flow of water respectively. The main advantage of this system is the backflushing potential and low energy cost.

In the spiral wound MBR, the spiral-wound membrane is coiled through a perforated tube from which the effluent passes out and is most commonly used in two processes, *i.e.* reverse osmosis (RO) and nanofiltration (NF). As the installation of this system is easier and the cost is low, it has been studied frequently and can also be used in series or in parallel order in plants exhibiting higher efficiency/capacity. Plate and frame MBRs are made up of flat-sheets membrane with separators/support membranes and are frequently used in water treatment plants.[27] The last two membranes have pleated filter cartridges and tubular configurations and are not commonly used in industry.

## 12.3 Effect of MBR on Microorganism and Pollutants and Reuse Options

MBRs have an integrated microfiltration membrane and have high potential to remove microbiological material (*e.g.* coliforms, faecal coliforms, bacteriophages).[28,29] In an MBR, even if full disinfection is not possible, with the addition of a small quantity of residual chlorine, disinfection is possible allowing its subsequent utilization. However, it should be noted that a crucial screening protocol has to be designed and implemented prior the distribution/release of water for its reuse.[30,31] In Sanguanpak *et al.*,[32] membrane fouling and micro-pollutant removal using MBRs in treating landfill leachate has been discussed elaborately. The MBR has been gaining huge research potential globally mainly due to two factors, *i.e.* decentralized treatment and reuse of water, and the majority of the presently operating plants are in small to medium size units (Table 12.1). MBR technology is more efficient than methods such as ultrafiltration and biologically aerated filtration. The MBR had the potential to treat wastewater and reduce the BOD to 10 mg $mL^{-1}$ and could comply with reuse standards, whereas with a biologically aerated filter the BOD was 5% higher than the reuse standard. Due to high removal levels

**Table 12.1** The various types of MBR and their utility in removal of various effluents.

| No | Type of MBR | Type of pollutant | Reference |
|---|---|---|---|
| 1. | Flat-sheet membrane sequencing batch bioreactor | Real samples of leachate were taken from a compost plant | 33 |
| 2. | Enhanced MBR | Wastewater collected from different car wash facilities | 34 |
| 3. | Pilot-scale membrane bioreactor with a ceramic membrane | Moroccan domestic wastewater | 35 |
| 4. | Membrane bioreactor at pilot-scale | Woolen textile wastewater | 36 |
| 5. | Integration of membrane bioreactor and nanofiltration | Real hospital wastewater | 37 |
| 6. | Continuous flow pre-denitrification MBR (A/O-MBR) pilot unit | Amoxicillin removal | 38 |
| 7. | Membrane bioreactor–advanced oxidation process combined treatment | Pharmaceutical removal | 39 |
| 8. | Melanin-covered *Escherichia coli* in a membrane bioreactor | Continuous removal of chloroquine from water | 40 |
| 9. | Aerobic membrane bioreactor | Recycling and reuse of domestic wastewater for irrigation | 41 |
| 10. | Submerged-membrane bioreactor | Ablution grey water | 42 |

in MBRs the cost for downstream chlorination is minimized as the majority of the cost is due to oxidation of the organics rather than disinfection of microbiological contaminants. The MBR systems that are commercially available include package treatment plants, these are Clereflo MBR (Conder Products, UK) and ZeeMOD® (Zenon Environmental Inc.).[31]

## 12.4 The Quality of the Effluent Water after MBR Treatment

MBRs in various countries has been designed to meet the requirement of nutrients and organic content in the water as per the standard norms. Improvements in MBR technology have enhanced its functioning and resulted in an efficient treatment for wastewater effluent. As described by Sun *et al.*[43] most MBR technology ensures the removal of COD (>95%) and biodegradation. The MBR is resistant to the rarely occurring influent impact due to the presence of the membrane, and nutrient removal from the effluent in an MBR is dependent on the pre-anoxic and anaerobic configurations of the system that are set prior to the membrane tanks.[44] The MBR allows the efficient removal of contaminants and membrane retention increases biomass concentration which also contributes in the removal of nutrients *via* various biological processes such as nitrification, denitrification *etc.*

The other most concerning factor while treating he effluent is the maintenance of hygiene, and the presence of microorganism (pathogenic) is of the utmost concern.[45–47] MBR technology has been used for the efficient removal of various microorganism (pathogenic bacteria and viruses).[48,49]

Trace organic pollutants are present in sewage (*e.g.* endocrine disruptor chemicals, pharmaceuticals, personal care products *etc.*).[50–52] Trace organic pollutants removal of >95 and 80% has been reported for 34 and 53 trace organic pollutants of the 7979 that were reported. Further, only 11 exhibited <50% removal by the MBR. MBR technology when compared with the conventional activated sludge without tertiary treatment has enhanced treatment efficiency for certain trace organic pollutants (TOPs) due to the complete retention of the suspended solids and high concentration of sludge at longer solids retention time.[53,54] The biodegradation of trace organic pollutants depends on their hydrophobicity; they are easily removed by both conventional activated sludge and MBR technology. It should be noted that the MBRs for trace organic pollutants removal perform best using biological degradation.[54] The hydrophobic trace organic pollutants are absorbed by the sludge. Conventional activated sludge may perform better for the removal of he hydrophobic trace organic pollutants due to shorter solids retention time and high rate of sludge discharge. However, in case of the weakly hydrophobic trace organic pollutants that can be adsorbed by the particles and colloids, the MBR can enhance the removal and effluent quality due to the complete retention of the suspended solid and partial retention of the colloids by the membrane.[3,55] Despite the above-mentioned potential of the MBR to remove the trace organic pollutants there are still certain number that cannot be treated either by conventional activated sludge or by MBR technology, thus additional treatment such as the powered activated carbon and ozonation has to be integrated with the process to remove trace organic pollutants from the effluent to maintain safety standards and quality of the treated water.[54] Lastly the potential of MBR technology to remove microplastics (*i.e.* plastic particles of <5 mm) has garnered much attention in the scientific community. Microplastics harm life both on land and in water.[55] Conventional secondary sedimentation has been inefficient in the removal of microplastics, as a result the latest technological advances are need for their removal.[55,56] It has been observed that MBR has the potential to remove 99.9% of microplastics due to the high retention potential of the membrane. Thus, MBR technology has numerous advantages over other treatment techniques and can be effectively be used for the treatment of wastewater effluent (Table 12.2).

## 12.5 The Cost Associated with MBRs

The capital cost and footprint in the case of MBRs consists of costs associated with the construction, pipeline work and non-engineering work. The various costs associated with the construction of the bioreactor include 40, 10, 20 and 30% for tanks, pipelines/canals, membrane modules and miscellaneous equipment respectively[66] (Figure 12.2).

It should be noted that an MBR with larger capacity has low cost whereas an underground MBR has high capital cost. The footprint of an MBR is mainly associated with the area of land occupied by the tanks, the greenery area, roads and the buildings. The footprint and capital cost in the case of an industrial wastewater treatment plant are high because of the high concentration of feed and long process flow. As is the case for capital cost the footprint of an MBR also reduces with an increase in capacity.[66] The operating cost in case of the MBR is associated with the consumption of energy, chemicals, sludge disposal, labour costs and miscellaneous expenses (Table 12.3). The operational cost of an MBR depends on the treatment capacity: the operational cost decreases with an increase in capacity.

The sludge generated after MBR treatment is dewatered mechanically and conditioned chemically after which it is disposed either in landfill or *via* incineration in China. However, in a few cases it has also been re-used as fertilizer. A part of the expense in an MBR is contributed by aeration and sludge mixing.[67–69] In summary, the capital costs associated with an MBR are high compared with conventional activated sludge excluding tertiary treatment, however an MBR has a smaller footprint. With the advent of new technology and rigorous research, the reduction in cost alongside the development of the MBR has resulted in numerous advances that will allow multi-dimensional application of MBR in the future.

**Table 12.2** The efficiency of MBR in treating various wastewaters.

| No | Membrane bioreactor | Treatment | Reference |
|---|---|---|---|
| 1. | Membrane bioreactor was employed for the treatment of influent, final effluent and biosolids samples from wastewater treatment plant | Personal care product (PPCP) removal varied from −34% to >99% and 23 PPCPs had ≥90% removal. | 57 |
| 2. | Pilot-scale MBR was installed and operated for 1 year at a Swiss hospital. Among the 68 target analytes were the following: 56 pharmaceuticals, 10 metabolites and 2 corrosion inhibitors | The MBR influent contained the majority of the target analytes. The overall load elimination of all pharmaceuticals and metabolites in the MBR was 22%, as >80% of the load was due to persistent iodinated contrast media. No inhibition by antibacterial agents or disinfectants from the hospital was observed in the MBR. | 17 |
| 3. | A pilot-scale hybrid MBR was developed by introducing biofilm carriers into a conventional MBR and operated for about 1 year for municipal wastewater treatment | The comparative study results indicated that at a constant hydraulic retention time of 10 h and sludge retention time of 10 d. Hybrid MBR improved organic removal. Effluent COD dropped to 24.5 mg $L^{-1}$ in the hybrid MBR compared with conventional MBR (44 mg $L^{-1}$), and the COD removal rate increased from 90.4% to 94.2%. Regarding $NH_4^+$–N, TN and TP, the hybrid MBR improved the removal rate by 4.2, 13.7 and 1.7%, respectively. | 58 |
| 4. | Pilot anaerobic MBR was used to treat wastewater and waste organic solvents originating from pharmaceutical and chemical industries for 580 days | COD removal was up to 97% when the influent concentration was increased by the addition of methanol (up to 25 g $L^{-1}$ as COD). Lower or variation in COD removal (≈78%) was observed when the anaerobic MBR was operated with incoming pharmaceutical wastewater as sole carbon source. The addition of waste organic solvents (>2.5 g $L^{-1}$ as COD) to the influent led to low COD removal efficiency or even to the breakdown of anaerobic digestion. | 59 |
| 5. | Activated sludge process coupled with hollow fibre membrane for solid–liquid separation was applied to treat low-strength domestic wastewater | The effluent turbidity and COD were well within the limits (<0.5 nephelometric turbidity units (NTU) and 3–5 mg $L^{-1}$). The transmembrane pressure drop was <20 cmHg even after 2 months of operation. The system can be used as a household wastewater treatment system. | 60 |

(*continued*)

**Table 12.2** (*continued*)

| No | Membrane bioreactor | Treatment | Reference |
|---|---|---|---|
| 6. | MBR and rapid sand filtration was used for the removal of microplastics from the final effluent of an urban wastewater treatment plant and these two technologies were monitored for 18 months | Microplastics were statistically significantly reduced after both technologies, but a significant difference was not observed in both techniques. Microplastics removal efficiency was 79.01 and 75.49% for MBR and rapid sand filtration (RSF), respectively. The removal was higher for microplastic particulate forms, 98.83 and 95.53%, than for fibrres, 57.65 and 53.83% for MBR and rapid sand filtration, respectively. The maximum microplastics average size significantly decreased from MBR (1.39 ± 0.15 mm), to RSF (1.15 ± 0.08 mm) and influent (1.05 ± 0.05 mm) (F-test = 4.014, $P = 0.019$). | 61 |
| 7. | Sponge-membrane bioreactor combined with ozonation process was used to remove antibiotics from hospital wastewater | Antibiotics were eliminated by 45–93%, tetracycline was completely removed (100%) when operated at a flux of 10 LMH. After ozonation the efficiency was >90% for trimethoprim, norfloxacin and erythromycin. It was >80% for ofloxacin and ciprofloxacin and >60% for sulfamethoxazole. | 62 |
| 8. | The upflow anaerobic sludge-forward osmotic MBR for simultaneous wastewater treatment, membrane fouling reduction, and nutrient recovery was developed | The removal of COD, $PO_4^{3-}$ and $NH_4^+$ was >95% with low membrane fouling. Halotolerant *Fusibacter* (ferment organics to acetate) increased from 0.1% to 5% in a saline environment. Acetoclastic *Methanosaeta* resulted maximum methane production. | 63 |
| 9. | Sequencing-batch MBR for the treatment of swine wastewater | Nine compounds categorized into three groups were detected of which sulfonamides and tetracyclines removal was >90%, fluoroquinolones was <70% and organic matter and nutrients removal was >60%. | 64 |
| 10. | Aluminium dioxide ceramic membrane was used in a single-stage anaerobic fluidized-bed ceramic MBR for low-strength wastewater treatment and was operated for 395 days | A membrane net flux as high as 14.5–17 L $m^{-2}$ $h^{-1}$ was achieved by periodic maintenance and adding 25 mg $L^{-1}$ of sodium hypochlorite solution. An average SCOD in the membrane permeate of 23 mg $L^{-1}$ was achieved with a 1 h hydraulic retention time. Biosolids production averaged 0.014 ± 0.007 gVSS/gCOD removed. | 65 |

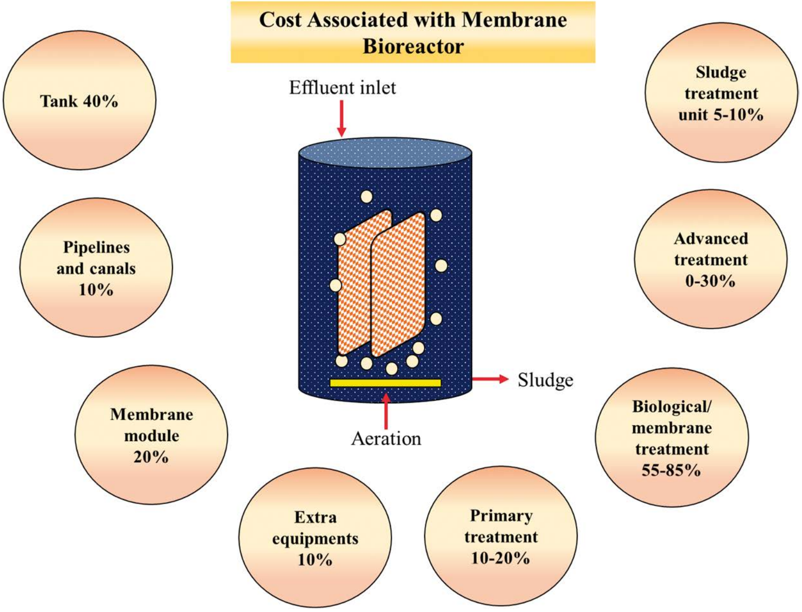

**Figure 12.2** Schematic representation of the costs associated with a membrane bioreactor.[66]

**Table 12.3** The operations cost associated with an MBR system.[66]

| Operation | Associated cost |
|---|---|
| Energy consumption | 40–60% |
| Chemical consumption | 10–30% |
| Sludge disposal | 5–15% |
| Labour costs | 10–30% |
| Miscellaneous | 5–20% |

## 12.6 Limitations and Advantages of Membrane Bioreactors

Membrane fouling is a very critical issue for MBRs.[70] MBRs suffers the major disadvantage of the membrane fouling, which is the accumulation of particles, macromolecules, colloids and salts on the membrane. In a review article Meng *et al.*[71] studied the status of membrane fouling and reported that in the year 2010 to 2015 ≈600–700 research articles were published with respect to wastewater treatment and this has increased significantly in the year 2019–2020. Studies with respect to MBRs have recently diverted towards their practical use at large scale, along with reduction in the cost associated with them, so that easy and economical implementation of MBR technology is becoming feasible.[72,73] In addition, research focused on using different material has increased over the past few years, along with wastewater treatment and anti-fouling membranes.[74]

MBRs have advantages over the conventional activated sludge process in that the treated water quality is very good, the biodegradation potential is high, they have a small footprint, are easy to operate, are stable, have high effluent quality, allow total removal of bacterial strains existing in the treated effluent and have absolute biomass retention.[75,76] As a result of these advantages the MBR has been used frequently in the treatment of municipal and industrial effluent and exhibits tremendous future potential as well.[77,78]

## 12.7 Advancement in MBR Technology

MBR technology has advanced considerably in the past three decades, especially since 2000. Research on the design, modification, and integration of new treatment techniques, adapting multidimensional approaches *etc.* has seen a tremendous increase in the current scenario. The extension of pilot-scale MBR to large and super-large scale too has increased exponentially. As mentioned above, the MBR has the potential to remove various component pollutants s present within the effluent and also helps remove pathogenic microorganisms and microplastics. Despite its numerous advantages the major drawback of the MBR is the cost associated with its implementation, which exceeds that of conventional activated sludge without tertiary treatment. However, with technological advances cost and energy consumption of MBRs have both has been reduced significantly in recent years and these issues are still being investigated globally. The constant efforts of the researchers globally have contributed significantly for to the development of MBR-based technologies and numerous milestones and landmarks have been reached over time. Thus, overcoming the limitations, such as the membrane fouling, high cost, energy consumption, and optimizing the process and focusing on core competitiveness, small footprint, flexibility, stable effluent, removal of pollutants, will enable use of BMR technology in even broader areas of application.

## 12.8 Conclusion

MBR technology has been the core focus of many research groups for the past few decades and has contributed significantly to advances in the field of bioreactor technology. The drawbacks associated with MBRs have been intensively studied, resulting in many possible solutions being developed and implemented for the successful treatment of various pollutants. MBR technology, once its drawbacks are overcome, is undisputedly the best technology to date for the treatment of the effluent and various other pollutants.

## Conflict of Interest

The authors declare no conflict of interest.

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## CHAPTER 13

# *Membrane Bioreactors for Separation of Persistent Organic Pollutants From Industrial Effluents*

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## 13.1 Introduction

In the past few decades, humanity has witnessed depletion of water sources across the globe due to several factors such as agricultural and industrial activities, urbanization, climate change, population growth and incessant consumption of water. This has compelled researchers across the globe to

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

look for new fresh water sources.[1] The natural aquatic ecosystem is time and again tainted with a class of chemical substances called micro-pollutants which is an enormous group containing synthetic organic compounds, such as pesticides, industrial chemicals, personal care/cosmetic products, detergents, food additives and even some naturally occurring substances such as oestrogen. These micro-pollutants are discharged into water bodies without any suitable treatment from industrial, agricultural and even domestic sectors. Such contamination of natural water bodies raises alarming concerns for the environment as well as human health because these chemical substances are capable of generating damaging effects on ecosystems and can poison fresh water resources even when present at trace concentrations (ng $L^{-1}$–μg $L^{-1}$).[2]

The European Union (EU), has listed >100 000 chemicals under the label micro-pollutants, of which ≈30 000–a 70 000 chemicals are used on a daily basis for various activities. Many countries in the EU, and Canada, have applied a number of regulations and laws for proper discharge of wastewater containing micro-pollutants, however there are neither firm implementation of these regulations nor any strict standards set for discharge of such pollutants.[3] Around 45 chemical substances, including polycyclic aromatic hydrocarbons (PAHs), phthalates, pesticides, metals and endocrine disruptors, have been listed as priority substances by EU Directive 2013/39/EU.[4] Additionally, 17 organic compounds of emerging concern (CEC), have been added to the watch list of substances for proper scrutiny prior to discharge (Decision 2015/495/EU).[5] Although most pharmaceuticals, steroid hormones and personal care products (PCPs), and are not yet designated as pollutants, the list of CECs includes five pharmaceutical compounds. Micro-pollutants are not just toxic but can also bio-accumulate owing to their recalcitrant nature. It is important to recognize and understand the biological effects and actual impact of such compounds on human health and the environment so as to set regulatory standards and design suitable water treatment and recycling methods to limit their release into the environment.

From this perspective, conventional activated sludge processes (CASP) are often found to be inefficient for complete elimination of micro-pollutants like POPs.[6] Moreover, most of the wastewater treatment plants (WWTPs) are not well equipped to analyse the exact levels of POPs in the source wastewater.[5] Hence, it has become necessary to reform the CASP system in WWTPs for improved management and control of micro-pollutants. Some adaptation in the operating conditions, such as hydraulic retention, aeration, vigorous mixing, addition of surfactants and bioaugmentation, are recommended by researchers in order to achieve enhanced remediation of pollutant-laden water. However, the results are not very pleasing in the case of micro-pollutants.

Physicochemical techniques such as nanofiltration (NF), adsorption on carbonaceous solid substances, advanced oxidation processes (AOPs), photo-catalytic degradation, ozonation and photo-oxidation have also been applied for removing micro-pollutants. But these processes too have their limitations such as high cost, high energy requirement, use of insensitive environmental conditions, generation of secondary sludge, requirement of toxic chemicals *etc.* Moreover, POP-contaminated water may be surface or ground water, potable or wastewater, in turn necessitating a treatment process suitable for all types.[7] Membrane bioreactor (MBR) technology often adapts suitable techniques based on the nature of micro-pollutants. Compared with conventional methods, modern water treatment techniques utilized in MBR technology and recent innovation in MBR-integrated systems are comparatively advanced, elaborate and fruitful. This chapter presents typical studies related to MBR technologies and cost analysis for their operating systems for the efficient removal of micro-pollutants. The terms POPs and micro-pollutants have been used interchangeably throughout the chapter.

## 13.2 Sources and Toxicity of POPs

Table 13.1 shows a list of commonly detected micro-pollutants along with their average concentration found in wastewater and surface water bodies. Depending on several factors such as usage of products, manufacturing techniques, production rate, per capita water consumption per day, rate of generation of wastewater and its discharge, ambient conditions *etc.* the quantity of micro-pollutants reaching WWTPs may vary.[5]

### 13.2.1 Occurrence of Micro-pollutants in Groundwater and Drinking Water

Apart from surface water, ground water also gets contaminated by micro-pollutants mainly because of seepage from sewer systems, septic tanks, and interaction between surface and ground and water through soil. In addition to this, soil permeation of runoff water from agricultural lands containing various pesticides and other chemicals and landfill leachate increases the level of micro-pollutants in ground water. Yet, the extent of ground water contamination with micro-pollutants is comparatively lower than that of surface water. The most common micro-pollutants present in ground water are sulfamethoxazole, triclosan, carbamazepine and non-steroidal anti-inflammatory drugs (NSAIDs). These compounds are ubiquitously present in surface as well as ground water and wastewaters, thereby confirming the association of the occurrence of these micro-pollutants in various aquatic systems.

### 13.2.2 Impact of Micro-pollutants on the Environment

Micro-pollutants are hazardous to the ecosystem and toxic to aquatic organisms, other animals and even human beings. Most micro-pollutants are either genotoxic, mutagenic or oestrogenic. Owing to their non-biodegradable and bioaccumulative nature, micro-pollutants can cause potential damage to

**Table 13.1** Micro-pollutants commonly found in municipal wastewater and surface water. Reproduced from ref. 5 with permission from Elsevier, Copyright 2018.

| Categories | Micropollutants | Application | Average concentration in surface water (ng L$^{-1}$) | Average concentration in wastewater (ng L$^{-1}$) |
|---|---|---|---|---|
| Biocides | 2, 4, 5-T | Herbicide | 67 | 13 |
| | 2, 4-D | Fungicide | 16 | 81 |
| | Atrazine | Herbicide | 54 | 201 |
| | Atrazine-desethyl | Herbicide | 373 | — |
| | Bentazone | Herbicide | 315 | 12 |
| | Carbendazim | Herbicide | 3 | 30 |
| | Chlortoluron | Herbicide | 40 | 25 |
| | Dichlorprop | Herbicide | 45 | 424 |
| | Diuron | Microbiocide | 20 | 116 |
| | Glyphosate | Herbicide | — | 90.6 |
| | Hexazinone | Herbicide | — | 4.2 |
| | Irgarol (cybutryne) | Herbicide | — | 68.8 |
| | Isoproturon | Herbicide | — | 9.6 |
| | Linuron | Herbicide | — | 12.4 |
| | MCPA | Herbicide | — | 9.6 |
| | Mecoprop-p | Herbicide | — | 26.3 |
| | Metolachlor | Herbicide | — | 13.8 |
| | Simazine | Herbicide | — | 3.2 |
| | Terbutylazine | Herbicide | — | 0.8 |
| | Terbutylazine-desethyl | Herbicide | — | 40.1 |
| | Triclosan | Herbicide | — | 0.3 |

| | | | | |
|---|---|---|---|---|
| Detergents, dishwashing liquids, personal care products (fragrances, cosmetics, sunscreens) and food products | Acesulfame | Food additive | 4010 | 22 500 |
| | Buprenorphine | Personal care product | — | 3.9 |
| | Caffeine | Food additive | — | 191.1 |
| | Chlorpromazine | Personal care product | — | 0.1 |
| | DEET, *N*,*N*′-diethyltoluamide | Personal care product | — | 678.1 |
| | Duloxetine | Personal care product | — | 0.1 |
| | Flutamide | Personal care product | — | 0.1 |
| | Gadolinium | Personal care product | — | 115 |
| | Loperamide | Personal care product | — | 29.3 |
| | Maprotiline | Personal care product | — | 0.4 |
| | Methylbenzotriazole | Personal care product | — | 2900 |
| | Miconazole | Personal care product | — | 0.2 |
| | Sucralose | Food additive | 540 | 4600 |
| Disinfectants, pharmaceuticals (prescriptions, over the counter drugs, veterinary drugs) | Alfuzosin | Alpha-blockers | — | 2.8 |
| | Alprazolam | Antidepressant | — | 1.3 |
| | Atenolol | β-Blocker | 205 | 843 |
| | Azithromycin | Antibiotic | 12 | 175 |
| | Bezafibrate | Lipid-lowering drug | 24 | 139 |
| | Bisoprolol | β-Blocker | — | 41.6 |
| | Bupropion | Antidepressant | — | 1 |
| | Carbamazepin-10, 11–dihydro-10,11-dihydroxy | Transformation product | 490 | 1551 |
| | Carbamazepine | Antiepileptic drug | — | 832.3 |
| | Carbamazepine | Anticonvulsant | 13 | 482 |
| | Ciprofloxacin | Antibiotic | — | 96.3 |
| | Citalopram | Antidepressant | — | 33.8 |
| | Clarithromycin | Antibiotic | 30 | 276 |
| | Clindamycin | Antibiotic | — | 70.4 |
| | Clofibric acid | Lipid-lowering drug | — | 5.3 |
| | Clonazepam | Anticonvulsant | — | 1.6 |
| | Codeine | Morphine derivate | — | 70.6 |

(*continued*)

**Table 13.1** (*continued*)

| Categories | Micropollutants | Application | Average concentration in surface water (ng L$^{-1}$) | Average concentration in wastewater (ng L$^{-1}$) |
|---|---|---|---|---|
| | Cyproheptadine | Chemotherapeutic agent | — | 3.9 |
| | Diatrizoate (amidotrizoic acid) | Contrast medium | 206 | 598 |
| | Diclofenac | Analgesic | 65 | 647 |
| | Diclofenac | Analgesic | 65 | 647 |
| | Diltiazem | Antiarrhythmic agent | — | 10.7 |
| | Diphenhydramine | Antihistamine | — | 11.7 |
| | Eprosartan | Antihypertensive | — | 226.8 |
| | Erythromycin | Antibiotic | 25 | 42 |
| | Ethinylestradiol | Synthetic estrogen | 5 | 2 |
| | Fenofibrate | Lipid-lowering drugs | — | 1.1 |
| | Fexofenadine | Antihistamine | — | 165 |
| | Flecainide | Antiarrhythmic | — | 45.5 |
| | Fluconazole | Antifungal medication | — | 108.2 |
| | Fluoxetine | Antidepressant | — | 2.1 |
| | Gemfibrozil | Lipid-lowering drug | — | 137.7 |
| | Haloperidol | Psychiatric medication | — | 32.2 |
| | Hydroxyzine | Antihistamine | — | 1.1 |
| | Ibuprofen | Analgesic | 35 | 394 |
| | Iohexol | Radiocontrast agent | — | 158 |
| | Iomeprol | Contrast medium | 275 | 380 |
| | Iopamidol | Contrast medium | 92 | 377 |
| | Iopromide | Contrast medium | 96 | 876 |
| | Irbesartan | Antihypertensive | — | 479.5 |
| | Ketoprofen | Analgesic | — | 86 |
| | Levamisole | Antihelminthic | — | 40.6 |
| | Lincomycin | Antibiotic | — | 31.2 |
| | Mefenamic acids | Analgesic | 7 | 870 |
| | Memantine | Antidementia agent | — | 22.8 |
| | Metformin | Antidiabetic | 713 | 10 347 |
| | Metoprolol | β-Blocker | 20 | 166 |
| | Mianserin | Antidepressant | — | 1.5 |

| | | | | |
|---|---|---|---|---|
| | N4-Acetylsulfame thoxazole | Transformation product | 3 | 67 |
| | Naproxen | Analgesic | 37 | 462 |
| | Orphenadrine | Antihistamine | — | 3.9 |
| | Oxazepam | Anxiolytic | — | 161.7 |
| | Penicillin V | Personal care product | — | 28.7 |
| | Ranitidine | Antihistamine | — | 68 |
| | Repaglinide | Antidiabetic medication | — | 3.1 |
| | Risperidone | Neuroleptic | — | 6.9 |
| | Rosuvastatin | Statin | — | 31 |
| | Sertraline | Antidepressant | — | 2.1 |
| | Sotalol | β-Blocker | 63 | 435 |
| | Sulfadiazine | Antibiotics | — | 3.5 |
| | Sulfamethoxazole | Antibiotic | 26 | 238 |
| | Sulfamethoxazole (JRC) | Antibiotic | — | 142.3 |
| | Sulfamethoxazole (VITO) | Antibiotic | — | 280.2 |
| | Telmisartan | Antihypertensive | — | 367.5 |
| | Terbutaline | Antiasthmatic | — | 1.1 |
| | Tiamulin | Antibiotics | — | 3.3 |
| | Tilmicosin | Antibiotics | — | 3.1 |
| | Tramadol | Analgesic | — | 255.8 |
| | Triclosan | Disinfectant | — | 74.8 |
| | Trihexyphenidyl | Antidementia agent | — | 0.2 |
| | Trimethoprim | Antibiotic | 13 | 100 |
| | Venlafaxine | Antidepressant | — | 118.9 |
| | Zolpidem | Hypnotic | — | 1.5 |
| Hormone active substances (effect on hormone balance) | Bisphenol A (BPA) | Additive | 840 | 331 |
| | Oestradiol | Natural oestrogen | 2 | 3 |
| | Oestrone | Natural oestrogen | 2 | 15 |
| | Nonylphenol | Additive | 441 | 267 |
| Pesticides | Carbaryl | Insecticide | — | 1.6 |
| | Diazinon | Insecticide | 15 | 173 |
| | Diethyltoluamide (DEET) | Insecticide | 135 | 593 |
| | Dimethoate | Insecticide | 22 | — |
| | MCPA | Insecticide | — | 149.9 |

wild-life and humans. In a case study it was observed that feminization in male fish was induced due to exposure to endocrine disrupting compounds (EDCs).[4,5] An unremitting release of EDCs in the environment, even at low concentrations, can cause such developmental and reproductive abnormalities in highly sensitive organisms. Moreover, it can also lead to an amplification of antibiotic resistant organisms in the environment. The ever-growing and arbitrary use of antibiotics both in human and animal health sectors has resulted in the development and evolution of organisms carrying antibiotic resistant genes. Growth of population, dependence on pharmaceutics and constant release of micro-pollutants into various natural ecosystems is likely to further enhance the progression of antibiotic resistant genes and microorganisms in the near future.

### 13.2.3 Toxicity Induced by Micro-pollutants

The level of risk to the environment due to different hazardous substances depends on their physical and chemical properties, their nature and mostly on their affinity for water and solid matter, which in turn can significantly affect their bioavailability. The threat to living organisms due to such harmful substances depends on the intensity of exposure, mobility of these substances and their capability of bioaccumulation and bio-magnification in the food chain. The micro-pollutants in water bodies are ingested by marine organisms and get accumulated in their tissues (bioaccumulation), often resulting in a higher pollutant concentration inside the organism's body as compared to the concentrations present in the environment. A wide range of different environmental conditions such as pH, temperature, salinity, turbidity *etc.* also affect the bioavailability of micro-pollutants. Other than the physicochemical properties, sensitivity of a species can also affect its ability to bioaccumulate micro-pollutants in its tissues. The ability to bioaccumulate compounds may vary from species to species even if they are exposed to the same concentration of particular pollutants. In fact individuals of the same species may show a different rate of accumulation of specific substances for the same period of exposure. For any given species certain factors such as age, body weight and size, sex and their physiological state, play an important role in the rate of accumulation of pollutants.

The information available regarding the concentration levels of POPs in treated effluents is not sufficient for calculating the risk posed by them to aquatic ecosystems. The analysis of target and non-target compounds result in some basic information regarding the hazard caused to humans as well as to the environment. Owing to the complex nature of mixed compounds in treated sewage, along with their degraded and transformed products, it is difficult to determine the effect of such a bottom-up approach.[8] Ecotoxicological studies are an excellent tool for gauging the dangers resulting from the presence of harmful byproducts and intermediates in treated wastewater. The ecotest results can determine the actual threat level posed to the organisms by a certain ecosystem. The test results are based on the determination of the dose of the chemical substance that can induce some predefined effects on the indicator organism (*e.g.*, $LC_{50}$, lethal concentration resulting in death in 50% individuals of the population; $EC_{50}$, effective concentration which can produce measurable effects in 50% of individuals in a population; $IC_{50}$, inhibition concentration that inhibits growth in 50% of individuals in a population). Compounds toxic to selected indicator organisms along with their highest concentration recorded in treated effluents are shown in Table 13.2. The majority of these compounds have been found to be pharmaceuticals.

According to a previous study,[9] the microalga *Pseudokirchneriella subcapitata* experienced maximum toxicity from exposure to citalopram and naproxen and minimum from acetaminophen, gabapentin, irbesartan and valsartan. Organisms like *Hydra attenuate, Lemna minor* and *Vibrio fischeri* (bacteria) have also been found to show sensitivity towards benzotriazole and diclofenac. Acetaminophen also reportedly exerted a toxic effect on *Daphnia magna.* According to previous studies, X-ray contrast media like iopamidol, iopromide *etc.* posed no risk to aquatic organisms when present in environmentally relevant concentrations. However, whether these compounds exert any detrimental effect in combination with other pollutants present in effluent is yet to be determined.[9,10]

Most of the POPs present in effluents reportedly disrupt endocrine processes by counteracting or mimicking natural hormones.[9,11] Bisphenol A, brominated flame retardants, organic tin compounds, pesticides, phthalates, polychlorinated biphenyls and some pharmaceuticals are examples of endocrine disrupting POPs.[12] Conventional processes of wastewater treatment are incapable of complete removal of such compounds, especially those having polar nature.[13] These compounds may affect living organisms even in trace concentrations.[12] The European Commission priority list includes 66 active substances having confirmed endocrine-disrupting activity.[9] Moreover, these compounds also exert genotoxic effects over an entire population for generations. Hence it is essential to perform genotoxicity assays for ecosystems that are constantly exposed to such pollutants.

EDCs found in wastewater are often percolated from microplastics which is a growing and quite troublesome pollutant in the EU.[14,15] Microplastics are a group of organic polymers prepared from different petroleum compounds with a maximum particle size of 5 mm. Studies indicated that WWTPs play a significant role in discharging microplastics to the environment. Microplastics ending up in effluents and subsequently in the marine environment have been raising major concerns because of their ubiquity, recalcitrant nature and possibility of bioaccumulation, thus entering different trophic levels with ease after undergoing numerous transformations.[24,26] Treatment processes implemented in contemporary WWTPs are not efficient enough for the complete removal of microplastics. However, many studies have shown 80–90% removal efficiency for an average microplastic concentration of 0–447 particles per litre.[16]

**Table 13.2** Toxicity parameters of compounds that were identified at the highest concentration levels in treated wastewater. Reproduced from ref. 9, under the terms of the CC BY 4.0 license.

| Compound | Toxicity (mg L$^{-1}$) | Species | Additional information |
|---|---|---|---|
| 1*H*-benzotriazole | 1.18 | *Desmodesmus subspicatus* | |
| | 231 | *Scenedesmus subspicatus* | Growth |
| | 102 | *Scenedesmus subspicatus* | Biomass |
| | 41.65 | *Vibrio fischeri* | Luminescence |
| | 107 | *Daphnia magna* | Immobilization |
| | 25.9–76.9 | *Daphnia magna* | Reproduction |
| | 102 | *Ceriodaphnia dubia* | Mortality |
| | 15.8 | *Daphnia galeata* | Immobilization |
| | 65 | *Pimephales promelas* | |
| | 25 | *Pimephales promelas* | Mortality, static |
| | 25.7 | *Pimephales promelas* | Mortality, static |
| | 27.5 | *Lepomis macrochirus* | Mortality, juvenile, static |
| | 25 | *Lepomis macrochirus* | Mortality, juvenile, static |
| | 3.94 | *Lemna minor* | |
| | 8.3 | *Chlorella sorokiniana* | Growth |
| 4-Methyl-1*H*-benzotriazole | >15 | *Oncorhynchus mykiss* (epithelial cell lines) | In mixture (1 : 1) with 5-methyl-1*H*-benzotriazole |
| | 21 | *Vibrio fischeri* | |
| | 118 | *Ceriodaphnia dubia* | |
| | 63 | *Pimephales promelas* | |
| Acesulfame | >1000 | *Daphnia magna* | |
| | >1000 | *Lemna minor* | |
| | >1000 | *Scenedesmus vacuolatus* | |
| Acetaminophen | >160 | *Oryzias latipes* | |
| | >160 | *Oryzias latipes* | |
| | 26.6 | *Daphnia magna* | |
| | 30.1 | *Daphnia magna* | |
| | 34.99 | *Daphnia magna* | |
| | 549.7 | *Vibrio fischeri* | |
| | 657.5 | *Vibrio fischeri* | |
| | 363.3 | *Vibrio fischeri* | |
| | >100 | *Pseudokirchneriella subcapitata* | |
| | >100 | *Artemia salina* | |

| | | | |
|---|---|---|---|
| Bromazepam | 1.5 | *Danio rerio* | |
| | 0.0001 | *Daphnia magna* | |
| | 0.0001 | *Daphnia magna* | |
| Caffeine | 290.2 | *Desmodesmus subspicatus* | Population growth |
| | 265 | *Sinapis alba* | Root length |
| Citalopram | 3.3 | *Pseudokirchneriella subcapitata* | |
| | 1.6 | *Pseudokirchneriella subcapitata* | Growth inhibition |
| | 0.505 | *Skeletonema marinoi* | |
| | 3.9 | *Ceriodaphnia dubia* | |
| | 4 | *Ceriodaphnia dubia* | Reproduction |
| | 30.14 | *Daphnia similis* | |
| | 30.14 | *Daphnia magna* | |
| | 22.81 | *Daphnia magna* | |
| | 7.44 | *Daphnia magna* | |
| | >100 | *Artemia salina* | |
| | 0.000405 | *Leptoxis carinata* | |
| Darunavir | 43–100 | Green algae | |
| | >43 | *Pseudokirchneriella subcapitata* | In pharmaceutical product Prezista |
| Diatrizoate | 613.92–0.61392 × $10^{-5}$ ($10^{-3}$–$10^{-11}$ M) | *Tetrahymena pyriformis* | Na-diatrizoate |
| | 613.92 (0.001 M) | Ciliate | Population growth |
| Diclofenac | 1950 | *Raoultella* sp, *strain DD4* | |
| | 14.31 | *Vibrio fischeri* | Sodium salt |
| | 416.67 | *Staphylococcus warneri* | |
| | >1300 | *Pseudomonas aurantiaca*<br>*Serratia rubidaea* | |
| | 782.11 | *Sorghum bicolor* | Sodium salt |
| | 7.5 | *Lemna minor* | Total frond area |
| | 72 | *Desmodesmus subspicatus* | Sodium salt |
| | 68 | *Daphnia magna* | Sodium salt |

(*continued*)

**Table 13.2** (*continued*)

| Compound | Toxicity (mg $L^{-1}$) | Species | Additional information |
|---|---|---|---|
| Efavirenz | >0.012 | *Pseudokirchneriella subcapitata* | In pharmaceutical product Stocrin |
| | 0.012–96.9 | *Green algae* | |
| | >0.76 | *Microcystis aeruginosa* | In pharmaceutical product Stocrin |
| | $1.03 \times 10^{-5}$ | *Oreochromis mossambicus* | Liver damage, histology-based assessment |
| Gabapentin | 50 | *Oncorhynchus mykiss* | |
| | >500 | *Daphnia magna* | |
| | >100 | *Daphnia magna* | |
| | >100 | *Pseudokirchneriella subcapitata* | |
| | >100 | *Artemia salina* | |
| | >100 | *Skeletonema marinoi* | |
| Iopromide | 10 000 | *Pseudokirchneriella subcapitata* | In pharmaceutical product Ultravist |
| | >1000 | *Daphnia magna* | |
| | >100 | *Danio rerio* | |
| Irbesartan | 460 | *Pseudokirchneriella subcapitata* | In pharmaceutical product Aprovel |
| | >100 | *Daphnia magna* | |
| | >100 | *Pseudokirchneriella subcapitata* | |
| | >100 | *Artemia salina* | |
| Lamivudine | 49.06 | *Pseudokirchneriella subcapitata* | In pharmaceutical product, Kivexa with formoterol and abacavir |
| | >96.9 | *Pseudokirchneriella subcapitata* | In pharmaceutical product Zeffix |
| | 96.9 | *Pseudokirchneriella subcapitata* | In pharmaceutical product Epivir |
| Metformin | 64 | *Daphnia magna* | |
| | >320 | *Desmodesmus subspicatus* | |
| | 110 | *Lemna minor* | |

| | | | |
|---|---|---|---|
| Metronidazole-OH | >100 | Aerobic bacteria | Metronidazole |
| | >100 | Aerobic bacteria | Metronidazole |
| | 243 | *Vibrio fischeri* | Metronidazole |
| | >64 000 | *Pseudomonas putida* | Metronidazole |
| *N*-Acetyl-4-aminoantipyrine | 10 | *Daphnia magna* | |
| Naproxen | 174 | *Daphnia magna* | Naproxen-sodium |
| | 43.64 | *Ceriodaphnia dubia* | Naproxen-sodium |
| | 66.37 | *Ceriodaphnia dubia* | |
| | 43.54 | *Thamnocephalus platyurus* | Naproxen-sodium |
| | 84.09 | *Thamnocephalus platyurus* | |
| | 2.68 | *Hydra attenuata* | |
| | 54.64 | *Brachionus calyciflorus* | Naproxen-sodium |
| | 24.2 | *Lemna minor* | Naproxen-sodium |
| | 3.7 | *Pseudokirchneriella subcapitata* | Naproxen-sodium |
| | 39.31 | *Pseudokirchneriella subcapitata* | |
| | >320 | *Desmodesmus subspicatus* | Naproxen-sodium |
| | 18.5 | *Vibrio fischeri* | |
| | 17.92 | *Vibrio fischeri* | |
| Sucralose | 1800 | *Daphnia magna* | |
| | >93 | *Mysid shrimp* | |
| | >1800 | *Daphnia magna* | |
| | >1800 | Green algae | |
| | 114 | *Lemna gibba* | |
| | 93 | *Americamysis bahia* | |
| Tramadol | 130 | Unspecified fish | Tramadol HCl |
| | 73 | *Daphnia* spp. | Tramadol HCl |
| | 170 | *Daphnia magna* | |
| | >4000 | *Pseudomonas putida* | Tramadol HCl |
| Valsartan | 85 | *Desmodesmus subspicatus* | |
| | >100 | *Salmo gairdneri* (*Oncorhynchus mykiss*) | |
| | >580 | *Daphnia magna* | |
| | >100 | *Daphnia magna* | |
| | >100 | *Pseudokirchneriella subcapitata* | |
| | >100 | *Artemia salina* | |

## 13.3 MBRs for Efficient Treatment of POPs

MBRs are regarded as a recent and innovative technology for the removal of micro-pollutants from effluents and wastewater. They may have a compact design and structure depending on the volume of wastewater that needs to be treated. MBRs have a very dense population of microbes on the membrane surface that comes directly into contact with the effluent, thus ensuring complete removal of contaminants before the wastewater passes out through the membrane filter. The sieving structure of the membrane helps to block pollutant particles that have a higher molecular weight than that of the cut-off of the membrane, thus bringing particles into the vicinity of the microorganisms inside the MBR for complete microbial degradation. This feature of MBR gives it an exceptionally high rate and efficiency of removing micro-pollutants and therefore provides MBRs with an advantage over other conventional biological water treatment systems.[17]

In the recent past different types of MBRs have been designed and employed for the removal of a wide range of pollutants including carbonaceous compounds, nutrients, particulate matter and pathogenic microorganisms.[18] Such pollutants are easy to remove *via* conventional water treatment methods, however the removal of micro-pollutants, especially persistent organic pollutants (POPs), such as those coming from sources like, pesticides, PCPs, pharmaceuticals, chemical industries, surfactants, steroid hormones *etc.* is often very difficult. Hence, comprehensive analysis of the fate and rate determining factors for the removal of micro-pollutants during the effluent treatment process is a crucial step for any of treatment facility in order to avoid discharge of untreated or partially treated wastewater into the environment.

As mentioned above MBRs can be adapted for the removal of various classes of micro-pollutants such as pharmaceutical compounds, pesticides, EDCs *etc.* Studies have reported up to 99% removal efficiency for 15 endocrine disrupting compounds, at a concentration range of 1–5 $\mu g\ L^{-1}$ using MBR technology.[19] MBR systems have even shown complete removal of some micro-pollutants from PCPs including salicylic acid and propyl paraben: 99, 97 and 70–80% of triclosan, atenolol and beta blockers, respectively, were successfully removed using this system. However, in the case of pharmaceutical compounds, treatment performance and removal efficiency of MBRs may vary. For instance, antibiotics such as erythromycin, ofloxacin and sulfamethoxazole, and analgesics like ibuprofen lorazepam, carbamazepine citalopram and primidone were removed at rates ranging between 75 and 95%,[1] although there are certain pharmaceutical compounds that are difficult to remove using MBR technology. Thus, the overall removal efficiency of MBR systems for different micro-pollutants can be said to follow the order: PCPs > EDCs > beta blockers > pharmaceutical compounds > pesticides.[17,19]

## 13.4 Major Processes of Pollutant Removal Occurring in MBRs

Different physical and biochemical processes are involved in an MBR system for the removal of micro-pollutants from wastewater. They include physical retention of pollutant particles by the membrane, microbial degradation, air stripping, adsorption and biosorption, and photo-transformation. For the removal of non-polar pollutants, membrane retention and sorption of solids are the main underlying mechanism.[1] When the pore size of the microfiltration membrane exceeds the micro-pollutant particle size, the availability of area for sorption is effectively reduced. Yet a considerable rate of sorption occurs owing to the formation of a secondary layer of micro-pollutants deposited on the membrane surface.[20] However, sorption becomes very limited in the case of polar pollutants, and hence microbial degradation plays a major role in their removal.[1] The highly volatile organic compounds that are present in trace amounts in wastewater can be removed by MBRs through volatilization or air stripping. For the removal of hydrophobic and hydrophilic pollutants, biosorption and biodegradation can be applied respectively. These mechanisms however have some limitations due to the numerous intermediate compounds and by-products or secondary metabolites formed during sorption and biodegradation.[21]

### 13.4.1 Sorption

This is a phenomenon, where the micro-pollutant particles associate with the solid phase (activated sludge) by adhesion. Some pollutants are easily adsorbed onto the sludge. There are two major underlying mechanisms for the sorption of pollutants on primary and secondary sludge – they are adsorption and absorption. Here, adsorption refers to the electrostatic interaction between the negatively charged surface of microorganisms with the positively charged functional groups of micro-pollutants, whereas, absorption is the hydrophobic interaction of the pollutants with the lipophilic cell membrane of the microbes and the lipid fractions of the sludge.

The ratio of concentration of pollutant present in the solid to the concentration present in the aqueous phase (at equilibrium) is called the solid–water distribution coefficient ($K_d$). $K_d$ is often used to determine the ratio of equilibrium concentration of micro-pollutants adsorbed and in solution.[7] Previous studies have reported minimum sorption of hormones and musk fragrances, *i.e.* compounds having a $K_d < 500$ L kg$^{-1}$.[7] A low value of the octanol water partition coefficient (log $K_{ow}$) suggests the hydrophobic nature of the target pollutants. These pollutants are first adsorbed by the activated sludge and then removed by biodegradation.[7] Normally, the $K_d$ value of primary sludge is a bit higher than that of activated sludge, which clearly suggests higher adsorption and lower degradation of pollutants by the primary sludge.

### 13.4.2 Biodegradation

Bioremediation is an integrated and sustainable approach towards employing microorganisms, such as bacteria and fungi, for the treatment of both solid wastes and wastewater that are rich in organic pollutants and generated from various sources.[22] Bioremediation is gaining much appreciation as an innovative tool in the field of environmental science and engineering owing to its eco-friendly nature, cost effectiveness and comparatively high efficiency. The advantage of this technology is that it allows microorganisms to acclimatize to the toxic environment created by hazardous wastes, resulting in the natural development of new and toxin-resistant strains. These new strains are hence capable of metabolically transforming a variety of toxic chemical substances into a less harmful form.[23–25]

In the past, several types of biological treatment systems were developed, such as activated sludge, sequencing batch reactors, bioslurping, trickling filters, rotating biological contactor, biological aerated filters and bioaugmentation.[26] Biological methods are mostly dependent upon the enzymatic and metabolic efficiency of microbes for pollutant degradation.[27,28] However, bioremediation by the indigenous microbial population has proven to be the most eco-friendly, energy-saving and cost-effective process.[29,30] The most beneficial characteristic of biological processes is that their end-products are nontoxic. Mostly harmless gases like nitrogen, carbon and hydrogen are generated as end-products of microbial degradation and can easily be assimilated into the environment.[30] The biodegradation potential of indigenous microorganisms can be further improved by optimizing certain process parameters such as bioavailability, rate of adsorption and mass transfer. However, more inclusive research is essential for the implementation of bioremediation techniques on a large scale and for analysis of the environmental consequences.

#### *13.4.2.1 Modes of Biodegradation*

Among various different processes reported in the past, biological oxidation gives the best result in terms of complete degradation of pollutants present in effluent.[31] Evaluation of previous reports implies that bacterial species are competent at degrading different contaminants over a wide range of environmental factors (like pH, temperature, salinity, *etc.*) in comparison to fungal or algal species. This superior biodegradation potential displayed by bacterial community can be credited to their rapid rate of growth and reproduction along with simple culture techniques.[32] Studies have indicated that MBR technology for wastewater treatment provides some specific advantages like reduced carbon footprint, low sludge production, removal of organic micro-pollutants with low molecular weights (which are otherwise difficult to remove), and better separation potential and superior quality of effluent post-treatment.[33] Therefore, the MBR technology is currently favoured and recommended by many researchers over conventional sludge-based chemical processes. The one thing that limits wide-scale implementation of MBR technology is the lengthy treatment period.

### 13.4.2.2 Suspended Cultures and Immobilized Cultures

Currently, immobilized microbial cell technology is gaining much interest and appreciation as the most suitable method for treatment of wastewater rich in reactive azo dyes and their metabolites. Cell immobilization aids with increased concentration of biomass, improved process stability, amplified hydraulic loading rates, reusability of biocatalysts and enhanced microbial activities in the immobilized state, as compared to CASP and suspended cultures.[34] Moreover, Immobilized cell cultures (ICC) can be efficiently employed for solid–liquid phase separation in the settling tanks, and even eliminate hitches related to bulk amount, unlike suspension cultures.[34]

Immobilized cells are therefore often referred to as biocatalysts, and have been shown to have greater efficiency for pollutant degradation, greater resilience to fluctuations in environmental factors such as pH and salinity of the effluent, ambient temperature, varying concentrations of toxic chemicals *etc.*[34] With all the advantages they offer, ICCs or the biocatalysts are regarded as an appropriate technique for large-scale effluent treatment. A detailed comparative analysis of immobilized and non-immobilized biocatalyst-mediated processes is presented in Table 13.3.

### 13.4.2.3 Biocomposites

Advances in the field of biotechnology and nanotechnology have empowered researchers to develop different types of nano-biocatalysts, immobilize cells, enzymes and other biochemical substances into nano-environments, manoeuvre the process parameters affecting macroscale reactions *etc.* Studies in the recent past have shown that nano-biocatalysts exhibit improved biomolecule loading capacity, appreciably superior efficiency of mass transfer, enhanced biomolecule activity and stability and higher tolerance to fluctuations in experimental parameters. The huge surface area of nano-materials provides a greater surface-to-volume ratio and hence can sustain much higher concentrations of immobilized cells and biomolecules compared to other materials with planar surfaces. Some of the advantages offered by nanotechnology for immobilization of biomolecules include development of nano-biocatalysts with a high percentage of solid content without using any surfactant or toxic chemicals, preparation of well-defined and homogenous supports, and convenient modification of nano-particle size as required. Various nano-materials are being extensively examined and studies are being conducted for concurrent immobilization of several biomolecules on the same substrate for synthetic *in vitro* applications.[5]

### 13.4.2.4 Factors Affecting Bioremediation Processes

Bioremediation is an efficient technique, although the process is often complicated because of the toxic, multi-phased hydrophobic nature of pollutants such as petrochemical wastes. Previous studies of petrochemical waste

**Table 13.3** Comparison of immobilized and non-immobilized biocatalytic processes. Reproduced from ref. 35 with permission from Macmillan Publishers Ltd, Copyright 2015.

| Properties | Non-immobilized biocatalytic processes | Immobilized biocatalytic processes |
|---|---|---|
| Biomass growth (for cell biocatalysts) | Biomass reaches high concentrations in a short time that complicates the control of process | Biomass growth remains same along the process |
| Contamination | Risk of contamination by reaction mixture | Minimizes or eliminates product contamination |
| Cost of design | No additional cost is necessary | Additional cost for design of support material and technique |
| Downstream process | Difficult separation due to biocatalyst/substrate/product mixture | Facilitates separation from the production medium |
| Industrial application | Can be applied in various industrial production processes | New techniques and support materials need to be improved for application in different industries |
| Mass transfer and diffusion limitations | Biocatalyst can interact with environment with no limitation | Mass transfer is limited due to the support material |
| Movement (for cell biocatalysts) | Free movement—high mobility | Limited movement due to physical/chemical interaction with support material |
| Overall cost-effectiveness | Loss of valuable biocatalysts | Valuable biocatalysts can be reused |
| Productivity | Low productivity (kg product/kg enzyme) | High catalyst productivity (kg product/kg enzyme) |
| Recovery and reuse | Minimal or null reuse of biocatalyst | Efficient recovery and reuse |
| Stability | Low stability | Enhanced operational stability against different operational conditions (temperature, pH) |

degradation have recognized a number of physical, chemical and biological factors that affect the rate of biodegradation. These factors include pH, initial concentration of the pollutant, temperature, accessibility of inorganic nutrients, biochemical composition of soil and water, adaptation by microbes *etc.*[30,36,37] Bioavailability of the organic pollutants to the microbial population is another important factor that determines the rate of biodegradation.[30] The solubility and bioavailability of hydrocarbons can vary, based on their physical and chemical nature as well as temperature.[63] There are some microorganisms that can release biosurfactants and are hence capable of effectively removing petroleum hydrocarbons.[38]

### *13.4.2.5 Drawbacks of Bioremediation*

While bioremediation has proven its potential and worth in laboratory-scale effluent treatment of waste-containing water, it often yields disappointing results in real-time wide-scale application due to harsh field conditions.[5] Selection of microorganisms is another critical factor for successful biodegradation. For instance, only a microbial population that can grow and survive in a habitat containing petrochemical wastes can be employed for the biodegradation of petrochemicals; other species will not be able to survive or adapt to such harsh environments. Therefore, it is a crucial step to identify and isolate the locally adapted species and strains from a particular habitat for a specific type of pollutant. In laboratory experiments the initial concentration of the contaminants are controlled and kept the same for different contaminants. However, in real effluent the distribution of contaminants is heterogeneous.[30] Natural surface sensors are found in certain bacteria which help them in moving towards pollutants or away from them. These sensors can determine the distance between target chemicals and the point of assemblage of microorganisms.[30] One other problem with the utilization of microorganisms is their lesser degradation efficiency. Usually, a single microbial species cannot effectively degrade petrochemical waste and therefore a consortium of different microbial populations is required. Consortia of different bacterial strains and coupling of bacteria and fungi have been found to carry out efficient degradation of volatile organic compounds and cyclic aromatic hydrocarbons. However, an excessive quantity of nutrients can potentially inhibit the degradation activity of the microorganisms. Moreover, the rate of biodegradation of specific contaminants is often hindered by interactions among different substrates.[30]

### *13.4.2.6 Biodegradation of POPs*

Biodegradation is significantly dependent upon the redox condition of the effluent for the removal of micro-pollutants in MBR technology.[5,39] The process of degradation follows pseudo-first order kinetics. The aerobic conditions inside the MBR system favour the growth of microbes and hence create suitable conditions for biodegradation as well. Previous studies have reported >80% removal of acetaminophen, ibuprofen, fenoprofen, 17α-ethynylestradiol, fenofibric acid, tonalide and roxithromycine using MBR sludge.[5] A similar negative charge of activated sludge and anti-inflammatory drugs causes repulsion, resulting in very limited sorption, and hence biodegradation is the chief method for removal of such compounds.[5]

Some other compounds like diazepam, carbamazepine, indomethacin, lipid regulators and beta blockers are persistent pollutants and show very limited biodegradation (<20%) and their discharge reduces the efficiency of continuous MBR operation.[5] To overcome this problem, the sludge retention time was increased and found to produce better results for the biodegradation of mefenamic, naproxen, gemfibrozil, diclofenac, acid and indomethacin.[5] Both sorption and biodegradation have been found to be simultaneously involved in the removal of musk fragrances in an MBR. Moreover, the rate of biodegradation has been found to be totally dependent upon effluent composition, sludge origin, sludge age, aeration and microbial consortium.[5]

### 13.4.3 Stripping/Volatilization

Stripping is used for the removal of gaseous pollutants and volatile compounds present in aerobic WWTPs. The process of stripping mainly depends on hydrophobicity and vapour pressure.[1] However, the phenomenon of volatilization will only be considered significant in the case of a high H/log $K_{\mathrm{ow}}$ value.[5,33] Volatilization is insignificant for most pharmaceutical compounds and oestrogens because of their low H-value and hydrophobicity; however, celestolide can be noticeably removed by an air-stripping method.[5]

## 13.5 Factors Affecting MBR Efficiency

There are several different factors that determine the effectiveness of an MBR system for the removal of micro-pollutants from wastewater. The biological factors that influence MBR operations are as follows: age and concentration of the sludge, sludge retention time (SRT), operating conditions and the environment inside the membrane compartments (which may be either aerobic, anaerobic or anoxic), effluent composition and a few other physicochemical factors such as ambient temperature, conductivity, organic matter concentration, ionic strength, *etc.*

### 13.5.1 Physicochemical Properties of POPs

Other than the prevailing conditions inside the MBR, the physicochemical characteristics of the micro-pollutants also greatly affect the performance of the MBR.[1] Studies have indicated that a bench top MBR system is suitable for the removal of certain micro-pollutants, like oestrone and 17α-ethynyloestradiol up to 80 and 99%, respectively.[1] A previous study reported a removal efficiency of 8–38% for diclofenac with an increasing SRT of between 20 and 48 days, whereas successful removal of clofibric acid was achieved only after acclimatization of the microbial population to the activated sludge.[1] Some other micro-pollutants such as ketoprofen and naproxen, which possess double aromatic rings, are effectively removed by increasing the SRT along with the presence of a varied microbial population that can degrade the aromatic rings once they are acclimatized. Though it is tricky to establish a correlation between removal efficiency and a contaminant's complexity, it can still be deduced that electron donating compounds such as aliphatic monocyclic aromatic hydrocarbons can be easily biodegraded in MBRs compared with electron withdrawing polycyclic compounds.[40]

## 13.5.2 Operating Conditions

Various researchers have reported how different operating conditions of the MBR can lead to increase/decrease in its pollutant removal efficiency resulting in poor effluent quality post-treatment, membrane fouling, excessive energy consumption *etc.*

### *13.5.2.1 Sludge Retention Time*

The average retention of activated solid sludge inside the MBR system is referred to as SRT.[1] Among the different physicochemical parameters influencing MBR operation, SRT is the most significant parameter. The common problem of membrane fouling during wastewater filtration is controlled by adjusting the SRT. In numerous studies it has been found that the performance and efficiency of MBR systems and effluent quality post-treatment are directly proportional to the SRT.[1] Another study reported an improvement in acidic pharmaceutical wastewater treatment simply by increasing the SRT from 15 days to 65 days.[1] Another study showed an 11% increase in the removal efficiency of 17α-ethynyloestradiol by extending the SRT by >20 days.[5]

High SRTs are capable of enhancing the removal efficiency of micro-pollutants by lowering the sludge yield and improving the concentration of mixed liquor suspended solids (MLSS). Generally, for the majority of different types of micro-pollutants, an SRT ranging between 20 and 30 days is adequate for their successful removal through MBR systems.[1] However, as the MLSS gets too viscous, high energy input is needed so as to prevent membrane fouling. When the SRT reaches beyond a critical point it results in severe fouling and ageing of the membrane.[1]

### *13.5.2.2 Solution pH*

pH is a very important parameter for any biochemical reaction and a pH range of 6–8 is best suited for biological wastewater treatment processes.[1] Efficient removal of micro-pollutants has been observed for pH 5–9.[5] Moreover, functional groups of compounds have also been found to significantly affect POP removal efficiency.[5]

### *13.5.2.3 Redox Conditions*

By operating MBR systems under diverse redox conditions, high microbial activity can be achieved. It has been reported that micro-pollutants like naproxen, ibuprofen and 17α-ethynyloestradiol can be degraded to a great extent under aerobic conditions whereas certain compounds like tonalide and galaxolide can be degraded under both aerobic and anoxic condition.[5] Many studies have shown that anoxic conditions are suitable for the removal of micro-pollutants from effluents.[1] For example, biodegradation of diuron was found to be 60% and 95 under aerobic and anoxic conditions respectively.[41] Partial removal of some micro-pollutants like bezafibrate, gemfibrozil, ketoprofen and diclofenac can be obtained through nitrification. Removal of certain trace micro-pollutants results from the enrichment of some nitrifying bacteria enabled by a high SRT in the MBR system.[42]

### *13.5.2.4 Temperature*

The growth and activity of microorganisms are highly affected by fluctuations in temperature even though the removal of micro-pollutants such as ibuprofen, naproxen, acetaminophen and bezafibrate takes place at room temperature using the MBR system. For the removal of carbamazepine and diclofenac, insignificant changes in were removal efficiency were reported at room temperature.[1] At a temperature of 20–35 °C, the pH was found to be stable at 8 for the removal of most hydrophobic micro-pollutants in an MBR system, while with an increase in temperature up to 45 °C a sharp decrease was observed in the removal rate. This decline which was observed in the removal efficiency may be credited to a decrease in sludge disintegration. Moreover, a rise in temperature from 20 to 45 °C led to an enhancement of soluble microbial products which in turn resulted in membrane fouling.[5] However, for certain antibiotics such as atenolol, ibuprofen and sulfamethoxazole, sulfamethoxazole and erythromycin, temperature variation within the range of 18–23 °C showed beneficial results.[5]

## 13.6 Integrated MBR-based Processes

Modern approaches involving integration of MBR systems with other processes, such as AOPs, membrane distillation, granular MBR systems, bio-entrapped MBRs *etc.*, are gaining much attention nowadays. MBRs integrated with other wastewater management processes can help improve the permeate quality, resolve membrane fouling issues and boost the removal efficiency for micro-pollutants. Figure 13.1 presents a brief schematic diagram of different types of integrated MBR systems that are already being utilized for wastewater treatment.

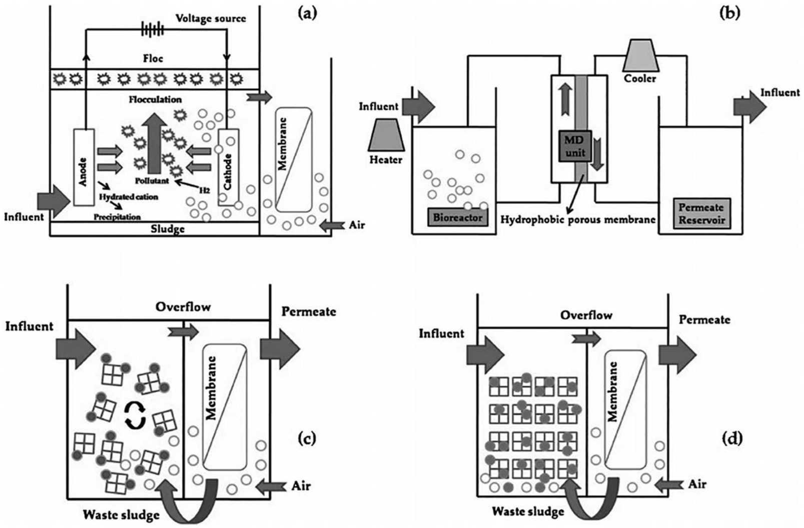

**Figure 13.1** Schematic diagram of some hybrid MBR systems: (a) electrocoagulation augmented external side stream membrane bioreactor system, (b) membrane distillation bioreactor (MDBR) with an external side stream membrane, (c) biofilm-membrane bioreactor (BF-MBR) and (d) bio-entrapped-membrane bioreactor (BE-MBR). Reproduced from ref. 5 with permission from Elsevier, Copyright 2018.

## 13.6.1 AOPs-MBR

AOPs are usually known for their ability to remove diverse organic pollutants from wastewater by altering them to readily biodegradable intermediates. However, the presence of suspended solids in wastewater can cause major problems by scavenging hydroxyl radicals.[33] In this vein, MBR plays an essential role in eliminating suspended solids from effluents thereby accelerating the rate of the degradation process. AOPs also help in overcoming membrane fouling and extending membrane life with improved performance. The efficiency of AOPs integrated with MBR technology depends upon the concentration and nature of the pollutants present in the wastewater. For example, if the concentration of recalcitrant pollutants is higher than that of biodegradable organic pollutants in wastewater, AOPs are applied prior to the biological treatment step so as to convert the recalcitrant compounds into their easily degradable forms. Integration of electrocoagulation with MBR has also shown successful removal of organic and inorganic contaminants from wastewater stream. In the process of electrocoagulation, metal ions and hydrogen gas are generated at the anode and cathode respectively, which promotes effortless removal of the flocculated pollutant particles. Such an integrated system has reportedly enhanced the quality of permeate flux and increased membrane life. However, integrated application of techniques like electrocoagulation and electro-Fenton with an MBR system reportedly resulted in excessive sludge generation.

### 13.6.2 Reverse Osmosis and Forward Osmosis Membrane Systems

Conventional MBRs often retain contaminants within the bioreactor. Moreover, an increase in SRT is found to enhance membrane fouling. The combination of MBR with osmotic techniques is found to produce superior quality of water with low energy requirement.[33] Enhanced removal efficiency was observed when an MBR system was conjugated with forward osmosis (FO) at low hydraulic pressure.[33] In an osmotic membrane coupled bioreactor (OMBR), sludge quality and membrane fouling can influence the overall performance of the system. In such integrated systems, low water flux and accumulation of salts are two additional challenges that need to be overcome.[33] Ding *et al.*[43] reported the improved removal rate of phosphorus and nitrogen from wastewater by applying an anaerobic membrane bioreactor (AnMBR) integrated with FO systems.

A combination of reverse osmosis (RO) and FO systems has been previously implemented for wastewater treatment, where FO was responsible for pumping the wastewater while RO was employed for separating and recycling the draw water.[5] FO does not have the drawbacks of high energy consumption and osmotic gradient, and hence shows better recovery. However, RO is considered to be more inexpensive and hence is preferred. The integration of these two systems can help overcome their individual limitations.

### 13.6.3 Granular MBR

Aerobic granular sludge systems have recently gained popularity for efficiently treating effluents rich in organic micro-pollutants'.[44,45] These systems are capable of achieving simultaneous nitrification and denitrification inside the reaction chamber owing to their compact, spherical and granular structure.[68] A previous study reported the removal of synthetic micro-pollutants from wastewater by conjoining a membrane airlift bioreactor (MABR) with a sequencing batch airlift reactor (SBAR).[5] In SBAR technology, aerobic granules are cultivated for managing high-aeration nitrification and low-aeration denitrification processes, whereas in MABR both aerobic and anoxic zones occur simultaneously. Aerobic granular sludge membrane bioreactors also demonstrate reduced membrane fouling during the removal of pharmaceuticals and PCPs from wastewater.[5] These integrated MBRs also aid in reducing COD and nitrogen, ammonium and total phosphorus.

### 13.6.4 Membrane Distillation Bioreactor (MDBR)

These are integrated systems where a thermophilic bioprocess is combined with a membrane distillation method.[33] Microporous and hydrophobic membranes release water vapour in the process due to a thermal gradient, thereby generating superior quality of water. As compared to MBR systems, MDBRs are capable of achieving far better removal efficiency of organic wastes from municipal wastewater in addition to reducing sludge formation. Moreover, they reduce membrane fouling and are extremely cost-effective. A high-performing MDBR system was reported to reduce total organic carbon (TOC), salt concentration and greenhouse gases along with excellent removal of organic water contaminants.[1]

### 13.6.5 Biofilm/Bio-entrapped Membrane Bioreactor

In biofilm-MBR, the suspended solid concentration is minimized due to the incorporation of biosupport within the MBR, which in turn decreases membrane fouling. An enhanced removal efficiency rate for ammonia and total nitrogen along with simultaneous reduction of membrane fouling was achieved by applying a biofilm-MBR integrated system.[5] In this system there is a specific rate of oxygen utilization which facilitates significantly improved microbial activity in the biofilm-MBR. Another study compared two different types of integrated method for pharmaceutical wastewater treatment,[5] *i.e.* the salt marsh sediment membrane bioreactor (MSMBR) and the bioentrapped membrane reactor (BEMR). In BEMR, the activated sludge used was entrapped in bio-carriers. Nevertheless, this entrapped activated sludge could not be sustained under hypersaline conditions. However, the MSMBR was capable of degrading persistent compounds with reduced membrane fouling.

A comparative analysis of POP removal efficiency achieved with different integrated processes is shown in Table 13.4.

## 13.7 Membrane-based Separation of Treated Water from Mixed Liquor

Membrane filtration systems for the separation of contaminants have added new dimensions to conventional water treatment technologies. Recent advancement in the design and development of novel membranes have made extra flexibility and improved efficiencies easily achievable. However, the addition of membranes into bioreactors necessitates a choice between low energy utilization and fouling control.[47]

Membrane filtration basically has two aspects which help to differentiate it from other conventional techniques of filtration. The first advantageous aspect is the asymmetric structure of the membrane, which has minute pores on the feeding surface that greatly reduces the pressure

**Table 13.4** Removal efficiency (%) of micro-pollutants utilizing MBR and integrated-MBR systems. Reproduced from ref. 45 with permission from Elsevier, Copyright 2017.

| | | Micropollutant removal (%) | | | | |
|---|---|---|---|---|---|---|
| Type of compound | Compound | MBR | MBR-NF | MBR-RO | MBR-powdered activated carbon (PAC) | MBR-granular activated carbon (GAC) |
| Analgesics non-steroidal anti-inflammatory and anti-pyretics (NSAIDs) | Acetaminophen | 95.1–99.9 | 91.0–99.9 | 99.6–99.9 | — | — |
| | Diclofenac | 15.0–87.4 | 87.5–97.0 | 88.3–95.9 | > 98.0 | — |
| | Ibuprofen | 73.0–99.8 | 99.4–99.8 | 99.4–99.8 | — | — |
| | Ketoprofen | 3.7–91.9 | — | — | — | > 98.0 |
| | Naproxen | 40.1–99.3 | 78 | — | 87.3 | >98.0 |
| Antibiotics | Erythromycin | 25.2–90.4 | — | >99.0 | > 88.0 | — |
| | Sulfamethoxazole | 20.0–91.9 | 90 | >99.0 | 82 | — |
| Anti-depressant and anti-epileptics | 17α-Ethynyloestradiol | 0–93.5 | >71.0 | >71.0 | 86.7 | — |
| | 17β-Oestradiol | >99.4 | >71.0 | — | 92.4 | — |
| | Bisphenol A | 88.2–97.0 | 95 | 96 | — | — |
| | Carbamazepine | 42–51.0 | 81.0–93.0 | 84.8–99.0 | 80.0–99.0 | >98.0 |
| | Diazepam | 67 | — | >99 | 80.0–90.0 | — |
| | Oestrone | 76.9–99.4 | >76.0 | >76.0 | — | — |
| Beta-blockers | Atenolol | 5–96.9 | 85 | >99.0 | — | — |
| | Metoprolol | 29.5–58.7 | 71.2 | >99.0 | >99.0 | — |
| Lipid regulator and cholesterol lowering drugs | Bezafibrate | 88.2–95.8 | — | — | — | — |
| | Clofibric acid | 25.0–71.0 | — | — | — | — |
| | Gemfibrozil | 32.5–85 | — | — | — | — |

gradient across the membrane, thereby eradicating membrane plugging tendency. The second aspect is application of a strong crossflow over the operating surface of the membrane system, which prevents the build-up of filter cakes.[48]

Based on the pressure gradient across the membrane, membrane filtration techniques can be categorized as microfiltration, ultrafiltration (UF), nanofiltration (NF) and RO. RO and NF are based on the fundamental principle of membrane separation where water (containing micro-pollutants) is pressurized and forced out through a semi-permeable membrane resulting in desalination of the water. UF and NF membrane systems have gradually emerged as an ecofriendly and economical separation technology for a wide range of contaminants and micro-pollutants commonly found in wastewater. Application of these membranes is discussed in the following sections.

### 13.7.1 Ultrafiltration Membranes

For over a century UF has been regarded as an exceptional tool for mechanical separation of waste materials from a mixture of compounds present in effluents. This process involves forcing of solutions at different pressures through a membrane. More specifically, the hydrostatic pressure induces the movement of liquid through a semipermeable membrane.[49] This separation process is targeted at removing high molecular weight molecules and suspended solids. The removal efficiency will depend on the molecular weight cut-off (MWCO) which is specific for any given membrane. The molecule structure, charge and hydrodynamic conditions are some other important factors that can substantially influence the filtration results.[50] The major underlying mechanism of UF is size exclusion; however, based on the nature of the compounds present, interaction between the membrane and particles can negatively impact the efficiency of the process. The benefits of UF in comparison to conventional purification and disinfection processes are its simplicity and cost effectiveness owing to low energy consumption, fewer control methods, less use of chemicals, mild temperature requirement and superior quality treatment.

However, the performance of UF is often slightly downgraded due to a compromise between the selectivity and permeability of the membrane.[51] Hence to achieve effective results for the treatment of multicomponent wastewater, integration with other process is always recommended. Processes like heterogeneous catalytic oxidation, reverse filtration and sorption are typically used in combination with membrane technologies, especially for low molecular weight micro-pollutants.[52,53]

Spray coating is another cost-effective strategy applied for the development of multifunctional UF membranes, where thin films are coated on different substrates thus omitting the limitation posed by substrate size and shape.[54,55] Layer-by-layer deposition is an *in situ* method used for gaining control over the membrane synthesis process.[56] This method, can improve permeability and rejection efficiency while increasing the number of active sites. Moreover, initiating a strong interaction between the membrane matrix and active materials can reduce leaching and loss of active materials.[56]

The key criteria guiding the efficiency of UF membranes include rejection performance and stability. The key characteristics of a UF membrane are its permeance, rejection capacity and typical pore size of 1–100 nm. This helps in effectively intercepting molecules of size ranging from 0.5 to 1000 kDa. Permeance varies directly with porosity and pore size, and changes in these parameters may lead to a decrease in rejection performance. Therefore, optimization of permeance and rejection performance indicates a trade-off between membrane permeability and selectivity.[51,57] Pure water permeance of a UF membrane ranges from dozens to hundreds of $\mathrm{Lm^{-2}h^{-1}}$.[58] In the case of multifunctional UF membranes, loading of active materials can negatively affect the porosity of the membranes thereby influencing the operational pressure and causing a decline in rejection performance. Stability of the membrane matrix and the active materials is also a key parameter affecting the operational life of the membrane.[51] Application of UF membranes integrated with an MBR set-up for POP removal from effluents is shown in Table 13.5.

### 13.7.2 Nanofiltration Membranes

NF membranes have been in use since the 1980s and continue to gain interest owing to their versatility as a separation tool. The pore size of NF membranes should be <1 nm, which matches up with an MWCO within the range 100–5000 Da.[59] NF membranes display a mild surface charge due to dissociation of the functional groups and sorption of charged solutes. Active functional groups present in polymeric NF membranes, such as carboxylic and sulfonic acid, result in charged surfaces in the vicinity of an aqueous feed solution. Moderate operational pressure, no phase change, high selectivity, relatively high rejection of multivalent inorganic salts and cost effectiveness are some of the appealing characteristics of NF membranes.[59] Moreover, NF membranes are typically characterized by physicochemical compatibility with process liquors, pore-size distribution, surface chemistry and cost effectiveness. The membrane consists of three functional layers: an active layer, a porous layer for support and a macro-porous structure underneath. The properties of the active layer determine the permeability and selectivity of a particular membrane, whereas the supporting layer contributes to the mechanical properties of the same. Based on membrane structure and pore shape, NF membranes can be classified as isotropic micro-porous, nonporous, asymmetric, ceramic and liquid membranes.[48] The working area per unit of membrane surface is found to increase for plate and frame, tubular membrane, spiral wound and hollow fibre membrane modules in order of their mention.

In NF processes part of the feed is made to pass through a semi-permeable membrane.[48] The inlet stream is divided into two – the permeate, that is the filtered portion of the stream, and the retentate, which is the non-filtered

**Table 13.5** Ultrafiltration (UF) and nanofiltration (NF) membranes for micro-pollutant removal.

| Process | Membrane type | Effluent | Removal (%) | Reference |
|---|---|---|---|---|
| MBR-UF | Indigenous ceramic membrane | Cosmetic effluent | Colour (99.22); Triclosan (98.56); Surfactant (99.74) | 60 |
| MBR-UF + NF | Tubular polyether -sulfone UF membrane; Polyamide thin-film composite NF membrane | Phthalates (PAEs); Bisphenol A (BPA) | >99 for both PAEs and BPA | 61 |
| MBR-NF | Commercially available poly-meric membrane | Hospital wastewater | COD (94); colour (98) nitrogen (83); iron (99) | 62 |
| MBR-UF | Flat-sheet polymeric membrane | Pharmaceuticals and organic micropollutants | 90–98 | 63 |
| MBR-UF | Flat-sheet membrane | Pharmaceuticals | >95 | 64 |
| MBR-UF | Polypropylene hollow-fibre membrane | Amoxicillin | 95 | 65 |
| MBR-UF | — | Municipal landfill leachate | Complete removal of ammonium nitrogen; >97 removal of TOC and COD | 66 |
| MBR -UF/ NF/RO | Plate and frame type, hollow-fibre, submerged UF membrane; Thin-film composite polyamide RO/NF membrane; | Oestrogenic and androgenic steroid hormones | >95 by RO and NF; Residual pollutant conc. lower than USEPA and WHO permissible standards | 67 |
| MBR-UF | Hollow-fibre polyvinylidene fluoride membrane | Domestic wastewater | Pharmaceuticals (>84); COD (98) | 68 |
| MBR-NF | Positively charged polyamide hollow-fibre NF membranes | Pharmaceuticals, personal care products and environmental oestrogens | 81 to ≈91.26 | 69 |
| MBR-UF + ozonation/RO/ adsorption using activated carbon | Flat-plate type polyethersulfone UF membrane | Fruit processing wastewater | Best results with adsorption as post treatment; 2,4-D (98.6); atrazine, carbendazim and diuron (>99) | 70 |
| MBR-UF | Hollow-fibre hydrophilized polyvinylidene-fluoride UF membrane | Olive processing wastewater | Total organic carbon (≥86.4); total poly-phenols (89.1); turbidity (99) | 71 |
| MBR-NF | Commercially available flat-sheet NF membranes prepared from polyamide thin-film composites | Trace organic contaminants | 90–99 | 72 |

or rejected portion. NFs can effectively remove a wide range of organic wastes, however chlorine disinfection for removal of microbial growth is an important aspect reported in NF distribution systems.[48] Other major factors controlling the efficiency of NF membrane systems are pH and initial concentration of waste substance.[48] Proper selection of membrane material and favourable operating conditions can delay the fouling process. Moreover, high pressure can help in maintaining a steady flux rate, but sometimes cleaning becomes necessary so as to keep the membrane performance optimum. Cleaning is important under the following situations: when permeate flux falls below 10%, when the salt concentration in the permeate increases by 10%, or when the net driving pressure (NDP) increases by 15%.[48] However, cleaning is recommended on a regular basis even before the above conditions arise.[48] Application of NF membranes integrated with an MBR set-up for POP removal from effluents is shown in Table 13.5.

## 13.8 Different Tools for Process Optimization

Wastewater treatment processes on real industrial scales is more complex than simulated conditions on a laboratory-scale. A number of process parameters, configurations, effluent characteristics and operational conditions play a crucial role in large-scale implementation. Sustainable control over the treatment systems requires constant monitoring and stabilization of circumstantial conditions. Interpretation of the relationship between input and output variables using statistical tools have always helped in gaining better control of the overall treatment process. However, due to lack of detailed information on the causes and consequences of pollutant formation, such statistical models might fail to accurately interpret environmental conditions that are instinctively non-linear in nature.[73] Hence, it becomes necessary to conduct a thorough analysis of complex inter-parameter interactions with a large number of experimental attempts in the laboratory prior to field application. Results obtained from these analytical studies can assist in developing a suitable representative models that can help in predicting the various possible outcomes. Best results can be achieved with any process under optimized conditions. Earlier studies have investigated the effect of single parameters on process efficiency because it is expensive to undertake the large number of experiments necessary to explicate the synergistic effects of multiple variables on a process.[74,75]

Various advantages have been gained from soft computing-based approaches to control of real-time process parameters. These advantages are cost effective process optimization, protection of the system from various risks posed by fluctuation in effluent characteristics, rapid measurement of pollutant loads and developing a strategy for providing continuous early-warnings.[76] Recently, soft computing tools like response surface methodology (RSM) and artificial neural network (ANN) have been used to examine process optimization.

### 13.8.1 Response Surface Methodology (RSM)

RSM is mainly used for optimization of various factors through a number of experiments generated by the software (referred to as runs) to achieve a desired result, *e.g.* removal of dye.[34] For process optimization certain ranges of independent variables are used as inputs. On the basis of these inputs, the software then suggests a number of experiments to be performed manually. The results (in terms of the desired output) are entered into the system, from which the software creates a statistically best-fit model for the process concerned. The said model can predict the responses against which the results obtained are plotted in order to determine accuracy of the optimized conditions. This software also gives graphical data on the process concerned. Applying RSM helps to eliminate repetitive analysis with minimum noise. The most suitable model is chosen according to the analysis of variance.[74] Derringer's desirability function is used to approximately calculate the optimum values of independent variables. In this case, the range and maximum of input and output variables, respectively, are applied as goals.[75]

### 13.8.2 Artificial Neural Network (ANN)

ANN, also known as neurocomputing or parallel distributed processing (PDP), is used for simulation and modelling processes where symbolic and algorithmic solutions are not applicable.[34] ANN designs are based on the available knowledge regarding the human nervous systems, although the two are different in almost all aspects. An ANN model consists of processing units distributed in parallel that remain well connected with each other. An ANN model is used to determine whether the outcome of a designed process is in accordance with theoretically predicted results.[34] An ANN model usually consists of input, hidden and output layers.[75] Various functions like "logsig", "poslin", "tansig" "purelin", "satlin" *etc.* are generally chosen as transfer functions for guiding the hidden and output layers. Data obtained through experiments are standardized using algorithms like gradient descent with adaptive learning rate (Traingdx), scaled conjugate gradient (Trainscg), Levenberg–Marquardt (Trainlm), Resilient (Trainrp), *etc.* before process optimization.[75] The algorithm yielding the highest value for the coefficient of determination ($R^2$) is considered to be the best fit to the experimental data.[75]

### 13.8.3 Comparative Analysis of Different Optimization Approaches

Comparative analysis of the efficiency of different processes of optimization may be determined in terms of the following parameters.[75,77]

$$\text{Absolute average deviation (AAD\%)} = \left( \frac{1}{n} \sum_{i=1}^{n} \left( \frac{Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}}{Y_{\mathrm{i,E}}} \right) \right) \times 100 \qquad (13.1)$$

$$\text{Average relative error (ARE)} = \frac{100}{p}\sum_{i=1}^{n}\left(\frac{Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}}{Y_{\mathrm{i,E}}}\right) \tag{13.2}$$

$$\text{Coefficient of determination } (R^2) = 1 - \sum_{i=1}^{n}\left(\frac{\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right)^2}{\left(Y_{\mathrm{i,P}} - Y_{\mathrm{A}}\right)^2}\right) \tag{13.3}$$

$$\text{Hybrid fractional error function (HFEF)} = \frac{100}{n-p}\,\frac{\sum_{i=1}^{n}\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right)^2}{Y_{\mathrm{i,E}}} \tag{13.4}$$

$$\text{Marquart's percentage standard deviation (MPSD)} = 100 \times \sqrt{\frac{1}{n-p}\,\frac{\sum_{i=1}^{n}\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right)^2}{Y_{\mathrm{i,E}}}} \tag{13.5}$$

$$\text{Mean absolute error (MAE)} = \frac{\sum_{i=1}^{n}\left|Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right|}{n} \tag{13.6}$$

$$\text{Pearson's Chi-square measure } (\chi^2) = \sum_{i=1}^{n}\left(\frac{\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right)^2}{Y_{\mathrm{i,E}}}\right) \tag{13.7}$$

$$\text{Root means square error (RSME)} = \sqrt{\frac{\sum_{i=1}^{n}\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right)^2}{n-1}} \tag{13.8}$$

$$\text{Sum of the absolute errors (SAE)} = \sum_{i=1}^{n}\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right) \tag{13.9}$$

$$\text{Sum of the squares of errors (SSE)} = \sum_{i=1}^{n}\left(Y_{\mathrm{i,P}} - Y_{\mathrm{i,E}}\right)^2 \tag{13.10}$$

Here, $n$ denotes the number of data obtained experimentally. $Y_{\mathrm{i,P}}$, $Y_{\mathrm{i,E}}$, and $Y_{\mathrm{A}}$ respectively indicate the response predicted by the selected techniques, the response obtained experimentally and the mean of responses obtained experimentally. $R^2$ is calculated by the least-squares regression.

AAD is relatively a more direct approach for determining the deviation between software predicted and experimentally obtained responses. Values of $R^2$ should be closer to 1 for best fit. Moreover, values of AAD% for any process should be as low as achievable.[75] Moreover, the optimization approach supporting lower values for all other parameters will be considered as the most efficient process of all tested ones.[75]

## 13.9 Determination of the Cost Effectiveness of the MBR Process

MBR treatment of effluents reportedly incurs less cost in comparison to other contemporary processes applied for widescale effluent treatment.[78] Regardless of the fact that MBR system are high-energy operations, very limited or almost no extensive study has been carried out for determining the energy consumption pattern of this process. In the global market, the net worth of MBR systems was estimated to be around $425.7 million in 2014 and was predicted to reach $777.7 million in 2019.[1] The operational cost of an MBR usually exceeds that of the traditional activated sludge process because of the high energy required for aeration provided to decrease membrane fouling in the case of the former (≈60–70% of the overall price).[79]

The total energy needed to treat 1 $m^3$ of the effluent by an MBR system is ≈1 kW $h^1$ while for an RO system the total energy required is roughly between 3 and 4 kW h.[80] However, the cost of energy incurred for operating an MBR is higher that of CASP.[1] In an AnMBR system, the high operating energy requirement can be compensated by biogas recuperation.[81]

The annual cost for operating a conventional water treatment plant with a capacity of 20 851 $m^3$ per day is estimated to be €618 602. However, the annual cost incurred by an activated sludge process with 15 days SRT is estimated to be $241 000.[5] The cost of sludge-based treatment processes is reportedly inversely proportional to the cost incurred for aeration of the set-up.[5] According to a previous study, an AnMBR integrated with a conventional anaerobic reactor requires nearly 0.058 kW h $m^{-3}$ of energy for fluidization of both reactors.[5] This energy requirement can be met with 30% of the methane generated during AnMBR operation.[5]

Almost, a decade ago, membrane prices were comparatively greater than the cost of energy consumed by an AnMBR system.[5] Progress in automation of the process over the years have diminished the cost of labour. In recent times, the price of membrane replacement is estimated to be ≈10–14% of the total cost of the overall operation.[1] Course bubbling aeration for continuous membrane cleaning, better aeration regimes and intermittent bubbling or air cycling are a few useful strategies recommended for reducing the overall operational cost.[5]

## 13.10 Conclusion

POPs have been efficiently removed from different effluents by using MBRs. Integration of this technology with other processes, such as advanced oxidation processes, adsorption, ozonation *etc.*, has reportedly increased the micropollutant removal efficiency of the MBR process. Micro-pollutant removal efficiency of MBRs may also increase with the addition of enzymes. However, application of isolated enzymes may lead to their resistance towards the target pollutants. Moreover, toxic byproducts and metabolites formed from microbial degradation of micro-pollutants also reduces the efficiency of MBR technology. These issues may be mitigated with immobilization of microbial cells or enzymes. Furthermore, process efficiency may be enhanced by coupling the bioreactor with UF or NF modules. NF membranes yield permeates of quality superior to those yielded by UF membranes. However, flux values of NF membranes are lower than those of UF membranes, which makes the latter more popular for widescale real-time effluent treatment. Process optimization discussed herein will also help optimize the efficiency of the MBR process. However, further investigations are required for improving aeration, fouling prevention and cost effectiveness of MBR technology.

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CHAPTER 14

# Anaerobic Membrane Bioreactors for Industrial Wastewater Treatment

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## 14.1 Introduction

The discharge of domestic and industrial wastewater into the environment adversely affects the ecosystem, human health, hygiene, sustainable development and contributes to climate change. Energy recovery from wastewater is one approach to decrease the adverse impact and accomplish more prominent resource recuperation. The most widely recognized method of energy recovery from fermentable and easily degradable compounds is anaerobic digestion, which involves the conversion of organic carbon into biogas in the absence of oxygen. A diverse metabolic group of anaerobes

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[†] Both first and second authors have equal contribution.

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

carry out the sequential decomposition through syntrophic interaction (eqn (14.1)–(14.10)). The external physicochemical conditions selectively determine both the microbial communities and their respective metabolism modes in the bioreactor. The anaerobic membrane bioreactor (AnMBR) has emerged as a promising option in contrast to aerobic wastewater treatment technology. Several types of reactor configuration, including batch, semi-continuous, and continuous mode of operation, have been reported in the literature to treat wastewater. In continuous mode, reactors have also been used in one-stage or multistage and one-phase or multiphase manner. In industrial wastewater of high organic strength, both batch and semi-continuous reactor configurations are commonly practiced. In addition to the above high-rate anaerobic reactors, such as completely stirred tank reactors (CSTR), up-flow anaerobic sludge blanket (UASB), and expanded granular sludge bed (EGSB), hybrid reactors coupled with a membrane module are also recommended for the treatment of industrial wastewaters (Ozgun *et al.* 2013).[21]

Anaerobic methods of wastewater treatment are influenced by various parameters, irrespective of the processes or technology. The primary factors are the physicochemical properties of the membrane, transmembrane pressure, membrane flux, pH, temperature, solids retention time (SRT), hydraulic retention time (HRT), carbon to nitrogen ratio (C/N), mixed liquor suspended solids (MLSS), and organic loading rate (OLR). Several contaminants, including heavy metals, toxic chemicals, and xenobiotics, may have a toxic or inhibitory effect on AnMBR performance. Xenobiotics are synthetically prepared, recalcitrant chemical compounds used in households and industries and include antibiotics, drugs, surfactants, emulsifiers, solvents, personal care products, and household chemicals. These compounds are not easily recognized or metabolized by microbes. Moreover, certain classes of these compounds have been categorically designed to inhibit microbes, such as antibiotics and personal care products.

Anaerobic degradation has been commonly used to treat wastewater sludge, rural compost, and food waste. Wastewater can be viewed as an inexhaustible biogas resource to achieve more sustainable resource recovery and lower energy footprint. Thus, several industries, including food, fermentation, and pharmaceutical industries, have started using the AnMBR technique to treat their high strength wastewater. The steady-state operation of AnMBR is relatively less energy-intensive than that of an aerobic MBR due to the absence of aeration and the utilization of process-generated biogas as a source of energy to achieve a net reduction in energy consumption. This chapter covers the basic understanding and underlying mechanisms of AnMBRs with a particular focus on the current status and recent developments in their design and operation. The chapter also discusses the application of AnMBR to treat several industrial wastewaters and landfill leachate, energy requirements, and the operational costs involved.

## 14.2 Fundamentals of the Anaerobic Degradation Process

The anaerobic digestion process begins with the hydrolysis of the organic materials, followed by acidogenesis, acetogenesis and finally, methane production, *i.e.* methanogenesis (Figure 14.1). Of these four stages, hydrolysis and methanogenesis are considered as the rate-limiting steps due to the relatively slow degradation kinetics of several substances, including inactive microorganisms, slow-growing methanogens, and extracellular polymeric substances. During the first stage of hydrolysis, small water-soluble organic compounds break down to simpler low molecular weight compounds. In contrast, complex high molecular weight organic matter such as proteins, carbohydrates and fats are converted into monosaccharides, fatty acids, and amino acids by unique facultative and/or obligate anaerobic hydrolytic bacteria.[1] Several factors, including temperature, pH, hydrolyzing mass concentration and size/type of particulate organic matter, affect the microbial activity and subsequently control the rate of hydrolysis.[2]

During the second stage of anaerobic digestion (acidogenesis), soluble sugars, amino acids, and fatty acids are converted into short-chain volatile fatty acids, such as formic, butyric, propionic, and acetic acid, alcohols, aldehydes, $H_2$, and $CO_2$. Like hydrolysis, the anaerobic reactor's operational

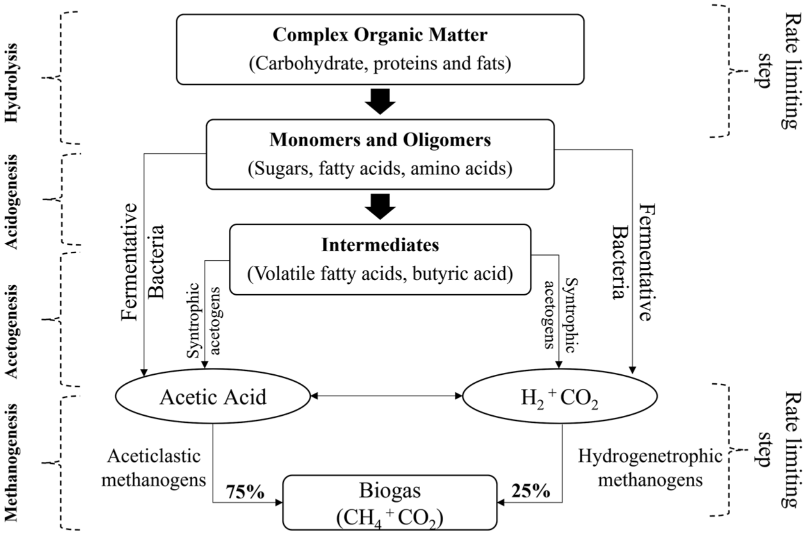

**Figure 14.1** Anaerobic treatment in AnMBRs. Reproduced from ref. 6 with permission from Elsevier, Copyright 2019.

conditions can affect the rate of acidogenesis.[2] Interestingly, the same facultative and/or obligate anaerobes responsible for hydrolysis also participate in acidogenesis. The majority of these acidogenic microbes belonging to the genus *Clostridium*, *Micrococcus*, *Pseudomonas*, and *Flavobacterium* proliferate rapidly under favourable reactor conditions at high pH.[2,3] However, during the long operation period, accumulated volatile fatty acids in the reactor reduce the pH of the system, which further hampers the growth of methanogens.

During the third stage of degradation, acetogenic bacteria such as *Clostridium*, *Acetobacterium*, and *Sporomusa* convert volatile fatty acids, alcohols, and hydrogen into acetate.[3,4] Both obligate $H_2$ producing bacteria, and homoacetogens participate in acetogenesis.[4] While the former group of bacteria oxidizes butyrate, propionate, and long-chain fatty acids to acetate, the latter group utilizes $H_2$ and $CO_2$ to produce acetate. The last step of anaerobic digestion, *i.e.* $CH_4$ production, is achieved in two ways, as highlighted in Figure 14.1. Approximately 70% of methane is produced from acetate by several aceticlastic methanogens such as *Methanosarcina* and *Methanosaeta*.[4] In another pathway, hydrogenotrophic methanogens convert carbon dioxide and hydrogen into methane.[3] The $CH_4$ production rate is mainly controlled by the population and diversity of archaea, the concentration of degradable or non-degradable substrate, and other toxic compounds.[5]

## 14.3 Stoichiometry of Anaerobic Biodegradation

Anaerobic digestion takes place in the absence of oxygen at oxidation reduction potential (ORP) between −100 and −400. The anaerobic digestion of glucose to $CH_4$ and $CO_2$ has a relatively lower free energy change ($\Delta G^{\circ\prime}$ −390 kJ mol$^{-1}$) in comparison to the aerobic decomposition of glucose ($\Delta G^{\circ\prime}$ −2870 kJ mol$^{-1}$), primarily due to the conservation of energy in the product in the form of $CH_4$ (eqn (14.1)). Overall the stoichiometry of anaerobic digestion suggests that 1 unit of carbon upon anaerobic digestion yields 0.95 units of carbon in the form of biogas ($CO_2$ + $CH_4$) and 0.05 units of carbon as microbial biomass.[7] Similarly, based on the stoichiometry calculations, 1 kg of chemical oxygen demand (COD) from wastewater generates 0.1 kg of microorganism, 0.42 kg of $CH_4$ (0.628 m$^3$ at NTP), 0.442 kg of $CO_2$ (0.239 m$^3$ at normal temperature and pressure (NTP)), 0.086 kg of $NH^{4+}$, and 0.292 kg of $HCO_3^-$ (eqn (14.2)).[8]

$$C_6H_{12}O_6\ (\text{glucose}) \rightarrow 3CH_4 + 3CO_2\ (\Delta G^{\circ\prime}\ {-390}\ \text{kJ mol}^{-1}) \tag{14.1}$$

$$\begin{gathered}0.025C_8H_{17}O_3N\ (\text{wastewater}) + 0.084H_2O \rightarrow 0.004C_5H_7O_2N \\ (\text{microorganism}) + 0.115CH_4 + 0.044CO_2 + 0.021\ NH_4 + 0.021\ HCO_3^-\end{gathered} \tag{14.2}$$

The anaerobic digestion process sequentially decomposes fermentable macromolecules to volatile fatty acids (VFAs) such as valerate, iso-valerate, butyrate, iso-butyrate, propionate, iso-propionate, acetate, and formate (eqn (14.3)). Subsequently, VFAs are mineralized to gases such as $CO_2$, $H_2$, $H_2S$, $NH_3$, $CH_4$, NO*x*, and $H_2O$ (eqn (14.4)–(14.6)). Besides, various subsidiary reactions are known to occur, such as proteolysis for the degradation of proteins, alpha, and beta fatty acids. The following chemical reactions adapted from ref. 9 provides insight into the intermediary steps of anaerobic digestion.

$$\begin{gathered}C_6H_{12}O_6 + 2H_2O \rightarrow 0.7CH_3CH_2CH_2COO^- \text{ (butyrate)} + \\ 0.6\ CH_3COO^- \text{ (acetate)} + 1.3H^+ + 2CO_2 + 2.6H_2\ (\Delta G^{\circ\prime} -233\text{ kJ mol}^{-1})\end{gathered} \tag{14.3}$$

$$\begin{gathered}CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + 2H^+ + \\ 2H_2\ (\Delta G^{\circ\prime} + 48.3\text{ kJ mol}^{-1})\end{gathered} \tag{14.4}$$

$$\begin{gathered}CH_3CH_2COO^- \text{ (propionate)} + 2H_2O \rightarrow 3CH_3COO^- + \\ CO_2 + 3H_2\ (\Delta G^{\circ\prime} +76\text{ kJ mol}^{-1})\end{gathered} \tag{14.5}$$

$$\begin{gathered}CH_3CH(NH_3^+)COO^- + 2H_2O \rightarrow CH_3COO^- + NH_4^+ + CO_2 + \\ 2H_2\ (\Delta G^{\circ\prime} +2.7\text{ kJ mol}^{-1})\end{gathered} \tag{14.6}$$

$$4H_2 + 2CO_2 \rightarrow CH_3COO^- + H^+ + 2H_2O\ (\Delta G^{\circ\prime} -94.9\text{ kJ mol}^{-1}) \tag{14.7}$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O\ (\Delta G^{\circ\prime} -131\text{ kJ mol}^{-1}) \tag{14.8}$$

$$H_2 + S^\circ \rightarrow H_2S\ (\Delta G^{\circ\prime} -33.9\text{ kJ mol}^{-1}) \tag{14.9}$$

$$\begin{gathered}CH_3(CH_2)nCOOH + 2H_2O \rightarrow CH_3(CH_2)n - \\ 2COOH + CH_3COOH + 2H_2\end{gathered} \tag{14.10}$$

## 14.4 Classification and Membrane Configuration

Based on the membrane module's position in an anaerobic reactor, a hybrid system can be described as side-stream, submerged, or externally submerged. As shown in Figure 14.2A, the membrane module is present outside of the reactor in a side-stream configuration. A recirculation pump withdraws the MLSS from the bioreactor and subsequently forces it through an external membrane module at high pressure, cross-flow velocities to generate the permeate.[10] The retentate is returned to the bioreactor. Although the ease of handling and cleaning the membrane module is relatively easy compared to other configurations, maintaining transmembrane pressure (TMP) and elevated volumetric flow at the cost of high energy consumption brings an

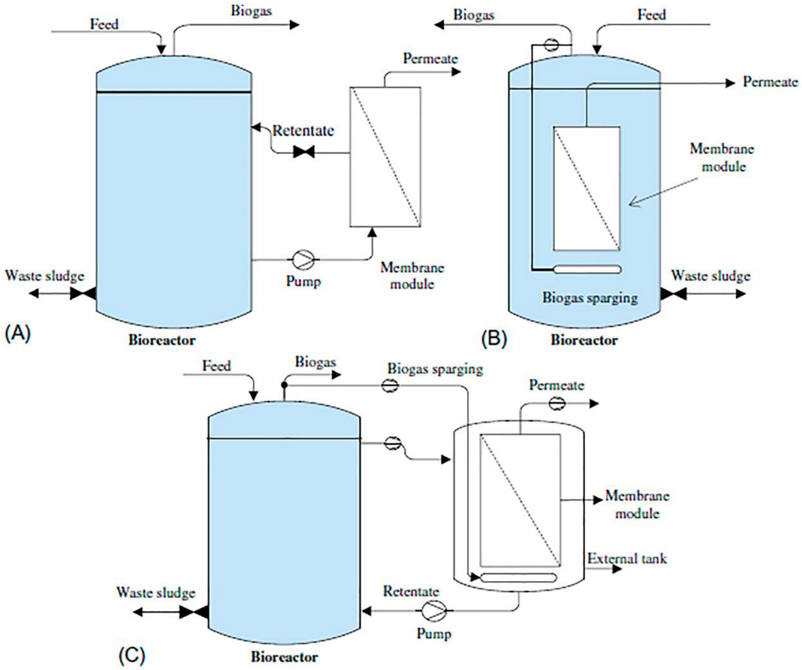

**Figure 14.2** Different configuration of AnMBRs: (A) side-stream configuration, (B) submerged configuration, and (C) submerged configuration (in a separate external tank). Reproduced from ref. 18 with permission from Elsevier, Copyright 2020.

economic burden.[6] High hydraulic shear force induced by the tangential flow reduces cake layer formation on the surface of the membrane, but it may further damage the aggregated anaerobic microbes into small sizes resulting in membrane fouling.[11] However, without disturbing the microbial community, the membrane can be easily replaced.

In the submerged AnMBR, the membrane module is immersed in the anaerobic bioreactor, as shown in Figure 14.2B. In this configuration, treated water/permeate is obtained either under vacuum or *via* gravity. The suspended biomass is retained in the bioreactor. Both cross-flow velocity and TMP are relatively low. This configuration is commonly used to treat low-strength wastewater, such as sewage.[12,13] The process-generated biogas (*i.e.* $CH_4 + CO_2$) is compressed and sparged below the membranes carrying the liquid upward, resulting in simultaneous cross-flow scouring across the membranes and mixing/homogenization.[6] The generated biogas further mitigates cake formation. In the third category, called externally submerged, the membrane is submerged in a tank placed outside the bioreactor, and a pump is used to return the retentate to the bioreactor (Figure 14.2C).[14] Unlike the previous configuration, the membrane in the external submerged configuration is operated under vacuum.[6]

As different groups of microorganisms grow under the different optimized conditions of temperature and pH at different stages of anaerobic degradation, several researchers have proposed two-stage AnMBR. In such a reactor configuration, acidogenesis and methanogenesis are carried out in an acidogenic and methanogenic reactor, respectively, such that both temperature and pH can be optimized separately in two different reactors for each consortium of microorganisms.[2] While hydrolytic bacteria work best in the pH range 4.5–6.5, acetogenic and methanogenic bacteria operate best at pH ranging from 6.5 to 7.0.[15] Similarly, the optimum temperature range for mesophilic digestion ranges between 30 and 40 °C, and for thermophilic digestion, it varies between 55 and 60 °C. Thus mesophilic bacteria may not survive at temperatures beyond 40 °C, but thermophilic bacteria work efficiently at temperatures beyond 50 °C.[6]

An AnMBR system can be designed by integrating suspended growth, biofilm, or granular sludge processes with a membrane separation unit. Anaerobic microorganism remain suspended in the wastewater in an anaerobic suspended growth system either in a CSTR or plug-flow reactor (PFR). Thus, integrating CSTR or PFR in the presence of a membrane separation unit leads to the design of integrated CSTR-AnMBR or PFR-AnMBR systems.[6] Here, a recirculation pump is used to recycle anaerobic sludge from the filtration zone to the CSTR and PFR bioreactor. However, biofilm systems have been reported to increase anaerobic digestion productivity.[16,17] Although plastic and clay pellets are commonly used for biofilm growth, increased biomass concentration with increased volumetric biological productivity is one of the significant advantages of other systems.[6] In the biofilm-AnMBR system, biomass effectively gets immobilized on packing material, resulting in reduced suspended biomass concentration in the membrane filtration zone. Thus, membrane fouling is significantly reduced and the performance of the membrane filtration is increased substantially. However, full-scale applications of such an integrated system are still scarce.

Much research has been conducted to test the suitability of granular sludge systems such as an UASB and EGSB for anaerobic wastewater treatment.[6] Such a system operates at increased and reduced biomass level in the bioreactor and filtration zone, respectively. The system's overall performance is improved by the excellent settling properties of the large size of granular sludge. Like other integrated AnMBR systems, a recirculation pump is used to recycle biomass from the membrane filtration zone back to the bioreactor zone.[2,19–21] Although laboratory-scale and pilot-scale applications of such configuration exist, full-scale application of these configurations is yet to be reported.

As mentioned earlier, several biomass types, including suspended growth, granular sludge, and bioreactors such as CSTR, PFR, UASB, EGSB, and biofilm reactors have been used to treat a variety of wastewater anaerobically. However, the success behind the right integration between the biofilm and the reactor mainly depends on the wastewater's strength. While a CSTR-AnMBR or PFR-AnMBR system is primarily suitable to treat low-strength wastewater, UASB-AnMBR, EGSB-AnMBR, and biofilm-AnMBR configurations are mainly used to treat wastewater of elevated concentration. Similarly, CSTR-AnMBRs and PFR-AnMBRs are easier to operate than AnMBR-UASB and AnMBR-EGSB systems, whose operational efficiency depends on the formation of granular sludge under environmental conditions. Although biofilm systems have several advantages, biofilm sloughing and biofilm overgrowth may block the flow of wastewater, resulting in operational failure.

## 14.5 Operational Considerations

### 14.5.1 Physico-chemical Properties of the Membrane

Membrane filters are primarily manufactured from three materials, namely polymeric, ceramic and metallic. Polymeric materials have been the common choice for most membrane manufacturing, accounting for nearly 75% of the total market. They are preferred due to the relatively lower costs, high packing density, and ability to mould into various shapes such as hollow fibre, flat sheet (plate or frame), and tubular. Various polymeric materials employed for the manufacture of membranes are polyvinylidene difluoride (PVDF), polyethersulfone (PES), polyethylene (PE), polypropylene (PP), polysulfone (PSF), polyethylene terephthalate (PET), chlorinated polyethylene (CPE), and uncoated polyetherimide (PEI).[22] The pore sizes of the membranes range between 0.018 and 1.0 μm. Of these, PVDF has been the most widely used material. The hollow-fibre membrane module is preferred due to having the highest packing density, and relatively lower capital cost, and pumping and dead volume, compared to flat-sheet and tubular membrane modules. On the other hand, flat-sheet and tubular membrane modules exhibit high physical and chemical stability at a lower rate of fouling, are amenable under higher viscosity of wastewater and MLSS, operationally easy to clean, and can have defective membranes replaced. However, compared to ceramic and metallic membranes, polymeric membranes exhibit the lowest permeability and structural vulnerability towards long-term, periodic physical and chemical cleaning.[21,23] Ceramic membranes are primarily made up of aluminum oxide/alumina ($Al_2O_3$) with pore size ranging from 0.05 to 0.5 μm, whereas metallic membranes are manufactured in 300–400 series stainless steel (SS) and Hastelloy-X.[24] They both exhibit relatively higher stability towards physical and chemical cleaning; structural stability at higher temperatures such as mesophilic and thermophilic conditions; resistance to corrosion, abrasion, and oxidation; relative ease to clean and backwash; higher hydraulic conductivity; easy recovery of permeability after cleaning of fouled membranes; and 10 times higher filtration flux (200–250 L $m^{-2}$ $h^{-1}$) (ceramic filters) in comparison to polymeric membrane filters. However, ceramic and metallic membranes are more expensive than polymeric membranes, limiting their installation and wastewater treatment applications.[20,23]

### 14.5.2 Transmembrane Pressure (TMP)

TMP is a key indicator for assessing the permeate flux (PF) as at low TMPs, the PF varies directly with the TMP but is independent at high TMP. Hence, the activity of the AnMBRs under threshold flux could be an ideal approach to control membrane fouling, particularly removable and irreversible fouling, because it applies less TMP, decreasing the cycles of chemical washing and subsequently membrane substitution.[18] When the MP surpasses the threshold flux level, a further increase of TMP is needed to compensate for the gradually formed cake layer's pressure drop. High TMP builds energy utilization and the recurrence of membrane cleaning or substitution. Although the threshold TMP for the critical flux is reported to vary between 80 and 260 kPa, its value for an AnMBR with a side-stream membrane typically ranges from 207 to 690 kPa.[14,21,25] With an increase in TMP, a decrease in cross-flow velocity is also reported, indicating the cake layer's growth on the membrane surface.[25]

### 14.5.3 Membrane Flux

Like TMP, membrane flux (MF) is a critical design parameter which governs the membrane capital cost, fouling rate and cleaning frequency. However, MF depends on the liquid viscosity and total resistance offered by the cake; as per Darcy's law, MF varies directly with TMP. Based on reported studies, several parameters, including membrane properties, sample properties, operating conditions (*i.e.* biogas sparging intensity, temperature), and process configuration, can affect PF value.[25] Many studies have suggested that thermophilic AnMBRs can sustain a higher PF than mesophilic AnMBRs due to low water viscosity under thermophilic conditions.[26] A similar observation was also reported under thermophilic conditions, possibly related to the formation of more biopolymer clusters at a high soluble microbial product (SMP) level.[27] Additionally, porous and more compact cake layers under thermophilic conditions are also reported in the literature. When side-stream AnMBRs were compared with submerged AnMBRs, a greater membrane permeation was reported for the former reactor, and the fluxes for submerged AnMBRs for different wastewaters ranged between 5 and 30 L $m^{-2}$ $h^{-1}$.[28] In general, AnMBRs are operated at low or critical permeable membrane fluxes, resulting in low membrane fouling and minimum energy expenditure. The effect of membrane pore sizes on permeate flux has also been correlated to the particle size of the wastewater in the literature. Generally, in the beginning, if high filtration MF is observed for membranes with large pore size, such membranes are more susceptible to membrane fouling due to internal pore blockage.[10,29] Wastewater characteristics further alter the MF by altering the membrane surface charge due to the adsorption of ions and charged particles present in the wastewater.[30] An average membrane flux of 10–14 L $m^{-2}$ $h^{-1}$ can be adopted as a standard design criterion for AnMBR plants, albeit an appropriate MF ought to be acquired from pilot-scale testing for specific wastewater.[31]

### 14.5.4 Membrane Configuration

The location of the membranes in the anaerobic bioreactors determines the rates of membrane fouling. The membranes are mounted and operated in three main configurations that are as follows. (1) External cross-flow. The membrane is positioned outside the bioreactor. The mixed liquor is withdrawn from the bioreactor and pumped at high pressure across the membrane surface to generate the permeate, whereas the retentate is returned to the bioreactor. Filtration is carried out at a high cross-flow velocity and TMP ranging from 1–5 m $s^{-1}$ and 207–690 kPa (30–100 psi), respectively. Moreover, the higher cross-flow velocity scours the membrane surface to prevent fouling.[22,23] (2) Internal vacuum. The membranes are submerged in a bioreactor and driven by a vacuum to generate the permeate. The membranes are operated at a relatively lower cross-flow velocity and TMP in the range of 0.6 m $s^{-1}$ and 21–103 kPa (3–15 psi), respectively. The membrane fouling is controlled with the help of biogas sparging, backflushing with permeate, membrane relaxation, and surface scouring with activated carbon and biogas. (3) External submerged. The submerged membrane is placed in a chamber outside the bioreactor and filtration is carried out under a vacuum. The mixed liquor is withdrawn from the bioreactor and pumped to the external chamber. Vacuum filtration generates permeate and the retentate is returned to the bioreactor. In an externally placed membrane configuration, the cleaning of membranes and replacement can be carried out without interfering with the bioreactor's treatment processes.[22,23]

### 14.5.5 Membrane Cleaning

The primary factor affecting the long-term, steady-state operation of an AnMBR is membrane fouling occurring under various biochemical conditions. As discussed before, fouling leads to a simultaneous increase in membrane resistance and reduced membrane flux. The fact remains that membranes cannot be operated eternally and need to be replaced after a certain period of operation depending on the intensity and irreversible nature of the fouling. Moreover, membranes account for between 46.4 and 72.3% of the total capital costs of a full-scale AnMBR;[20] therefore periodic replacement of membranes could result in higher capital costs, and downtime/intermission in wastewater treatment. Hence, periodic cleaning of membranes by physical and chemical methods is often administered to reduce their clogging propensity, simultaneously prolonging the usable lifespan of membranes. Fouling takes place both on the membrane surfaces and membrane pores. However, surface fouling is relatively easier to remove than pore fouling. The removal of fouling is accomplished by two main methods, termed physical cleaning and chemical cleaning. Cleaning is performed both online and offline. An online cleaning step is included within the treatment cycles without interruption and halting of bioreactor operations. On the other hand, an offline treatment step requires discontinuation/halting of the bioreactor operation followed by manual inspection and cleaning. The physical membrane cleaning methods are as follows: backwashing with permeate and clean water, backwashing with the injection of compressed biogas, surface scouring of membranes with biogas, ultrasonication, manual scrubbing of the membrane surface, and surface scrubbing with fluidized granular carbon. The factors controlling effective backwashing of membranes are intensity/rate of backwashing, frequency of backwash, and period of backwash. Backwashing for a longer period is considered more effective than high-frequency, short-period backwashing. Ultrasonic membrane cleaning methods generate high-frequency oscillations usually in the range 20–500 kHz frequency resulting in cavitation on the interface of membranes, foulant, and water, dislodging the physical structure of the fouling layer. They are relatively more effective in cleaning membrane surfaces rather than the pores of the membrane. The optimum power requirement for ultrasonic membrane cleaning is 0.18 W $cm^{-2}$ for a duration of 3 min $h^{-1}$.[32]

A wide range of chemicals is employed for the cleaning of membranes such as alkali (NaOH); acids ($HNO_3$, citric acid, HCl, $H_2SO_4$); oxidizing agents (NaOCl, $H_2O_2$, ozone); chelating agents (EDTA); surfactants (sodium dodecyl benzene sulphonate (SDBS), polyethylene-oxide, Tween 20); ammonium hydrogen fluoride, *etc.* Alkali is targeted towards the solubilization and/or disintegration of organic matter present in biofilms, extracellular polymeric substances (EPS), and SMP, while acids target the hydrophobic organic compounds and break metal-associated structures including metal–organic foulant complexation and inorganic scales. Oxidizing agents increase the hydrophilicity of polymeric organic contaminants, destroy the cell wall structure, and ultimately kill the microbes. On the other hand, surfactants reduce the hydrophobicity between foulants and chemicals, simultaneously increasing the contact and efficacy of chemicals, and the solubilization of proteins in the foulant, and destroying the microbes biofilm structure. EDTA disrupts biofilm/slime structure by chelating with various metal ions and salts.[33,34] Various factors considered in the chemical washing of membranes include the concentration of chemicals, chemical solubility and efficacy of chemicals at various temperatures, frequency and period of chemical cleaning, reaction/contact time of the chemicals with foulant, resistance of the foulant to the chemicals, deleterious effects of the chemicals on the microbes inhabiting the bioreactor, adverse effects of chemicals on the physical structure and integrity of the membranes, and secondary fouling induced by the residual chemicals.[34,35]

### 14.5.6 EPS, SMP, Biofilm Layer

An AnMBR offers longer SRT than conventional anaerobic digesters by preventing sludge washout during start-up and operation. Higher SRT in the bioreactor results in a higher concentration of mixed liquor volatile suspended solids (MLVSS), macromolecular matter, colloids, SMP, EPS, humic substances, and viscosity. The concentration of SMP and EPS in the bioreactor has been reported to exhibit a higher membrane fouling rate. It causes membrane pore blocking by gel formation and seeps into pores and spaces of the cake layer. A higher SRT and MLVSS enhances biofilm formation on the membrane surface, also called a filter cake. The filter cake is a porous biofilm layer that contains 1.5-times higher EPS than the bulk. It is a complex network consisting of microbes, SMP, EPS, humic substances, water, lipids, inorganic compounds such as magnesium struvite ($MgNH_4PO_4{\cdot}6H_2O$), potassium struvite ($MgKPO_4{\cdot}6H_2O$), and calcium carbonate ($CaCO_3$).[14] The filtration resistances exhibited by a relatively thicker filter cake and thinner biofilm were reported to be $308 \times 10^{11}$ and $32.5 \times 10^{11}$ $m^{-1}$, respectively.[36] The gradual growth of filter cake leads to increased filtration resistance and a simultaneous reduction in the filtration flux. These problems are often encountered in the treatment of high-strength wastewater. Higher organic loads require higher MLVSS to maintain a lower substrate/inoculum (S/I) ratio, eventually leading to high MLVSS in the bioreactor. An AnMBR is primarily operated at OLR <5 kg COD per $m^3$ per day. An AnMBR operated at a relatively lower permeate flux closer to the critical value leads to the initial formation of the loose filter cake that could be easily dislodged by backwashing. However, the maturation of the filter cake leads to a simultaneous rise in the thickness of the filter cake, a surge in transmembrane pressure, an increase in the filtration resistance, and a reduction in permeate flux. In these conditions, dislodging the filter cake from the membrane surfaces is difficult and demands backwashing with chemicals. In contrast, permeate flux higher than the critical value leads to increased cake layer formation.[10]

### 14.5.7 Salinity

High salinity creates instability in microbial community diversity and leads to community migration towards halotolerant microbes, affecting the treatment quality. For instance, an increase in $Na^+$ concentration from 14 to 20 g $L^{-1}$ led to a reduction in specific methanogenic activity by 24%. Disaggregation of biomass flocs resulted in a 10-fold reduction in biomass particle size from 185 to 16 μm and a simultaneous increase in transmembrane pressure to ≈350 bar. The biomass disaggregation also led to a rise in the concentration of proteins in SMP, which is known to enhance membrane fouling and filter cake formation, and has an irreversible effect on membrane filtration.[37,38]

### 14.5.8 pH

pH is another important parameter that can significantly influence microbial growth and community structure, thus influencing anaerobic digestion. The optimum pH for anaerobic digestion is 6.8–7.2, although anaerobic digestion has been reported to prevail between pH 5 and 8.5. pH <6.8 enhances the accumulation of VFAs, whereas pH >8 causes microbial inhibition due to the volatilization of ammonia and sulfide inhibition. The optimal pH values for acetogens/acidogens and methanogens are 5.5–7.2 and 6.8–7.8, respectively.[2] As the pH range for the methanogens is very narrow, AnMBRs are commonly operated at neutral pH to favour the microbial community. However, acetotrophic methanogens operate at their optimum level when the system pH is maintained at 6.2. When the pH value reaches beyond 7.4, free ammonia hampers acetoclastic methanogens' activity, leading to reactor malfunction.[39] In general, the buffer capacity of AnMBRs is maintained by $CO_2$ and ammonia in the gas and liquid phase, respectively, which is a function of wastewater strength. Increased $CO_2$ concentrations beyond the reactor's buffering capacity can lower the pH, leading to acidification. Similarly, increased ammonia concentration can accumulate acetate and propionate and decrease the pH.[40] Thus, it is important to opt for two-phase AnMBRs where pH can be optimized separately for both acidogenesis and methanogenesis by adding a base such as sodium hydroxide to the influent stream.

### 14.5.9 Temperature

Anaerobic methods of wastewater treatment have been reported at a wide range of temperatures, *i.e.* psychrophilic (−20 to 20 °C), mesophilic (20–45 °C), and thermophilic (45–80 °C). However, mesophilic conditions, ideally at 35 ± 2 °C, is the preferred range of temperature as it provides the optimum balance between the rate of metabolism and operational costs. Nevertheless, most bioreactors are operated at room temperature (25 ± 2 °C) to reduce operating costs and complexities in the heating of bioreactors.[41] Psychrophilic conditions lead to a reduction in microbial activity and an increase in wastewater viscosity. On the other hand, thermophilic conditions cause microbial inhibition due to the volatilization of ammonia. An increase in temperature by 1 °C has been reported to increase the flux by 2%, attributed to the reduction in viscosity due to the increase in temperature. As a result, the flux increases in the following order of bioreactor operation/conditions, namely, psychrophilic > mesophilic > thermophilic.[14]

### 14.5.10 Solids Retention Time (SRT) and Hydraulic Retention Time (HRT)

SRT determines the overall biodegradation kinetics and MLSS concentration of an AnMBR. Thus, it is also the deciding factor for membrane performance and its fouling. Although the SRT of an AnMBR is much higher than that of aerobic MBRs due to low sludge yield, the SRT of AnMBR was reported to vary between 19 and 680 days and 28–300 days for domestic and industrial wastewater, respectively.[42]

HRT is defined as the average residence time spent by the wastewater in a reactor. This operating parameter, in general, determines the system performance, which is also a function of temperature. The HRT of an AnMBR is reported to be relatively more extended than that of a typical aerobic reactor, and the value can go beyond 8 h.[14] Some studies have also reported SRT in the range of 10–20 days. In general, the HRT of an AnMBR ranges from 0.2 to 7 and 0.67 to 18 days for municipal and industrial wastewater treatment, respectively.[42] Both SRT and HRT can affect the membrane fouling, as EPS and SMP production and the concentration of MLSS are functions of

SRT and HRT. Thus, both parameters must be optimized in pilot-scale for individual wastewaters in varying operating conditions before field-scale application.

### 14.5.11 Carbon to Nitrogen Ratio (C/N) and MLSS

It is crucial to maintain optimum C/N to maximize microbial activity and avoid nutrient limitation or ammonia toxicity. At low C/N, wastewater is likely to produce high VFAs and total ammonia nitrogen at high pH (8.5), which can inhibit methanogenic activity.[43,44] This ratio is also reported to affect the performance of mesophilic and thermophilic digestion processes. Low C/N further reduces nutrient removal efficiency and increases membrane fouling.[45] At a high C/N ratio, several researchers have reported increased concentrations of EPS, polysaccharides, and protein[46,47]. The optimal C/N ratios for anaerobic digestion range from ≈20 : 1 to 30 : 1. Another critical parameter characterized by a mixture of biologically active solids is MLSS. Theoretically, no maximal concentration of MLSS for an AnMBR has been defined yet. However, for long-term operation, MLSS ranges from 10 and 15 g $L^{-1}$.[48] The typical range of MLSS for municipal and industrial wastewater ranges from 1–26 and 6–30 g $L^{-1}$, respectively.[42]

### 14.5.12 Organic Loading Rate (OLR)

Anaerobic digestion (AD) has been reported to handle wide ranges of OLRs ranging from 200 mg per L per day to 100 g per L per day, ideally operated between 1 and 30 g per L per day. AD is a multi-step, syntrophic process carried out by a metabolically diverse group of microbes with different growth rates. The entire process efficiently moves forward at a rate determined by the slowest metabolizing microbes, also called the rate-limiting step. In AD, the syntrophic reactions (*e.g.* conversion of butyrate and propionate into acetate) carried out by syntrophomonas, and methanogenesis (*e.g.* the conversion of acetate to $CH_4$ and $CO_2$) carried out by aceticlastic methanogens, are considered rate-limiting reactions due to their relatively lower metabolic rates and doubling times between 10–90 h, respectively. A sudden increase in OLR, especially at the higher OLR >1 g per L per day, leads to the overproduction of VFAs by the first set of organisms due to proportionately higher metabolizing capabilities. However, the conversion of butyrate/propionate to acetate and acetate to methane proceeds at a relatively slower rate than their production, creating an imbalance and accumulation of VFAs. Accumulation of VFAs leads to low pH (<6) in the bioreactor, resulting in microbe inhibition, foul odour, rancidity, halted processes, and residual wastewater pollutants.

### 14.5.13 Inhibition and Toxic Effect

The inhibition mechanism varies depending on the compounds; however, some of the common modes start with adsorption of xenobiotics to cell membranes, impairing substrate and metabolite transportation. Subsequently, agglomeration of cells, inhibition of proteins, lipids, cell wall, and nucleic acid synthesis results in complete inhibition. The xenobiotics exhibit a relatively higher inhibition of syntrophomonas and methanogens than the other group of microbes, resulting in a simultaneous reduction in $CH_4$ production and accumulation of VFAs. Various antibiotics such as doxycycline, tylosin, streptomycin, and neomycin inhibited the metabolic activities of propionic and butyric acid degrading bacteria, respectively, whereas chlortetracycline and chloramphenicol inhibited acetoclastic.[18] Similarly, thiamphenicol, amoxicillin, oxytetracycline and erythromycin, propranolol, clofibric acid, and sulfamethoxazole inhibited methanogenesis at concentrations >80, 60, 250, 30, 400, 300 mg $L^{-1}$, respectively. Other compounds such as surfactants and industrial chemicals invariably exhibit antimicrobial properties at higher concentrations. For example, linear alkylbenzene sulfonate (LAS), quaternary ammonium compounds (QAC) are commonly used surfactants in detergents that exhibit inhibition of anaerobic microbes at concentrations of 5 g LAS per kg of dry sludge and 25 mg $L^{-1}$, respectively.[49]

Anaerobic reactors are known to inhibit sulfate-reducing bacteria (SRB) that convert sulfate into sulfides. In aqueous media, the sulfide exists both in gaseous ($H_2S$) and dissolved states ($S^2$). A higher concentration of sulfides (*i.e.* COD/sulfate ratio <10) leads to corrosion of metal components and foul odour. Besides, sulfides exhibit a relatively higher inhibition of methanogens by interfering with the assimilatory metabolism of sulfur, altering the intracellular pH and scavenging acetates. The sulfides-related inhibition is accentuated at pH >7.8 and a sulfide concentration of 90 mg $L^{-1}$.[50,51]

Nitrogen is an essential component of cell mass, commonly present in wastewater as proteins, amino acids, unionized ammonia ($NH_3$), and ammonium ion ($NH_4^+$).[52] On the other hand, anaerobic digestion can only convert proteins and amino acids into $NH_3$ and $NH_4^+$. In an aqueous medium, $NH_3$ and $NH_4^+$ exist in an ionic equilibrium, governed by primary factors such as temperature and pH. Higher temperatures >45 °C and pH >8 shift the equilibrium towards the formation of $NH_3$, which is considered to be relatively more toxic than $NH_4^+$. Total ammonia ($NH_3 + NH_4^+$) concentration >1700 mg $L^{-1}$ has been reported to induce failures in anaerobic digesters.[52]

Fat, oil, and grease (FOG) primarily refer to the long-chain fatty acids (LCFA) comprising hydrocarbon chain length >8. Lower concentrations (*e.g.* ≤1000 mg COD-LCFA $g^{-1}$ $VSS^{-1}$) of LCFA can undergo mineralization in anaerobic reactors through beta oxidation pathways. However, higher concentrations of LCFA create process failures due to sludge floatation and washout; foaming; encapsulation of microbes creating a barrier to the transportation of substrates, gases, and metabolites; and the inability of the microbes to regulate the intracellular pH.[53,54]

## 14.6 Application of AnMBRs

The following section describes the application of an AnMBR for the treatment of municipal and industrial wastewater. The information has also been reported concisely in Table 14.1.

**Table 14.1** Treatment of municipal and industrial wastewater using an AnMBR.

| Bioreactor configuration | Wastewater | Scale | Membrane material | Pore size and surface area | Flux and TMP | Fouling control | Reference |
|---|---|---|---|---|---|---|---|
| Anaerobic reactor + cross-flow flat plate membrane separation unit | Food industry wastewater | 500 L | Polyether sulfonate | 20 000–70 000 kDA and 0.32 $m^2$ | 13.1–18.9 L $m^{-2}$ $h^{-1}$, 0.2 MPa | 0.5% NaOH (1 h in 10 days interval) | 55 |
| Anaerobic CSTR + cross-flow tubular UF membrane module | Concentrated whey permeate | 10 L | Polyvinylidene fluoride (PVDF) | 0.03 μm and 0.0114 $m^2$ | 8–11 L $m^{-2}$ $h^{-1}$, <350 mbar | Permeate backwash (16–22 L $m^{-2}$ $h^{-1}$), NaOCl (550 ppm, 2–4 h), citric acid (1% w/v, 2–4 h). | 56 |
| Anaerobic CSTR + submerged hollow fibre module | Brewery wastewater | 15 L | Polyvinylidene fluoride (PVDF) | 0.04 μm and 0.047 $m^2$ | 8 L $m^{-2}$ $h^{-1}$, <8.6 kPa | Biogas recirculation at 15.3 $m^3$ $h^{-1}$ $m^{-2}$, Citric acid (20 g $L^{-1}$, 15 min) followed by NaOCl (2 g L; 15 min) and water | 58 |
| Anaerobic CSTR + external flat-sheet UF membrane | Ethanol still stillage | 12 000 L | Polyvinylidene fluoride (PVDF) | 0.08 μm and 18 $m^2$ | 4.3 L $m^{-2}$ $h^{-1}$, 0.1–0.2 bar | Biogas and permeate recirculation (47–65 $m^3$ $m^{-2}$ $h^{-1}$ and 11–47 m $h^{-1}$), chemical cleaning at 100 days with NaOCl, HCl | 60 |
| UASB + CSTR + MF hollow fibre unit | Sugarcane vinasse | 15 L | Polyetherimide | 0.45 μm and 0.045 $m^2$ | 4.4 L $m^{-2}$ $h^{-1}$, <0.5 bar | Flushing membrane surface with water, chemical cleaning with NaOCl (500 ppm): 20 min, citric acid: 20 min | 59 |
| CSTR + tubular UF | Swine manure | 6 L | Polyethersulfone | 20 kDa and 0.038 $m^2$ | 5–10 L $m^{-2}$ $h^{-1}$, 0.7–0.2 bar | High cross-flow velocity, chemical cleaning with 0.5% EDTA combined with 1% $Na_3PO_4$ or 0.1 M $HNO_3$ (pH 2) for 1 h. | 57 |
| Anaerobic reactor + external cross-flow membrane unit. | Pharmaceutical and chemical industry | 50 L | Ceramic | 50 kDa and 0.25 $m^2$ | 8.4 L $m^{-2}$ $h^{-1}$, 0.7–0.2 bar | Cross-flow velocity (3 m $s^{-1}$). No physical or chemical cleaning | 61 |

(*continued*)

**Table 14.1** (*continued*)

| Bioreactor configuration | Wastewater | Scale | Membrane material | Pore size and surface area | Flux and TMP | Fouling control | Reference |
|---|---|---|---|---|---|---|---|
| UASB + external cross-flow membrane | Pharmaceutical wastewater | 180 L | Polyvinylidene fluoride (PVDF) | 0.02 µm and 1 $m^2$ | 20 L $m^{-2}$ $h^{-1}$, 40–60 kPa | Chemical cleaning by soaking membranes in NaOCl (0.5% and 12 h) | 62 |
| Jet flow anaerobic bioreactor + UF membrane | Domestic wastewater | 50 L | NA | 100 kDa and 1 $m^2$ | 3.5–12 L $m^{-2}$ $h^{-1}$, 1–2 bar | NA | 64 |
| AnMBR with submerged flat-sheet MF membrane | Domestic and simulated wastewater | 5 L | Polyethersulfone | 0.2 µm and 0.0387 $m^2$ | >3.5 L $m^{-2}$ $h^{-1}$, 10 kPa | Biogas recirculation at 4.67 L $min^{-1}$, Permeate backflushing. | 19 |
| Submerged anaerobic with hollow fibre | Synthetic wastewater | 3 L | Mitsubishi Rayon | 0.4 µm and 1 $m^2$ | 15 L $m^{-2}$ $h^{-1}$ and 0.4–0.5 bar | Biogas recirculation | 70 |
| Submerged anaerobic with Kubota flat plate | Synthetic wastewater | 3 L | Kubota | 0.4 µm and 1 $m^2$ | 15 L $m^{-2}$ $h^{-1}$ and 0.4–0.5 bar | Biogas recirculation | |
| Jet flow anaerobic bioreactor + UF membrane | Landfill leachate | 50 L | NA | 100 kDa and 1 $m^2$ | 2.5–8.3 L $m^{-2}$ $h^{-1}$ and 1–3 bar | Chemical cleaning using NaOH, sodium bisulfate (1 h), every 45 days | 68 |
| Submerged UF membrane reactor | Landfill leachate | 29 L | Polyvinylidene fluoride (PVDF) | 0.1 µm and 0.46 $m^2$ | 20–50 L $m^{-2}$ $h^{-1}$, 02–0.5 bar | | 69 |
| Anaerobic baffled reactor + flat-sheet MF membrane | Kraft evaporator condensate | 10 L | Polyvinylidene fluoride (PVDF) | 0.3 µm and 0.03 $m^2$ | 5.6–9.3 L $m^{-2}$ $h^{-1}$, <30 kPa | Biogas sparging (0.3–0.75 L $min^{-1}$) | 66 |
| Anaerobic reactor UF flat-sheet membrane | Textile wastewater | 10 L | Polyvinylidene fluoride (PVDF) | 0.4 µm and 0.12 $m^2$ | 2 L $m^{-2}$ $h^{-1}$, <40 kPa | Biogas sparging (20 L $min^{-1}$) | 67 |

### 14.6.1 Food Industry Wastewater

The efficacy of four cross-flow UF membranes with different molecular weight cut-offs (MWCO) made of polyethersulfonate, *i.e.* PES200, PES200, PES500, and PES700, in conjunction with an anaerobic reactor was investigated to treat wastewater from a food factory (flour, meat, vegetable, utensil, and floor).[55] The treatment scheme comprised a storage tank, followed by treatment in the anaerobic reactor, filtration in membrane modules, and a membrane cleaning system. The raw wastewater is screened in a 1 mm mesh before storage. Subsequently, the wastewater is pumped into the anaerobic reactor (0.4 $m^3$) for treatment. The mixed liquor from the anaerobic reactor is pumped through an externally placed cross-flow flat plate module (surface area 0.32 $m^2$) comprising eight parallel (300 × 68 × 0.7 mm each) membrane sheets. The fluid flowrate and cross-flow velocity of membranes were 1.4–1.5 $m^3\ h^{-1}$ and 1.02–1.09 $m\ s^{-1}$, respectively, with an applied pressure of 0.2 MPa. All modules were flushed daily for 30 min by permeate recycling, whereas chemical cleaning was performed with 0.5% NaOH solution for 1 h every 10 days. The characteristics of food wastewater were as follows, COD 2000–15000 mg $L^{-1}$, suspended solids 600–1000 mg $L^{-1}$, pH 5–6, and chromaticity colour 6000°–10 000°. The reactor was operated at a varied HRT of 16–100 h (OLR from 0.88–4.83 kg per $m^3$ per day) with pH and temperature maintained at 7.0 ± 0.2 and 37.0 ± 0.5 °C. At a loading rate of <2.0 kg $m^{-3}$, all four flat plate modules showed high efficiency of SS, colour, and COD removal, reaching >99.9, 98, and 90 5-log reduction, respectively. However, an increase in loading rate to 4.5 kg per $m^3$ per day exhibited a reduction in COD removal (<80%). Although different membrane properties had a minor influence on overall treatment and effluent quality, MWCO affected membrane flux, fouling, and cleaning frequency. During the study period, the irreversible fouling layer stabilized after 2–3 periods of chemical cleaning and flux recovery became constant. An increase in the order of membrane MWCO exhibited an indirect influence on permeate flux. The recovery of flux in PES200 and PES300 was 40–50%, and 20% in PES500. However, PES700 exhibited <10% flux recovery. Scanning electron micrographs of virgin PES700 showed a network of ridges and valleys, whereas EPS-bound biofilm with inorganic components was observed on the fouled membrane. A longer SRT of >50 days enhanced the rate of membrane fouling. Therefore, a relatively lower SRT, frequent backwash, and periodic cleaning with chemicals were necessary to maintain the permeate flux.

The feasibility of treating cheese whey in an AnMBR was investigated.[56] A 10 L continuously stirred tank reactor (CSTR) was coupled with an externally placed cross-flow tubular UF membrane module, operated in mesophilic conditions for 169 days, and agitated with a mechanical stirrer at 35 rpm. It was seeded with granular sludge from EGSB treated lactose-based wastewater. The pH and MLSS were maintained at 6.7–7.2 and 40 g $L^{-1}$, respectively, throughout the study period, and the SRT in the reactor was 50 days. The tubular membrane was made of PVDF and had a pore size and surface area of 0.03 µm and 0.0114 $m^2$, respectively. The permeability of the membrane was 1000 $Lm^{-2}$ hbar and was operated at a cross-flow velocity of 0.5 m $s^{-1}$ with 60 min filtration and a 2 min backwash cycle. The operating flux of the membrane was 8–11 L $m^{-2}$ $h^{-1}$ with an operational TMP of <350 bar. Concentrated whey permeate was collected and diluted to achieve a COD of 29.2 ± 3.3 g $L^{-1}$ with average carbohydrate and protein content of 14.1 and 1.4 mg $L^{-1}$, respectively. The other parameters in feed were (in mg $L^{-1}$) TSS 460, TKN 600 ± 135, $NH_4^+$-N 45 ± 14, TP 415 ± 45, $PO_4^{3-}$ 360 ± 55, *etc.* Urea was used as the source of supplemental nitrogen at a COD : TKN ratio of 50. A high COD removal efficiency of >90% was reported throughout the study period at an average OLR of 5 kg COD per $m^3$ per day with effluent COD of 365 mg $L^{-1}$. However, a reduction in treatment efficiency was observed in 139–160 days due to the limitations in supplemental nitrogen. Specific methane generation and sludge yield under steady-state operation were reported to be 0.24–0.30 $Nm^3$ per kg COD removed and 0.19 ± 0.03 g VSS per g COD removed, respectively. An optimum critical flux was investigated under varying MLSS (10, 20 and 32 g $L^{-1}$) and cross-flow velocity of 0.25, 0.5, 1, 1.4 m $s^{-1}$. The optimum critical flux was 36 L $m^{-2}$ $h^{-1}$ at 10 g $L^{-1}$ MLSS and 1.4 m $s^{-1}$ cross-flow velocity. Moreover, the study reported that improvements in critical flux could be made by increasing cross-flow velocity and decreasing MLSS.

The effect of high shear in a mixed anaerobic reactor equipped with an ultrafiltration membrane module on swine manure treatment was evaluated.[57] A lab-scale (6 L) reactor was operated for 300 days at a constant temperature of 37 °C. The UF membrane was made of polyethersulfone with a molecular weight cut-off of 20 kDa, 12 mm diameter, and a surface area of 0.0377 $m^2$. The membrane filters were operated at a TMP of 0.3–0.7 bar and membrane flux of 5–10 L $m^{-2}$ $h^{-1}$. The chemical cleaning of membranes was performed after 100 days of operation with a combination of 0.5% EDTA and 1% $Na_3PO_4$ or 0.1 M $HNO_3$ at pH 2 for 1 h. The swine manure was collected from an anaerobic sludge digester and blended to ensure uniformity. The AnMBR was inoculated with a 1 : 1 : 1 (v : v : v) mixture of sludge from a primary anaerobic sludge digester, UASB-treated brewery wastewater, and sludge dredged from a swine wastewater treatment lagoon. The reactor was initially operated at a loading rate of 1 g VS per L per day (≈1 g COD), which was subsequently increased to 2 and 3 g VS per L per day on days 53 and 186, respectively. The overall HRT of the system was 6 days. At an OLR of 1 g VS per L per day, the specific biogas production was 2–3 L per g VS per day, and effluent soluble COD was <200–250 mg $L^{-1}$. The overall total COD and soluble COD removal efficiencies were 96 and 86%, respectively, and total VFA in the reactor was <250 mg $L^{-1}$ acetic acid. The high cross-flow velocity (1.6 m $s^{-1}$) did not exhibit a deleterious effect on the reactor performance at an OLR of 1 g VS per L per day. At higher loading rates of 2 g VS per L per day and cross-flow velocity of 1.1 m $s^{-1}$, the system achieved 96% removal of soluble COD with a 2-fold increase in biogas production. However, higher cross-flow velocity >1.9 m $s^{-1}$ led to the accumulation of VFA, primarily attributed to the high shear stress causing breakage of microbial flocs and damage to cell structure, ultimately perturbing the syntrophic interactions between microbes. The optimal conditions for stable anaerobic digestion of swine manure were estimated to be OLR of 2.4 g VS per L per day and cross-flow velocity of 2 m $s^{-1}$.

### *14.6.1.1 Fermentation Industry Wastewater*

A study was conducted to assess the treatment potential of brewery wastewater in an AnMBR at a laboratory scale of 15 L capacity.[58] The system consisted of the mechanically mixed anaerobic digester with a submerged hollow fibre membrane module maintained at 37 °C. The membrane had a surface area of 0.047 $m^2$ and a pore size of 0.4 μm. Both synthetic and brewery wastewater was fed into the AnMBR at different stages of operation. In phase one, synthetic wastewater was fed for 140 days (including 20 days start-up time). The synthetic wastewater used was a mixture of beer, glacial acetic acid, yeast extract, ammonium chloride, $KH_2PO_{4,}$ and trace metal solution, to provide a total COD of 17 000 ± 600, TN 268 ± 18, $NH^{4+}$-N 101.0 ± 5.0, TP 66.0 ± 2.0, and $PO_4^{3-}$-P 55.0 ± 2.0 mg $L^{-1}$. During this phase, the stable MLSS concentration observed was 11.0 ± 1.0 g $L^{-1}$ with an SRT of 30 days and a critical flux of 9.26 ± 0.53 L $m^{-2}$ $h^{-1}$. In phase one, the membranes were operated at a flux 8 L $m^{-2}$ $h^{-1}$ with 10 min filtration and 1 min relaxation cycle. The biogas was injected to remove scouring at a rate of 15.3 $m^3$ $h^{-1}$ $m^{-2}$ of membrane area. The bioreactor's performance was challenged under various OLRs (g OD per L per day) of 2, 5, 7.5, and 10. The bioreactor attained an overall COD removal efficiency of >99% under all OLRs, with a permeate COD <100 mg $L^{-1}$. Changes in OLR caused a temporary increase in permeate COD that stabilized within 2–8 days of operation. At an F/M ratio of 0.95 ± 0.1 g COD per g VSS per day, specific growth rate and specific yield were 0.027 ± 0.0058 g VSS per g VSS per day and 0.028 ± 0.0036 g VSS per g COD, respectively. The average biogas yield was 0.64 ± 0.016 $m^3$ biogas per kg COD removed, whereas at different OLRs of 2, 5, 7.5, and 10, the biogas production rates were 18.0 ± 1.0, 52.0 ± 2.0, 79.0 ± 3.0 and 86.0 ± 4.0 L per day, respectively. The phase two operation was carried out with brewery wastewater for 90 days at an MLSS of 7 g $L^{-1}$, HRT of 44 h, OLR of 3.5–11.5 g COD per L per day, and similar membrane flux and filtration-relaxation cycles as phase one. Membrane backwashing was carried out occasionally only during an increase in TMP, at a flux of 8 L $m^{-2}$ $h^{-1}$. Chemical cleaning was carried out with citric acid at a concentration of 20 g $L^{-1}$ for 15 min, followed by 2 g $L^{-1}$ sodium hypochlorite for 15 min, and finally washed with deionized water for 10 min. Despite large variations in influent wastewater, COD in the permeate was usually <171 mg $L^{-1}$ (148–290 mg $L^{-1}$), *i.e.* >90% COD removal. The mean biogas production varied between 27.1 ±

1.8 to 44.0 ± 0.9 L per day with an average yield of 0.53 ± 0.015 $m^3$ biogas per kg of COD removed. The observed biomass yield and specific growth rate for the brewery wastewater treatment were 0.029 ± 0.001 g VSS per g COD and 0.022 ± 0.001 g VSS per g VSS per day, respectively. The membrane's critical flux was determined to be 8.64 ± 0.69 L $m^{-2}$ $h^{-1}$ with a gradual increase in TMP of 0.225 kPa per day. The accumulation of soluble and colloidal EPS (particulate protein and lipid) and SMP (>100 kDa) on membrane surfaces led to irreversible membrane fouling under sub-critical flux conditions. Therefore, frequent chemical cleaning was necessary to maintain long-term, stable operation of the bioreactor.

The performance of a two-stage submerged anaerobic membrane was evaluated for the treatment of sugarcane vinasse at 22 °C.[59] These bioreactors were operated sequentially, with acidogenesis in a UASB reactor followed by methanogenesis in a CSTR, mixed at 250 rpm with working volumes of 6.7 and 24 L, respectively. The HRT in the methanogenic reactor was 3.6 times higher than in the HRT acidogenic reactor. The CSTR consisted of 205 polyetherimide hollow fibre membrane modules with a pore size of 0.45 μm and a surface area of 0.045 $m^2$, operated at an average flux of 4.4 L $m^{-2}$ $h^{-1}$. After start-up, the acidogenic reactor was fed at an OLR of 2.5 g COD per L·per day at infinite/long SRT. The membrane fouling in the methanogenesis reactor (CSTR) was controlled with a filtration period of 8 min, followed by 40 s relaxation. During the operation period, the average VFA content in the UASB influent, UASB effluent, and CSTR permeate were 1995, 3541 and 987 mg $L^{-1}$ (as acetic acid), respectively. The COD and dissolved organic carbon (DOC) in UASB influent, UASB effluent and CSTR permeate were 15 727, 11 512, and 488 mg COD per L and 3544, 3533, and 178 mg DOC per L, respectively. At steady states, the pH in the acidogenic and methanogenic bioreactors were 4.2–4.6 and 7–7.5, respectively. The total COD removal in the combined system was 96.9 ± 0.7%, with a relatively lower contribution of 26.8 ± 5.5% by the acidogenic reactor. Similarly, the acidogenic reactor contributed 0.08–4.6% of the total methane generated in the combined system. The filtration performance was affected by the SMP and EPS released by acidogens. Backflushing for a span of 15 s after a permeation period of 15 min could achieve surface cleaning of membranes with no significant recovery of hydraulic permeability. The chemical cleaning of membranes was initiated at TMP >0.5 bar with a combination of NaOCl and citric acid. However, internal membrane fouling could not be completely reversed.

The feasibility of pilot-scale AnMBR for the treatment of thin stillage generated during ethanol production from corn was evaluated.[60] Here, the research investigated the attainable flux, fouling conditions, and MLSS and TMP influence on total flux across the membrane. The system comprised a 12 $m^3$ reactor, mixed at 1750 rpm, a recirculation tank, and an external membrane tank equipped with 20 flat-sheet Toray UF membranes. Each membrane was made up of polyvinylidene fluoride with an average pore size and area of 0.08 μm and 18 $m^2$, respectively. To scour the membrane, both generated biogas and permeate recirculated at a rate of

47–65 $m^3$ $m^{-2}$ $h^{-1}$ and 11–47 m $h^{-1}$, respectively. This reactor was operated under mesophilic conditions in a continuous fed-batch mode (5–15 min of feed-in intervals of 1 h), whereas the membrane was operated under a 9 : 1 min filtration and relaxation cycle. The initial MLSS of the anaerobic digestor was ≈26 g $L^{-1}$, and the reactor was acclimatized for 40 days before initiating the membrane filtration. Under steady-state conditions (with external membranes), the reactor was operated at an OLR and TSS of 4.5–7 kg TCOD per $m^3$ per day and 14.5 ± 5.4 g $L^{-1}$, respectively. At an average SRT and HRT of 300 days and 17 ± 4 days, the reported COD and TSS removal efficiency was >98%, respectively, with a $CH_4$ yield of 0.31 $m^3$ per kg COD removed. At steady state, the reported flux was 4.3 ± 1.1 L $m^{-2}$ $h^{-1}$ at an MLSS of 24 g $L^{-1}$ and TMP of 0.1–0.2 bar. The membranes exhibited irreversible fouling after 100 days of operation, irrespective of chemical cleaning with NaOCl and HCl.

## 14.6.2 Pharmaceutical Industry Wastewater

Treatment of pharmaceutical and chemical industry wastewater was tested in an AnMBR[61] where the efficacy of concentrated waste organic solvents (WOS) as potential co-substrates was studied. The volume of the bioreactor was 50 L. In contrast, the external cross-flow membrane unit consisted of two tubular membranes made up of $ZrO_2$–$TiO_2$, a diameter of 1 inch, 8 channels, MWCO 50 kDa, and a total area of 0.25 $m^2$. The reactor was operated at 35–37 °C, a constant flux of 8.4 L $m^{-2}$ h, TSS >10 g $L^{-1}$, and SRT of 120–450 days. The main constituents of wastewater were methanol and ethanol, responsible for >80–90% of total organic load in wastewater and total COD value between 0.55 and 10.6 g $L^{-1}$. The other constituent solvents were tetrahydrofuran, dichloromethane, acetone, ethyl acetate, tripropylamine, acetonitrile, toluene, isopropanol, acetone, and dimethylacetamide. Two batches of WOS were added as co-substrates with wastewater, namely WOS9 and WOS18. The AnMBR was operated for 580 days in three phases of varying substrates, influent composition, and organic load. In phase one (0–175 days), the reactor was fed with wastewater and operated in a continuous mode, with a volumetric loading of 0.6–4 g COD per L per day, HRT of 1.7–5 days. Under steady-state conditions, the effluent COD concentrations were 0.24–1.7 g $L^{-1}$, with an overall COD removal of 44–94% at an average of 78%. In phase two (191–214 days) the influent wastewater was amended firstly with methanol and subsequently with WOS9 at concentrations of 1–7 g $L^{-1}$ COD, respectively, resulting in an increase in COD from 3.24–7.54 g $L^{-1}$ to 5.4–7.6 g $L^{-1}$. The influent rate of wastewater was 14.3 L per day at an HRT of 3.49 days. The addition of methanol enhanced the COD removal to 89–93%. However, the addition of WOS 9 led to a reduction in COD removal efficiency by 19% within 8 days of co-substrate addition. The inefficient treatment was attributed to the accumulation of 480 mg $L^{-1}$ acetate and a simultaneous reduction in pH. Moreover, the addition of WOS 9 led to a decrease in populations of *Firmicutes* sp., *Crenarchaeota* sp., and *Actinobacteria* sp., with an increase in the relative abundance of *Chloroflexi* sp., *Cytophaga-Flexibacter* subphylum, and *Alphaproteobacteria* sp. In phase 3 (214–450 days) the reactors were operated in a continuous mode, fed with wastewater amended with a constant amount of methanol and WOS18. Similar to phase two, the addition of methanol at a concentration equivalent of 25 g $L^{-1}$ COD enhanced the removal efficiency (91–97%); however, a rapid drop in COD removal was observed (<60%) with WOS18 at an influent concentration of 5 g COD per L. The reduction in efficiency was attributed to the variations in incoming wastewater, elevated *N*,*N*-dimethylacetamide concentration (<2.5 g $L^{-1}$), reduction in viable methanogenic population from 27–42% to 6%. Overall, it was concluded that the treatment efficiency decreas es due to the varying composition of wastewater and influent of WOS. Moreover, membrane fouling was not reported up to an MLSS of 25 g TS per L; hence chemical cleaning was not performed throughout the operational period.

A pilot-scale AnMBR was employed to treat wastewater generated from a pharmaceutical company containing β-lactams under different OLRs.[62] The system consisted of a UASB and an external cross-flow UF membrane module. The working volume of the bioreactor was 180 L. The membrane was made up of a polyvinylidene fluoride hollow-fibre module with surface area and pore size of 1 $m^2$ and 0.02 μm respectively, with a critical flux of 20 L $m^{-2}$ $h^{-1}$. The reactor was operated in three stages corresponding to different HRTs (48.1 ± 1.0, 35.2 ± 0.9 and 23.9 ± 1.2 h) under 8 min suction and 2 min pause cycle. The SRT (250 days), cross-flow velocity (1.5 ± 0.2 m $s^{-1}$) and transmembrane pressure (40–60 kPa) were kept constant for all three stages. The influent wastewater contained several solvents such as tetrahydrofuran, nitrobenzene, bromobutane, bromopropane, aminophenol, and 1,3,5-tribromobenzen. During reactor operation, the total COD and BOD were 4746 ± 539 and 1397 ± 248, 5118 ± 801 and 1470 ± 136, 4428 ± 827 and 1307 ± 244 mg $L^{-1}$, in the first, second, and third stage, respectively. The concentration of antibiotics in the influent wastewater were as follows: amoxicillin (AMOX), ceftriaxone sodium (CEFT), cefoperazone sodium (CEFO), ampicillin sodium (AMPI) were in the ranges 19.53–24.02, 6.77–7.19, 2.0–2.54 and 8.78–10.52 mg $L^{-1}$ respectively. The effluent COD varied between 215 and 814 mg $L^{-1}$ (≈87.1–94% removal) for all three stages and increased with a decrease in HRT. Also, the average COD removal by the membrane module was higher (19.6 ± 2.7%) at lower HRT (23.9 ± 1.2 h) as compared to 11.1 ± 2.0% COD removal at higher HRT (48.1 ± 1.0 h). Similarly, an increase in OLR led to a simultaneous increase in VFA and alkalinity from 249 ± 25 and 2657–2992 mg $L^{-1}$ in stage one to 375 ± 61 and 1742 mg $L^{-1}$ in stage three, respectively. A similar trend was observed for antibiotic removal wherein, increase in OLR or reduction in HRT resulted in a reduction in antibiotic removal. Moreover, a major fraction of antibiotic removal took place in the UASB, whereas the UF membrane module had relatively less effect on antibiotic degradation. The average removal efficiencies of the antibiotics were as follows: CEFO (74.2 ± 6.3%) followed by AMOX (66.9 ± 6.9%), CEFT (44.8 ± 4.4%), and AMPI (32.8 ± 4.1%). The highest biogas yield of 0.167–0.349 L $g^{-1}$

COD removal was recorded in stage 3. The presence of 2000–4000 mg $L^{-1}$ sulfates in pharmaceutical wastewater contributed to 2.5–3.8% $H_2S$ in the biogas. In that study, details of membrane filtration and cleaning procedures were not discussed.

A bench-scale submerged flat-sheet anaerobic microfiltration membrane reactor was developed to treat simulated/standard and domestic wastewater (DWW) at psychrophilic temperatures (15 °C).[63] Furthermore, pyrosequencing techniques were used to assess the archaeal and bacterial community structures in suspension and biofilm to evaluate the selection of inoculating seeds for a psychrophilic AnMBR. The bench-scale AnMBR used in this study had a working volume of 5 L and contained two submerged housings, each incorporating two flat-sheet microfiltration polyethersulfone membranes with a pore size and an effective area 0.2 μm and 0.0387 $m^2$ (7.74 $m^2$ $m^{-3}$), respectively. The process-generated biogas was collected in a Tedlar bag and recirculated by a diaphragm pump at a flow rate of 4.67 L $min^{-1}$ (superficial gas velocity of 13.9 m $h^{-1}$) to reduce membrane fouling. The reactor was initially fed with simulated/standard wastewater for 351 days at a total COD 440 mg $L^{-1}$, soluble COD 290 mg $L^{-1}$, OLR 440–660 mg COD per L per day, HRT of 16–24 h, and membrane backflushing for 30 s after a filtration period of 30 min. The permeate characteristics were as follows: COD 36 ± 21 mg $L^{-1}$ (92 ± 5% reduction), 5-day biological oxygen demand ($BOD_5$) 18 mg $L^{-1}$ (92% reduction), and VFA concentration 18 ± 16 mg $L^{-1}$. The average biomass yield was estimated to be <0.10 g VSS per g COD. In the second phase, the reactor was fed with DWW at an OLR ranging from 170 to 393 mg COD per L per day for 40 days with membrane backflushing for 4 min after a filtration period of 4 h. The transition in feed constituents resulted in unstable performance attributed to higher variable concentrations of influent sulfate concentrations of 160 ± 100 mg $L^{-1}$. Despite lower OLR, only 69 ± 10% COD removal was observed along with ≈96% sulfate reduction. The author reported that the permeate quality met the EPA's standard for secondary effluent. *Methanosaeta* was the dominant genus in the reactor microbiome. The relative abundance of the different genera in suspension and biofilm was considerably different, such as *Methanobacterium* constituted 10.7 ± 2.2% in biofilm and 21.5 ± 2.2% in suspension. In contrast, the relative abundance of *Methanospirillum* was higher in biofilm (19 ± 3%) than in the suspended biomass (8.2 ± 1.1%). The relative population of acetolactic methanogens was higher than hydrogenotrophic methanogens in the suspension. The most abundant population in the microbiota belonged to the mesophilic psychrotolerant species, indicating the usefulness of using mesophilic inocula as a seed for low-temperature treatments.

The effectiveness of the anaerobic cross-flow UF membrane bioreactor for raw domestic wastewater treatment was investigated.[64] The jet flow anaerobic bioreactor had a working volume of 50 L and was operated under mesophilic conditions. In the reactor, the influent was dispensed through a nozzle located at the top of the inner tube. The bioreactor is bifurcated with the help of a baffled wall. The down-flow movement of the influent enhances the contact with settled sludge followed by up-flow movement. The reactor was coupled with a Technocon GmbH ultrafiltration module with a Stork WFFX 0281 membrane of 1 $m^2$ area and 100 kDa cut-off. The cross-flow velocity was maintained at 3 m $s^{-1}$, and the transmembrane pressure was varied between 1 and 2 bars. The permeate flux varied throughout the study period ranging from 13 to 3.5 L $h^{-1}$ $m^2$. The reactors were maintained under a stabilization and adaptation period comprising a low feeding condition of 20 L per day (0.23 g COD per L perday) for 1 month. After that, the OLR was progressively increased to the desired loading rate (15 h, 2 g COD per L per day) and HRT. Average influent COD, TOC, $BOD_5$ and total Kjeldahl nitrogen (TKN) concentrations were 685, 157, 356 and 156 mg $L^{-1}$, respectively. During the operation period of 170 days, average TSS, COD, and BOD removal were 100, 88, and 90%, respectively, along with 100% removal of total and faecal coliforms, faecal *streptococc*i, *Salmonella*, *helminths ova*, and protozoan cysts. During the study period, the reactors did not exhibit significant VFA accumulation, with the highest biogas production of 30 L per day at a COD of 2 g per L per day with an average biogas yield of 0.27 L $CH_4$ per g COD. During the study period, a steady decrease in flux was observed. It was concluded that AMBR-treated effluent conforms to WHO guidelines for unrestricted irrigation. The authors have not reported any cleaning measures taken during the operation period to reverse this phenomenon.

The application of submerged AnMBR for the treatment of dilute wastewater using two different membrane configurations was explored.[65] For this purpose, the authors employed three identical submerged AnMBRs, operated under mesophilic conditions, and maintained at pH 7. The first reactor was equipped with a hollow fibre membrane with an outer diameter of 540 μm and a wall thickness of 90 μm. The other two reactors were equipped with a Kubota flat-sheet membrane module of 0.1 $m^2$ area and 0.4 μm pore size. The feed reactors consisted primarily of glucose for reactors 1 and 2 (460 ± 20 mg $L^{-1}$ COD), and synthetic media: peptone (0.2 mg $L^{-1}$), meat extract (0.14 mg $L^{-1}$), urea (0.01 g $L^{-1}$), and $NaHCO_3$ (300 mg $L^{-1}$) for reactor 3. The biogas was sparged at a rate of 5 L $min^{-1}$ to reduce the propensity of membrane fouling. Throughout the experiment, the initial HRT of reactors was 48 h, which was reduced to 24, 12, 6, and 3 h, respectively. It was observed that removal efficiency decreased with decreasing HRT, with the highest treatment (95%) observed at HRT of 24 h. The peak biogas production was in the range 0.22–0.33 $m^3$ $CH_4$ per kg COD removed for all reactors. The initial flux in all three reactors was ≈15 L $m^{-2}$ $h^{-1}$; however, the average TMP was relatively higher in hollow fibre membrane than flat sheets under similar conditions. Membrane fouling was attributed to the presence of finer colloidal particles and the gel layer.

### 14.6.3 Recalcitrant Wastewater

A laboratory-scale, two-zone (top and bottom), vertically baffled, submerged AnMBR was designed to treat kraft evaporator condensate for 280 days.[66] The sludge was introduced in the bottom zone (3.5 L), and a flat-sheet membrane filter module made of polyvinylidene with an area of 0.03 $m^2$ and 0.3 μm pore size, and 70 000 Daltons was submerged in the top zone (6.5 L). The process-generated biogas was recirculated at a variable sparging rate from 0.3 to 0.75 L $min^{-1}$ to minimize the deposition of solids on the membrane surface. The temperature and pH were maintained at 37 ± 1 °C and 7.0 ± 0.2, respectively. The transmembrane pressure was maintained at <30 kPa. The physicochemical characteristics of kraft condensate were COD: 2.5–2.7 g $L^{-1}$, and Al: 0.176–0.4, Mg: 0.65–1.92, Na: 2.41–16.81, TKN 16.32–21.42 and TP 0.5–1.3 mg $L^{-1}$. The kraft condensate wastewater was amended with methanol to increase the OLR from 2.1 to 24 kg COD per $m^3$ per day (COD 5.6–10 g $L^{-1}$). The study was conducted at four different operational membrane fluxes, *i.e.* 5.6 ± 1.0, 7.1 ± 1.0, 12.5 ± 1.4, and 9.3 ± 0.8 L $m^{-2}$ $h^{-1}$. An overall soluble COD removal of 93–99% (50–200 mg $L^{-1}$ effluent COD) and $CH_4$ production of ≈0.35 L $g^{-1}$ COD (*i.e.* 85% methane in biogas) was achieved under all phases with a colourless permeate. In this study, sludge cake formation was the predominant cause of membrane fouling rather than membrane pore-clogging. Therefore, *in situ* membrane cleaning through biogas sparging at a lower rate (*i.e.* 0.75 litres per minute (LPM)) could result in a stable membrane flux.

A submerged AnMBR (11.4 L) fitted with a Kubota flat-sheet UF membrane module (filtration area 0.12 $m^2$ and pore size 0.4 μm) was used to decolourize textile wastewater containing azo dye.[67] This membrane module was operated with alternating cycles of 4 min of filtration followed by a 1 min relaxation cycle with biogas recirculation to remove scouring. The reactor was fed with synthetic wastewater comprising $NH_4Cl$ (30 mg N per L), $K_2HPO_4$ (10 mg P per L), $NaHCO_3$ (3.5 g $L^{-1}$), $FeCl_2$ (0.35 mg Fe per L) and $Na_2MoO_4$ (0.02 mg Mo per L) with 2.7 g COD per L per day at a HRT of 2.5 days. Reactive dye orange 16 was used as a model dye for all experiments, and its concentration was varied from 0.06 to 3.2 g $L^{-1}$. This reactor was operated for >150 days, and during this period, pH persisted at neutral values. The TSS, VSS, and TMP in the reactor were 20.3 ± 1.9 g $L^{-1}$, 14.5 ± 1.8 g $L^{-1}$, and <40 kPa, respectively. The removal of azo dye was >90% at a concentration of 60 mg RO16 per L. However, an increase in azo dye concentration up to 3.2 mg $L^{-1}$, led to the accumulation of VFA (≈2.5–3 g $L^{-1}$), resulting in the inhibition of anaerobic microbes, reduction in COD removal efficiency (<10%), and finally process failure. Re-acclimatization of the anaerobic microbes for 15 days was necessary to achieve process stability. Subsequently, 55–60% total COD removal could be achieved at an azo dye concentration of 3.2 g $L^{-1}$, indicating moderate potential for azo dye treatment using an AnMBR.

### 14.6.4 Landfill Leachate

The long-term performance of a pilot-scale AnMBR with cross-flow UF to treat landfill leachate is reported in the literature.[68] The anaerobic jet flow reactor had a working volume of 50 L and was operated under mesophilic conditions. The reactor was equipped with a 1 $m^2$ cross-flow UF membrane at 100 KDa cut-off. The membrane module was operated at a cross-flow velocity of 3 m $s^{-1}$, TMP of 1–2 bar, 8.3 L $m^{-2}$ $h^{-1}$ flux. In this study, the leachate was collected and stored at 4 °C until the analysis. Leachate was diluted during the operation to attain COD values of 15, 30, and 41 g $L^{-1}$, corresponding to OLRs of 2.24 ± 0.35, 4.66 ± 1.23, and 6.27 ± 0.78 g COD per L per day, respectively. The HRT was kept constant at 7 days. The total COD removal observed in three stages was 92.0 ± 1.3, 88.8 ± 6.8, and 90.7 ± 1.1%, respectively. The average biogas yield was 0.37–0.48 L $g^{-1}$. The increase in OLR resulted in the simultaneous rise in VFA in the permeate. However, an adaptation period of <10 days led to a recovery in treatment efficiency. Gas chromatography-mass spectrometry (GC-MS) analysis revealed complete removal of hexanoic acid, heptanoic acid, cyclohexane carboxylic acid, and octanoic acid. In contrast, compounds like hexadecane, docosene, octadecene, *etc.* persisted in the permeate at a relatively lower concentration. Fouling of membranes led to a gradual reduction in permeate flux from 8.3 to 2.5 L $m^{-2}$ $h^{-1}$, and chemical cleaning was performed using NaOH and sodium bisulfate for 1 h, followed by water. A subsequent chemical cleaning with citric acid and 0.5% EDTA solution was employed to recover the flux in case of failures with initial chemical cleaning.

A 29 L submerged AnMBR with a Zenon capillary ultrafiltration module was used with a pore size of 0.1 μm and filtration area of 0.46 $m^2$ to treat landfill leachate.[69] Experiments were performed at a temperature of 35 °C. The major constituents of landfill leachate used were (in mg $L^{-1}$): COD range 2800–5000, pH 8–8.9, alkalinity 4600–7900, chloride 1950–3650, and ammonia-N 750.4–840.0. The anaerobic microbes were primarily acclimatized in synthetic wastewater, fed at an OLR of 1 kg COD per $m^3$ per day at a HRT of 7 days. At steady-state, the reactor achieved a COD removal efficiency of 95% with a biogas yield of 12 L per day. Subsequently, leachate was introduced into the reactor in different dilutions (5–75% v/v) with synthetic wastewater. At a leachate dilution of 10–20% v/v, the COD removal was >90%; however, an increase in the strength of leachate to 30% v/v led to a reduction in COD removal efficiency from 95 to 78.8 and subsequently to 45% at influent leachate concentration of 75% (v/v). The optimum conditions for leachate treatment were as follows: 20% v/v of leachate mixed with synthetic wastewater, 2 days HRT and OLR of 2.5 kg per $m^3$ per day.

## 14.7 Energy Requirement and Operational Costs

The energy required by various upstream and downstream processes in a typical full-scale AnMBR is as follows:[1] pumping of sewage,[2] FOG removal,[3] screening and particulate removal,[4] operation of membrane filters (vacuum filtration/pressure filtration),[5] mixing or effluent recirculation,[6] physical cleaning of membranes with permeate or clean water or biogas,[7] chemical cleaning of membranes,[8] sludge pumping, and[9] heating of bioreactors up to mesophilic or thermophilic temperature. The membrane filtration and mitigation of membrane fouling consumes 85–90% of the total energy requirement of a typical AnMBR. Similarly, the energy requirement for recycling biogas or membrane tank sludge-feeding pumps accounts for 75% of the total energy demand. The specific energy requirement of an AnMBR varies with the configuration of membrane filters, operational and cleaning strategy, material properties of the membrane, and the physicochemical composition of wastewater. An AnMBR exhibited a particular energy requirement of 0.22 kW h $m^{-3}$ under scenarios with no energy recovery from biogas, whereas the recovery of energy from biogas reduces the specific energy requirement to 0.14 kW h $m^{-3}$.[22] The energy requirement for mixing and pumping in an AnMBR ranged between 0.1 and 0.3 kW h $m^{-3}$, whereas it was 0.12 kW h $m^{-3}$ during steady-state operation.[32] Overall, the specific energy requirement varies in the range 0.11–0.49 kW h $m^{-3}$. The explicit energy demand in an AnMBR varied between 0.03 and 5.7 kW h $m^{-3}$.[71] An energy demand of 0.03–3.57 kW h $m^{-3}$ by a submerged AnMBR was reported,[22] whereas the energy required to remove fouling was 0.80 kW h $m^{-3}$ for wastewater with a COD of 1.14 g $L^{-1}$. A specific energy demand of 0.69–3.41 kW h $m^{-3}$ by an AnMBR was reported, with 77–80% of the total energy consumed for biogas sparging and reduction in fouling.[23] Anaerobic digestion is susceptible to lower temperatures <20 °C. In colder countries or during winter, the bioreactors often demand heating to maintain higher degradation levels. The process-generated biogas can circumvent the energy demand for heating; however, it can only be viable with wastewater containing high organic matter of 4–5 g COD per L. Alternatively, high OLR can be achieved with low-strength wastewater by reducing the HRT. In contrast, operation of AnMBRs at low HRTs of <4h is practically challenging. The net cost for the treatment of sewage in an AnMBR at COD between 100 and 1200 mg $L^{-1}$ was reported to be between 0.42 and 0.35 € $m^{-3}$; however, subsequent removal of nutrients increases the net treatment costs above 0.51 € $m^{-3}$.[72]

## 14.8 Conclusions

The present chapter highlighted fundamental aspects of AnMBR, classification, operational consideration, and its application to treat several industrial wastewaters. Anaerobic digestion begins with the hydrolysis of organic compounds, with subsequent acidogenesis, acetogenesis, and methane production. The stoichiometry of anaerobic digestion suggests that 1 unit of carbon upon anaerobic digestion yields 0.95 units of carbon substrate in the form of biogas ($CO_2$ + $CH_4$). A hybrid system is operated that combines microbial decomposition of compounds followed by membrane filtration in various configurations such as side-stream, submerged, or externally placed submerged membrane, respectively. The submerged membranes have been the most commonly used configuration in AnMBRs. Similarly, polymeric materials, especially PVDF, have been widely used to manufacture membranes due to their relatively lower cost, ease of fabrication, low reactivity towards wastewater compounds, and resistance to mechanical fatigue. Irrespective of its construction material, the membranes suffer from bio-chemical fouling and clogging, resulting in lower flux and higher filtration resistance.

These parameters are process indicators; hence their threshold values require considerable attention to achieve efficient treatment processes, the simultaneous reduction in membrane fouling, and energy consumption. Various membrane-pore declogging strategies, such as permeate backwashing, chemical cleaning, and compressed biogas cleaning, are employed to reduce pore-clogging, fouling rate, cleaning frequencies, operation and maintenance (O&M) costs, and ultimately enhance the filtration life of the membranes. Operational failures due to membrane clogging remain the challenge. Innovative techniques to minimize fouling and membrane cleaning are necessary to increase the longevity of membrane filters. AnMBRs are preferred over the conventional form of anaerobic digesters due to significantly lower washout of microbes, leading to longer biomass residence time, discharge of high-quality effluent with low COD removal of SMPs and EPSs, smaller pore sizes of the membranes (<0.45 μm ensures lower microbial population and pathogens in the effluent), and low turbidity. AnMBRs have been implemented effectively in treating low-strength wastewater with OLR $< 5\ \mathrm{g\ L^{-1}\ d^{-1}}$; however, their robustness in handling high-strength wastewater $> 5\ \mathrm{g\ L^{-1}\ d^{-1}}$, is yet to be established. It has been relatively less successfully implemented with wastewater containing high COD, high suspended solids, high viscosity, salinity, humic acids, and surfactants. The effluent discharged by an AnMBR requires secondary or tertiary treatment due to residual nutrients such as N, P, and xenobiotics. The effluent discharged by AnMBRs contains a relatively low carbon/nitrogen (C/N) ratio and carbon/phosphate (C/P) ratio; therefore, residual nutrient removal from the effluent by post-treatment methods such as struvite precipitation becomes feasible. This could further create value-added products in addition to the biogas generated by the process. After their filtration life, the clogged membranes are discarded, creating a secondary hazardous solid waste pool of little/no value nonbiodegradable material. The lifecycle of membranes post-filtration is relatively less discussed and needs to be considered to prevent downstream pollution. Hence, the choice of a biological system with an AnMBR framework requires careful thought of the many variables involved and the strength of the wastewater.

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CHAPTER 15

# *Moving Bed Biofilm Systems: A Sustainable Approach for Industrial Wastewater Treatment*

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## 15.1 Introduction

Water is one of the indispensible resources for the survival of life on Earth. Rapid population growth promotes industrialization, which affects our quality of life, while simultaneously increasing the demand for safe drinking water. It is expected that 60% of the world population will face a water scarcity issue if the water consumption rate remains constant up to 2025.[1] The use of huge quantities of fresh water for different industrial practices not only reduces the fresh water level but also creates the problem of wastewater handling. Industrial growth plays a vital role in national economic development; however, industry is one of the major sources of water

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

pollution.[2,3] The wastewater generated from different industries contains enormous amounts of carcinogenic and mutagenic compounds that have many adverse effects on the environment. Therefore, the proper handling of toxic wastewater has become a major concern in recent years. Developing countries are confronting the problem of wastewater reclamation and reuse for different activities. Stringent wastewater quality standards and the demand for pure water have drawn researchers' and industrialists' attention towards the establishment of treatment plants that will use the least space. In this context, it is essential to consider social, technical, and economic factors before designing a system.

Biofilm systems have been used to treat toxic pollutants containing wastewater for the last few decades. Tricking filter, rotating biological contactor, and submerged fixed biofilm reactors have many drawbacks such as not having an effective working volume (*i.e.* trickling filter), susceptibility to mechanical failure (*i.e.* RBC), hydraulic instability (fluidized-bed reactor) *etc.* Earlier biofilm systems had some drawbacks, including high mass-transfer resistance, which leads to lower yields. Therefore, to overcome such limitations the moving-bed biofilm reactor (MBBR) system was developed in the late 1980s and early 1990s in Norway. The freely moving carrier-based biofilm system was found to provide an alternative solution to the other available systems. Nowadays, there is an increasing demand for the application of moving-bed biofilm systems to treat the different types of industrial wastewater because of its advanced features such as: less space required for the installation, stable operation, higher active biomass retention capability, no sludge bulking issues, better recovery from shock loading *etc.*[4,5] In addition to all the advantages, there are several other reasons for the preference of MBBRs over other available conventional methods. MBBR systems are based on the principle of an attached growth system in which the biomass is attached to the inert carrier medium to degrade the pollutant. It has the benefit of both an activated sludge process and a biofilm reactor. The MBBR technique consists of a submerged biofilm reactor along with the solid-liquid separation facilities that facilitate the treatment of different types of wastewater.

Wastewater coming from various industries (*e.g.* distilleries, paper and pulp, pharmaceuticals, petroleum refineries, textile, tannery) contains diverse group of toxic and poorly biodegradable compounds which limits the uses of biological treatment methods to treat the wastewater. A summary of the wastewater characteristics generated from the different industries is presented in Table 15.1.

## 15.2 Overview of the Moving-bed Biofilm Process

In the moving-bed biofilm reactor (MBBR) process, the biomass grows on the attached medium, as a biofilm. The carrier materials are less dense than water and have a high surface area, which allows more biomass to be attached to the support medium. The carrier media are kept moving inside

**Table 15.1** Summary of the different industrial wastewater characteristics.

| Industry type | Nature and characteristics of wastewater | Environmental impact | Reference |
|---|---|---|---|
| Distillery industry | High organic loading, phenolics, colloidal particles, melanoidins, proteins, lignin, sulfate, ammonia, phosphate high total solid | Skin allergies, headache, vomitting, stomach pain, reducing the dissolved oxygen level in the water, reduces the pH of the water stream, death of fish and many aquatic plants and animals | 9 |
| Petroleum refinery | Emulsified hydrocarbons, sulfide, ammonia, phenolic compounds, total dissolved solid, heavy metals, aromatic hydrocarbons | Leukaemia, chromosomal breakage, damage of human lung cells, reduction in chlorophyll content in aquatic plants | 1, 6 and 8 |
| Pharmaceutical industry | Heavy metals, high BOD and COD, sulfate and sulphide, antibiotics, drug precursors, chloride, nalidixic acid, polymeric materials | Carcinogenic, mutagenic, teratogenic, endocrine-disrupting effects on aquatic life | 11 |
| Textile industry | High TSS (total suspended solids), sulfide, chlorinated compounds, hardness, dyes, ammonia, starch, surfactants, fat, metal salt | Carcinogenic, mutagenic, destruction of aquatic ecosystem, | 12 |
| Tannery industry | Chloride, sulfides, ammonia, nitrates, nitrite, chromium, sulfate, synthetic tannins, suspended solids, phenolic compounds, sulphonated oils | Hinder the photosynthesis process, affect the eye, lungs, immune system, cellular injury in fish, retardation of microbial activity | 2, 13, 14 and 15 |
| Paper and pulp industry | Lignin, sulfate, phenol, high dissolved organics, alkylphenols, adsorbable organic halides, tannin, TDS (total dissolved solids), heavy metals, chlorophenol | Carcinogenic, mutagenic, headache, vomitting, nausea, diarrhoea, affect the aquatic ecosystem | 10 |

the reactor by aeration in the case of an aerobic reactor and by means of mechanical mixing in the case of anoxic and anaerobic reactors. An MBBR is one of the best alternatives to the conventional activated sludge process and it also possesses the useful feature of biofilters.

MBBR shows many advantages over the suspended growth process, such as robust design, higher biomass concentration, no sludge recirculation, compact design, better resistance to shock loading, and high solid retention time. It is better for the growth of slow-growing microorganisms, and allows the culturing of a diverse group of microbes requiring different environmental conditions in a single system.[15,17]

## 15.2.1 MBBRs Operated in Different Environmental Conditions

### *15.2.1.1 Aerobic MBBR*

An MBBR can be operated in an aerobic, anaerobic and anoxic environment. In an aerobic MBBR (Figure 15.1), external air is supplied into the system to help the movement of the carrier material in the reacting fluid and the growth of the microbes, and to oxidize the pollutants present in the wastewater. However, supply of a high amount of oxygen into the system leads to an increase in the operational cost. It also prevents the sludge settling. Aerobic reactors are most commonly used for the removal of carbonaceous matter and for nitrification. The nitrification process is carried out in two steps. Initially the ammonia is oxidized to nitrite by ammonium-oxidizing bacteria and then to nitrate through nitrite-oxidizing bacteria. *Nitrosomonas* is responsible for the ammonium oxidation whereas the *Nitrospira* and *Nitrobacter* genera are responsible for nitrite oxidation.[19,21] In an aerobic MBBR both autotrophs and heterotrophs are present. The autotrophic bacteria are known as the nitrifiers and are commonly present deep inside the biofilm. The heterotrophs consume the carbon content present in the system and generally grow on the outer region of the biofilm. Due to the slow growth rate and sensitive nature of the nitrifiers, the nitrification process can be easily inhibited by a high loading rate of toxic compounds into the system. The rate of nitrification is influenced by the dissolved oxygen (DO) concentration, total ammonium nitrogen concentration, organic load, alkalinity, pH and

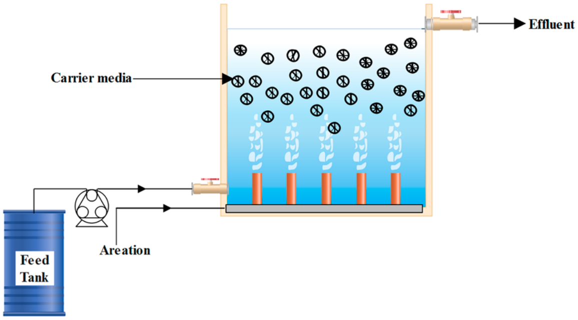

**Figure 15.1** Aerobic moving-bed biofilm reactor.

temperature. Approximately 75% of DO is used for ammonium oxidation whereas the other 25% is utilized for the conversion of nitrite into nitrate.[19] Nitrification rate is linearly dependent upon the DO concentration in the system. The performance of an aerobic reactor increases with increasing rate of aeration to the system, but excess air supply may hinder the carbon removal efficiency due to the erosion of the biofilm.[20] The optimum aeration rate can be decided by considering the type of wastewater, the characteristics of the carrier material and the volume of wastewater. An aerobic MBBR system shows better performance for the treatment of many industrial wastewaters such as pulp and paper mill wastewater, refinery wastewater, tannery wastewater *etc.*[8,13,27]

### *15.2.1.2 Anaerobic MBBR*

Anaerobic treatment is an economical, energy-intensive and sustainable wastewater treatment process used for the treatment of wastewater. In an anaerobic process (Figure 15.2), microbes degrade the pollutants present in the wastewater in the absence of oxygen. Insoluble organics and high-molecular-weight organic matter are degraded under anaerobic conditions *via* a series of reactions and produce carbon dioxide, methane and hydrogen gases, which can be further utilized as an alternative fuel. Although, anaerobic mineralization is a slow process compared to the other process, many recalcitrant compounds can be degraded by this process. The MBBR technique is used in anaerobic processes and has become a more prevalent wastewater treatment due its advantages over aerobic processes. Anaerobic MBBRs are more resilience to high organic load and can therefore be utilized as a preliminary treatment before other biological processes. An anaerobic MBBR can be used before an aerobic MBBR to reduce the organic load of the aerobic reactor. Hence, less energy will be utilized by the aerobic reactor. Morgan-Sagastume *et al.* (2019) used

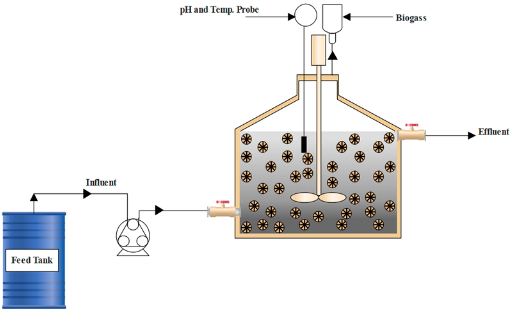

**Figure 15.2** Anaerobic moving-bed biofilm reactor.

an anaerobic MBBR (AnMBBR) to treat the oil-contaminated wastewater and found that it was able to handle high organic load in lower hydraulic loading conditions.[16]

#### *15.2.1.3 Anoxic MBBR*

In an anoxic process, microbes degrade pollutants into the nitrogen gas under the nitrate-reducing conditions. Nitrate acts as an electron acceptor whereas the organic compounds (such as organic alcohol, amino acids and fatty acids *etc.*) and inorganic compounds (hydrogen gas, elemental sulfur, thiosulfate, sulfide *etc.*) act as electron donors in this process. Therefore, both carbon and nitrogen can be removed in an anoxic reactor. The denitrification process occurs in four different steps. (1) Nitrate is reduced to the nitrite by the nitrate reductase. (2) Nitrite is reduced to nitric oxide by nitrite reductase enzyme. (3) Nitric oxide is reduced to nitrous oxidize by nitric oxide reductase. (4) Nitrous oxide is reduced to nitrogen gas by nitrous oxide reductase. Lower temperature, higher DO level and acidic pH hinder the second and the fourth steps in the denitrification process.[30] Application of an anoxic MMBR as a wastewater treatment system is a better option due to its efficient performance, less pH sensitive nature and low operational cost. Nitrate is present in many industrial wastewaters (coke oven effluent, petroleum refinery effluent, pulp and paper mill effluent) and its removal is crucial because of its toxic nature. Sahariah and Chakraborty (2012) used an anoxic fed-batch moving-bed reactor to remove the thiocyanate and phenol from coke oven wastewater and found that removal of thiocyanate increases with increasing nitrate concentration in the influent.[28] Mallick and Chakraborty, 2019 have used a fed-batch anoxic reactor to remove phenol, ammonia-nitrogen, nitrate-nitrogen and sulfide from petroleum refinery wastewater and to recover the sulfur from sulfide.[29] However, an anoxic MBBR system is preferentially used as a pre-denitrifying system for better utilization of carbon compounds.

## 15.3 Factors Affecting Reactor Performance

### 15.3.1 Carrier Filling Fraction

The carrier filling fraction is one of the design parameters that needs to be considered before designing an MBBR. The filling factor means the volume of carrier filled over the total volume of the reactor. The filling fraction should be $<70\%$.[18,20] The hydrodynamics of the MBBR is affected by a high filling fraction which ultimately hampers the system performance. The mixing efficiency is decreased by increasing the carrier filling fraction.[20] A significant quantity of the biomass in the carrier medium is maintained by the collision between the medium and the shear that arises due to the medium. This allows the microbes to utilize the inner surface area as an effective specific surface area for their growth. The effective utilization of the inner surface area of the medium is an important design parameter for the efficient operation of an MBBR system. Higher filling fraction (*i.e.* >67%) may retard the upward rolling pattern of water in an MBBR system.[5] Zhang *et al.* (2016) studied the effect of filling percentage (*i.e.* 10, 20, 30%) of carrier material (sponge cube) on the nitrification and the denitrification rate of an MBBR system operated in an aerobic environment.[17] The results revealed that the removal of total nitrogen and ammonia-nitrogen is quite insignificant when the filling percentage is increased from 20% to 30%. The optimum filling fraction is considered to be 20% for nitrification and denitrification. Denitrification rate is affected more by the filling fraction. Therefore, a larger filling fraction may not favour a higher transportation rate of the substrate in the reactor. The reason for the lower removal rate at higher filling fraction is the reduction in the suspended biomass concentration in the MBBR, which plays a vital role in the enzymatic hydrolysis and bio-flocculation.[18] Hence, the filling fraction is an important operational parameter of an MBBR system.

### 15.3.2 Dissolved Oxygen Level

DO level is an important factor for immobilized biomass rather than suspended biomass. However, a high DO level is required to avoid the diffusion limitations of the organic/oxygen in the inner layer of the biofilm and it also helps in the movement of the carrier materials throughout the reactor. In particular, the DO level in the reactor is the rate-determining step for the nitrification reaction. In an MBBR the DO concentration should be >2 mg $L^{-1}$ for the effective removal of organic matter working under aerobic conditions.[21] Greater bubble size may create more turbulence in the system, although on the other hand it decreases the DO level, whereas very smaller size air bubbles may not favour the floating of carrier material. Therefore, emphasis should be given to the design of the air diffuser to achieve suitable oxygen transfer efficiency, considering the important role of DO in the MBBR. McQuarrie and Boltz (2011) explained the advantages of a coarse-bubble diffuser: it less prone to scaling and fouling and requires low maintenance.[22] Proper oxygen supply and adequate movement of the carrier material in the reactor can avoid the biofilm sloughing from the carriers.

### 15.3.3 Biofilm Formation

Biofilm is defined as a layer-like aggregation of microbes with extracellular polymeric substances (EPS) attached to the inert carrier medium.[19] The microbial communities present in the biofilm will share the same environment with each other. The EPS make a significant contribution to biofilm development. The EPS produced by the extracellular enzymes protects the bacteria from antimicrobial agents and against the adverse effect of the environment. The EPS possess sorption ability which helps absorb and dissolve particulate matter from the outer environment. The EPS matrix is constituted of protein, lipids, polysaccharides, humic acids and nucleic acids. Water is the key component of the biofilm that helps in the transfer of the nutrients into the biofilm matrix. Biofilm formation and growth follows five steps: initially, attachment of the planktonic bacterial cells to the surface of the carrier medium due to van der Waals forces and weak electrostatic forces, adhesion of cells and formation of microcolonies, EPS development, and maturation of the biofilm and detachment of biofilm.[33] Microcolonies are comprised of EPS material (*i.e.* 75–90%), which can vary based on the participation of the bacterial species in biofilm formation.[23]

### 15.3.4 Characteristics of the Carrier Material

The possession of a buoyant carrier material plays a vital role in the application of the MBBR system. The rate of substrate transfer can be increased by developing a high specific surface area-based carrier medium, which is an advanced feature of MBBRs as compared with the conventional activated sludge treatment process. Therefore, the loading rate per carrier area is a crucial design parameter in MBBR (kg COD/m$^2$ day) operation.[24] Recently, different types of carrier media have been used in MBBR systems, such as polyurethane foam, kalden K1 media, biochip, ceramic biocarrier, low-density polyethylene and polypropylene, integrated low-density polyethylene–polypropylene *etc.*[7,8,19,26] The geometric shape, size and the selection of the material for the construction of the carrier medium should be done carefully in order to achieve a high specific surface area which has a direct impact on reactor hydrodynamics. However, the conventional approach used to design the larger surface area-based carrier materials may also lead to thicker biofilm growth, which may adversely affect the process parameters of the MBBR. Bassin and Dezotti, (2018) and Arbagol *et al.* (2020) discussed the design of Z type carrier media covered with grid to overcome the clogging problem by reducing excess biofilm growth.[19,25] The excessive biomass growth on Z type carrier media can be controlled by the abrasion caused by the collisions and hydraulic shear force acting on the biofilm. In a study by Bassin and Dezotti, two different types of carrier media (kalden $K_1$ medium and mutag biochip) were used in two MBBRs to investigate the effect on the attached biomass.[19] They concluded that along with the specific surface area, the size, shape and surface area should considered for the attaining better performance. Arbagol *et al.* (2020) has done a comparative study on the impact of different types of carrier media (Z-200, Z-400 and $K_5$) to restrain the biofilm.[25] He observed that thinner biofilm is formed on Z type carrier media compared to $K_5$ media, due to the higher turbulence caused by the aeration which ultimately affects the reactor kinetics. The Z type carrier medium is also able to maintain the biofilm thickness within its maximum predefined values. The physical properties of the carrier medium has significant effect on the biofilm thickness. At an inclination angle of 30–45° a stable thin biofilm layer can form.[20] Therefore, the appropriate carrier geometry can be predicted through computational fluid dynamics or by mathematical modelling, which facilitates the better mass transfer.

### 15.3.5 Hydrodynamics of the MBBR

Transportation of substrate and oxygen into the microbial cells accumulated inside the biofilm is a rate-limiting step in an MBBR, because the densely packed microbial biofilm restricts the flow of fluid into the interior region of the biofilm. Therefore, the rate of diffusion is slow and a concentration gradient may be generated in the biofilm. The study of bulk liquid hydrodynamics is very import for the effective design of an MBBR system. The hydraulic flow velocity is affected by the carrier shape and size and the turbulence caused by mixing. The chaotic motion of the carrier materials is caused by turbulence in the reactor, which promotes the growth of new biomass by sloughing of dead biomass. The required turbulence can be maintained through the fluid velocity in order to achieve better removal performance. A tracer study is generally carried out to check the hydrodynamic characteristics (stagnant zone, flow path and channelling) and the mixing behaviour of an MBBR.[19,34] It also helps to know the impact of increasing the filling fraction on the hydraulic regime of the reactor.

## 15.4 Recent Development in MBBR Systems

### 15.4.1 Development of Carrier Media

The carrier medium plays an important role in MBBR performance as discussed in Section 15.3.4. Therefore, to maintain uniform biofilm thickness is essential for maintaining the hydrodynamic conditions of the MBBR. Many recent developments are based on the development of carrier media for the MBBR system. Sonwani *et al.* 2019 developed modified carrier media by integrating two polymeric materials such as low-density polyethylene and polypropylene and polyurethane foam integrated with polypropylene for treating naphthalene containing wastewater.[26] They also performed a comparative study on the modified carrier material with simple polyurethane foam and concluded that the modified carrier medium shows the better removal efficiency for naphthalene. Z type carrier material was also introduced to get the desired biofilm thickness on the outside protected area of the carrier medium. Arbagol *et al.*, 2020 have performed a comparative study on the Z-200, Z-400 and $K_1$ media. The Z-200 and Z-400 are Z type carrier materials having different grid height.[25] Elliott *et al.*, 2017 explained the application of 3D printing technology in complex media design to get ultra high specific area with biomimetic shape.[31] They concluded that media can perform well in a heterogeneous flow environment. The newly designed carrier media using 3D printing technology are not appropriate for the industrial application because of their high production cost.

## 15.5 Merits and Demerits of the Available Moving Bed Biofilm Systems

Clogging of the bed is the major concern for fixed-bed biofilm systems which is not the case with MBBRs. Therefore, periodic cleaning is not required in the MBBR system. The system footprint is reduced due to its compact nature. The adhered biofilm is highly resistant to shock loading and toxic conditions. Sludge recirculation is not required in an MBBR.

Similarly MBBRs also possess some operational drawbacks such as higher energy is required in the case of aerobic an MBBR for external aeration. The feed pipe and carrier-retaining sieve becomes blocked due to excessive growth of the biofilm. The carrier materials may be destroyed due to the toxicity and high air flow in the system. Sometimes chemical scaling may occur on the carrier medium due to the presence of mineral salts in the wastewater, hence, the carrier material becomes heavier and settles at the bottom of the reactor, which may create a dead zone in the reactor.[32]

## 15.6 Conclusion and Future Perspectives

The MBBR system is a promising and widely acceptable wastewater treatment technique to treat different types of wastewater. MBBRs maintain higher biomass in comparison to the suspended growth process, with smaller footprint. Literature revealed that the single MBBR system is not sufficient for the treatment of industrial wastewater because of its heterogeneous nature. In future, more investigation is needed on treatment of industrial wastewater by MBBRs. As a result, the MBBR system is usually integrated with different biological treatment methods or physicochemical treatment methods to deal with real wastewater. Most research is focused on the removal of single pollutants or mixtures of two or three pollutants from the synthetic wastewater, which is quite different from real industrial wastewater. Hence, the results of synthetic wastewater containing single, and binary mixtures cannot be generalized for the treatment of industrial wastewater where multiple parameters affect wastewater characteristics. Future research should be conducted by considering all probable parameters and the overall range of pollutants present in wastewater. Process modification and addition of innovative accessories to speed up the system performance should be analysed carefully from economic and sustainability points of view.

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## CHAPTER 16

# *Recent Advances in the Biological Treatment of High-salt Wastewater*

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## 16.1 Introduction

It is highly desirable to develop advanced technologies to treat high-salt wastewater to address the challenging water shortage issues.[1] High-salt wastewater refers to wastewater containing organic matter and dissolved solids with a total content of >3.5%,[2] mainly produced from industrial sectors like chemical production, petroleum, printing and dyeing, and some enterprises even directly using seawater for process production.[1,2] High-salt wastewater features high salinity, high chemical oxygen demand (COD), strong acidity or alkalinity, high toxicity, complex chemical composition, and poor biodegradability.[3] Although a suitable concentration of

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

inorganic salts is necessary for microorganism growth, a high concentration of inorganic salts will significantly inhibit their activity, leading to a decline in the biological efficacy toward the treatment of high-salt wastewater.[4] Similarly, the use of physical–chemical treatment for high-salt wastewater does not yield improved treatment efficiency for organic matter removal compared with biological treatment, but does lead to increased operation costs.[2,5] Further, if discharged directly into the environment without sufficient treatment, these wastewaters can cause serious pollution to soil, surface waters, and groundwaters.[6] For these reasons, high-salt wastewater is considered as one of the most difficult-to-treat industrial wastewaters.

The existing treatment methods of high-salt wastewater can be divided into physical–chemical methods and biological methods. In general, although effective, these physical–chemical processes face several evident drawbacks, such as high cost and secondary pollution. Alternatively, biological methods may serve as a promising technology for the treatment of high-salt wastewater due to its low-input requirements, cost-effectiveness and environmental-safety.[7] It is well known that inorganic salts play an important role in enzymatic reaction and regulation of cell osmotic pressure during the growth of microorganisms.[8] However, high concentrations of inorganic salts can inhibit microbial growth. Hence, in the past, high-salt wastewater was diluted directly to achieve a salt mass fraction of <1% for microbial growth, which led to the waste of water resources, and increased investment and operation costs.[9] Currently, the treatment of high-salinity wastewater mainly focuses on direct biological treatment, rather than desalination and dilution.[1,6] Therefore, in addition to finding a suitable bioreactor for the treatment of high-salt wastewater, the research on purification and enrichment of halophilic microorganisms is also of crucial importance. In this chapter, some advances and developments with regard to the application of various biological treatment technologies for high-salt organic wastewater treatment in recent years are systematically reviewed. Meanwhile, the application of bioaugmentation technology and the research into halophilic microorganisms are described in detail. Moreover, potential applications of biological technologies in high-salt wastewater treatment are also discussed.

## 16.2 Application of Biological Treatment Technology

Similar to other biological treatment processes for sewage and wastewater, the biological treatment of high-salt wastewater includes adjustment systems, dosing systems, anaerobic systems, aeration systems, secondary settling tanks, sludge return and dehydration systems, and advanced treatment systems (see Figure 16.1). These processes mainly include a conventional activated sludge method, an anaerobic treatment method, a sequencing

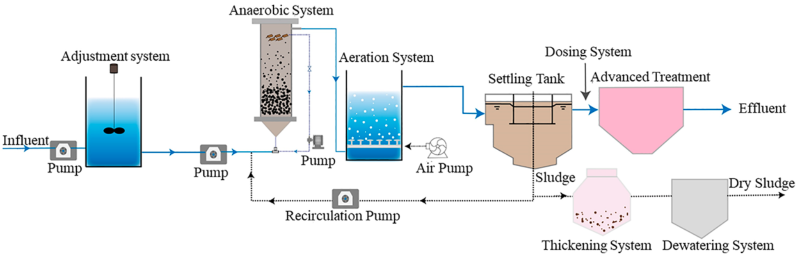

**Figure 16.1** Schematic diagram of biological treatment process for high-salt wastewater.

batch reaction (SBR) system, aerobic granular sludge, and cultivation of halophilic bacteria. These biological treatment technologies can be subdivided into anaerobic and aerobic treatments.

## 16.2.1 Aerobic Treatment of High-salt Wastewater

Although high salinity strongly inhibits aerobic biological efficacy, it is possible to make aerobic activated sludge moderately acclimated to high salinity.[9,10] Microorganisms can come into full contact with wastewater under aeration conditions, so that aerobic microorganisms can degrade organic matters in the wastewater. According to Hamoda *et al.*,[11] the salt concentration of high-salt wastewater is in the range 10–30 g $L^{-1}$ and the sludge retention time is in the range 3–20 d. The results showed that high-salinity wastewater has a significant inhibitory effect on uncultivated activated sludge. However, with the extension of culture time, the sludge concentration increased significantly, and the microbial community composition changed significantly as well. Since salinity has a great impact on microbial activity, it is important to cultivate salt-tolerant microorganisms for the treatment of high-salt wastewater. When treating high-salt fish canning wastewater by inoculating the microorganisms into an SBR, Capodici *et al.*[12] found that the autotrophic or heterotrophic microorganisms in the reactor exhibited high activity over 100 days of operation under conditions of 30 g $L^{-1}$ influent NaCl concentration. When investigating the efficiency of nitrogen removal in an aerobic SBR treating mustard tuber wastewater with salt concentration in the range 30–70 g NaCl/L, Wang *et al.*[13] found that special halophilic functional bacteria with multiple nitrogen removal pathways could be enriched within the reactor. The results showed that the aerobic process can adapt to ultra-high salt concentrations up to 70 g NaCl/L in the laboratory-scale. However, the operation of conventional aerobic wastewater treatment processes may be affected when the chlorine concentration exceeds 5–8 g $L^{-1}$ in actual applications. Table 16.1 summarizes the application limits of salt concentration in several treatment processes.[14,15] In general, the cultivation of microorganisms is achieved by slowly increasing the salt loading, thus making them adaptable to the actual

**Table 16.1** The limited salt concentrations of several aerobic treatment processes.

| Process | Sludge treatment | Activated sludge method | Biological filter | Two-stage contact oxidation method |
|---|---|---|---|---|
| NaCl (%) | 0.5–1 | 0.8–0.9 | 1–4 | 2.5–3.5 |

environment. In addition, the fluctuation of salt concentration has a great influence on the activities of aerobic microorganisms. Large fluctuations in salt concentration will lead to the inactivation of microorganisms, instability of the system and deterioration of effluent quality.[16] Hence, the pretreatment of wastewater is crucial for aerobic processes. In such cases it is necessary to strictly control the concentration and proportion of salt in the raw waters to secure a stable performance of aerobic processes.

### 16.2.2 Anaerobic Treatment

Many previous studies have confirmed that anaerobic biomass is more sensitive to salt toxicity than aerobic biomass.[9] Nonetheless, anaerobic treatment still has several advantages compared with aerobic processes, including limited energy consumption, reduced sludge yield, and the possibility to handle higher volumetric loading rates. Lefebvre *et al.*[17] found that the performance of the anaerobic reactor was closely correlated to the type of substrates under high-salt conditions. Methanogens can adapt to 60 g NaCl/L using ethanol as a substrate, while their tolerance for NaCl decreased to 10 g $L^{-1}$ using distillery vinasse. Even with an increase in NaCl concentration, microbial diversity can still remain at a high level. Rovirosa *et al.*[18] evaluated the performance of a laboratory-scale downflow anaerobic fixed-bed reactor for synthetic piggery wastewater diluted in 15 g $L^{-1}$ saline, and found that the COD removal efficiency exceeded 90% at a hydraulic retention time (HRT) of 96 h, but the COD removal efficiency decreased by 68% at a HRT of 12 h. According to previous studies,[19] a sodium concentration exceeding 10 g $L^{-1}$ strongly inhibits methanogenesis. In addition, additional operational and safety issues may arise due to the presence of sulfate-reducing bacteria in the treatment of sulfate-rich salt-containing wastewater in anaerobic treatment systems.[20] Sulfate is reduced to toxic sulfides by sulfate reducing bacteria in the presence of organic matter. The activity of methanogens in anaerobic systems can be inhibited by an increase in hydrogen sulfide, resulting in a decrease in pH and a deterioration in reactor efficacy. Sulfide is an inhibitor of anaerobic microorganisms at concentrations >300 mg $H_2S$/L.[21] Ferrous ions are commonly added into anaerobic systems to precipitate sulfides, thereby reducing the inhibition of methanogens by sulfide.

### 16.2.3 Combined Anaerobic–Aerobic Treatment Technology

Because of the complexity of industrial wastewaters, a single anaerobic or aerobic treatment process cannot meet the requirements for high-salt organic wastewater. An anaerobic–aerobic combined process integrates the

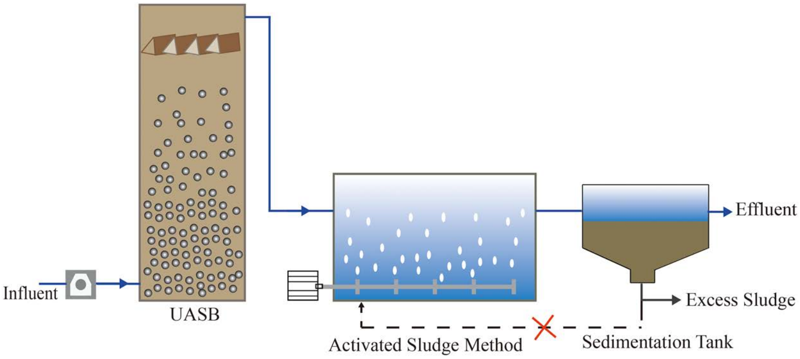

**Figure 16.2** Schematic diagram of the combination of up-flow anaerobic sludge bed (UASB) and activated sludge process. Adapted from ref. 9 with permission from Elsevier, Copyright 2006.

advantages of anaerobic and aerobic processes, with the aim of achieving efficient removal of organic matter. Furthermore, the treatment of high-salt organic wastewater with a combined process can achieve higher salinity tolerance of the system, thus improving the system's stability.[22] Lefebvre *et al.*[9] pointed out that a combination of an up-flow anaerobic sludge bed (UASB) and an activated sludge process showed enhanced performance towards the treatment of high-salt wastewater (see Figure 16.2). The particularity of the combined system lies in the sludge recirculation, which makes the hydraulic and solids retention times similar. In addition, the COD removal efficiency of the combined process reached up to 96%. On the other hand, the combined process makes it possible to address biological organics and nitrogen removal from saline wastewater. According to Kargi and Uygur,[23] COD and nitrogen removal efficiencies in the combined process reached 73% and 51%, respectively, without the addition of *Halobacter* strain at a salinity of 5%. Furthermore, adopting the combined process to treat high-salt organic wastewater can greatly reduce the cost of the treatment system.

## 16.3 Bioaugmentation Technology

### 16.3.1 Sludge Granulation Technology

Due to the poor settleability of flocculent sludge, conventional activated sludge methods for wastewater treatment still face several disadvantages, such as lower biomass concentration and larger land area requirement.[24] Compared with the suspended biomass process, biofilm-based technologies have several advantages, including lower footprint and higher biomass concentration.[25] Figure 16.3 summarizes several bioaugmentation technologies for the treatment of high-salt wastewater. As one of the biofilm-based technologies, sludge granulation technology is considered to be an effective method to mitigate the negative effect of high

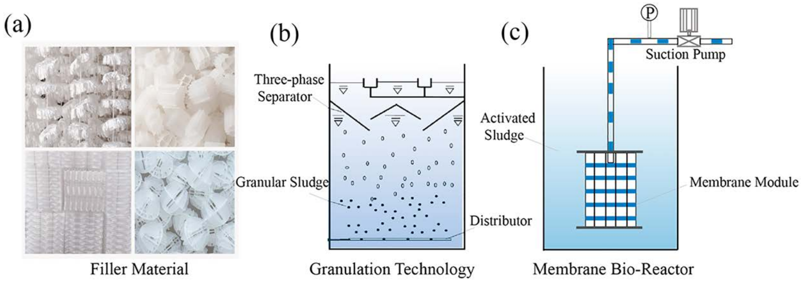

**Figure 16.3** Schematic diagram of bioaugmentation technologies: (a) bio-reactor filler material, (b) granulation technology, and (c) membrance bio-reactor.

salt concentrations on microbial activity in biological reactors. Moreover, with in-depth understanding of the mechanism of microbial metabolism and the structure of microbial aggregates, many efficient and stable bioreactors have been developed and designed to treat various types of wastewater.

In addition, the formation of granular sludge in these reactors is equally important. With high mechanical strength and weight, a high sludge concentration can be obtained in the bioreactor, and achieve decoupling of sludge retention time and HRT. By studying the influence of high salinity on microbial granule formation in a UASB system, Sudmalis *et al.*[26] found that stable granule formation is possible at a salinity level up to 20 g $Na^+$/L. In addition, aerobic granular sludge technology has also been and studied. Because of its spherical structure, anaerobic bacteria and aerobic bacteria can be distributed within the granular sludge simultaneously, which means that the aerobic granular sludge process makes it possible to address biological nitrogen and carbonaceous pollution in saline wastewater treatment.[27] By evaluating the effect of salt on the main conversion processes in an aerobic granular sludge process, Pronk *et al.*[28] found that simultaneous removal of organic matter and nitrogen can be accomplished at 20 g NaCl/L. However, when the salt concentration gradually exceeded 20 g $L^{-1}$, the nitrite oxidation process was completely inhibited. It is undeniable that anaerobic granulation technology is more applicable than aerobic granulation technology in actual wastewater treatment.

## 16.3.2 Biomass Immobilization Technology

Immobilization technology is recommended for saline wastewater treatment because of its high biomass concentration, high-quality effluent and low sludge production.[27] Moreover, higher biomass concentration improves the adaptability of microorganisms to increased salinity. Compared with simple anaerobic treatment, an anaerobic membrane bioreactor is a kind of immobilized technology, which effectively combines anaerobic treatment with membrane filtration, and is suitable for industrial and municipal wastewater treatment.[29] In the treatment of high-salt wastewater, membrane fouling, dissolved methane and microbial activity can be affected by the water salinity.[30] By studying the performance of an anaerobic membrane bioreactor for treating synthetic wastewater with various concentrations of NaCl (0–40 g $L^{-1}$), Chen *et al.*[30] found that the COD removal efficiency decreased from 96.4% to 77.7% as the salt concentration gradually increased from 0 to 40 g NaCl/L. Under elevated salt stress, the content and composition of soluble microbial products and extracellular polymer substances changed significantly, which can indirectly affect membrane fouling behaviour. After assessing the effect of increased salinity on the treatment of phenolic wastewater in an anaerobic membrane bioreactor, Munoz Sierra *et al.*[31] found that the removal efficiency of phenol could reach up to 99.9% when the salinity increased from 8 $Na^+$/L to 14 $Na^+$/L with a concentration gradient of 2 $Na^+$/L, whilst the performance of an anaerobic membrane bioreactor was hardly affected by salinity fluctuations in its long-term operation. Although there have been extensive studies on the treatment of saline wastewater by anaerobic membrane bioreactors, the applications of anaerobic membrane bioreactors in the treatment of high-salt wastewater are rather limited. The above problems are mainly attributed to membrane fouling. The physical and biochemical properties of activated sludge can be affected by high-salt wastewater, which can negatively influence membrane permeability and reduce biodegradability.[32] Moreover, in order to address the inhibition of high salinity on cell viability, microorganisms tend to secrete a large amount of extracellular polymeric substances (EPS). However, those free EPS are the key substances causing membrane fouling in MBR system.

## 16.4 Contaminants Removal Under High-salt Stress

### 16.4.1 Removal of Organic Matter

Organic matter in saline wastewater can be removed by activated sludge adapted to saline conditions, but the microorganisms are not effective in the treatment of saline wastewater at salinity exceeding 3%, because these microorganisms are sensitive to changes in ion concentration.[33] The biodegradation rate of organic compounds decreased with increased salt concentration. Lefebvre *et al.*[10] observed that the COD removal rate of a bioreactor was not affected by sudden exposure to 5–30 g NaCl/L, but a shock salinity loading up to 50 g NaCl/L could cause the COD removal rate to drop from 95% to 77%. Aslan and Sekerdag[34] investigated the effect of salt concentration on the performance of a UASB reactor, and found that the COD removal efficiency deteriorated significantly with increasing salinity from 0 to 50 g NaCl/L. In contrast, Tomei *et al.*[35] investigated a hybrid bioreactor-operated polymer tube for the biological treatment of saline wastewater, and achieved 90% organics removal in a synthetic saline wastewater containing 100 g NaCl/L. In addition, Corsino *et al.*[27] stated that both COD and BOD removal efficiencies were 90%, and were not affected at salinities up to 50 g NaCl/L by aerobic granular sludge, which was attributed to the excellent adaptability of aerobic granular sludge under adverse environmental conditions. The above results show that salinity has different effects on the removal of organic matter depending on the existing forms of sludge, metabolic substrates and reactor structures.

### 16.4.2 Denitrification of High-salt Wastewater

The removal of nitrogen in wastewater involves many microorganisms, including nitrite bacteria, nitrifying bacteria and denitrifying bacteria. The nitrification and denitrification processes are significantly affected under high salt stress.[36,37] High salt will inhibit the growth of nitrifying bacteria, resulting in a reduced nitrification efficiency. According to Wang *et al.'s*[13] experiment, with an increase in salinity from 3% to 7%, the total nitrogen removal rate decreased from 94.4% to 89.9%, and the ammoxidation functional microorganisms, nitrite bacteria or nitrifying bacteria, were severely inhibited. In addition, it is found that nitrifying bacteria are more sensitive to salinity than nitrite bacteria.[38] Nitrite accumulation occurs during the nitrification process as salt concentration increases gradually. In other words, short-range nitrification and denitrification can be achieved simultaneously in the treatment of high-salt wastewater, which can reduce oxygen consumption in the nitrification stage and organic material consumption in the denitrification stage. Most of the studies show that denitrification efficiency decreases with an increase in the salinity of the influent.[27] However, Yoshie *et al.*[39] found that the denitrification activity at a salinity of 10% was higher than that at a salinity of 1%. This is mainly due to three issues: (1) the different structure and experimental conditions of the system;[40] (2) the diversity of system microorganisms;[41] and (3) different dosing methods, such as one-time addition and batch addition.[16]

## 16.5 Halophilic Microorganisms for the Treatment of High-salt Wastewater

### 16.5.1 Halophilic Microorganisms

The applications of conventional biological treatment for high-salt organic wastewater have been severely limited because the high concentration of salt can inhibit the growth of microorganisms. Therefore, it is particularly important to strengthen the study on halophilic microorganisms that are capable of growing and carrying out their metabolic functions under high salinity conditions. Halophilic microorganisms have great metabolic diversity and include aerobic heterotrophs, denitrifies, sulfate reducers, and methanogens. Currently, the halophilic microorganisms have great potential in bioremediation processes due to their ability to degrade organic matter. According to the tolerance of microorganisms to salt concentration, they can be classified into four categories: non-halophilic bacteria, slightly halophilic bacteria, moderately halophilic bacteria, and extremely halophilic bacteria (see Figure 16.4). Halophilic bacteria have a special physiological structure and contain special substances in the cells that enable them to grow at high-salt concentrations. Table 16.2 lists the typical microorganisms mentioned in the treatment of saline wastewaters with the aim of comparing their salinity tolerance. For halophilic bacteria, the concentration of ions in and out of cells is basically equal, which can prevent the dehydration of cells in the presence of extracellular high-salt solution.[42] Moreover, halophilic bacteria have the ability to concentrate potassium ions and resist sodium ions, which means that there will not be too many sodium ions entering the cells in a high-salt solution dominated by sodium ions.[9] In addition, potassium plays a more important role in the physiological activity of halophilic bacteria than do sodium ions, so halophilic bacteria can maintain stable cell structure and grow well in a high salt solution.

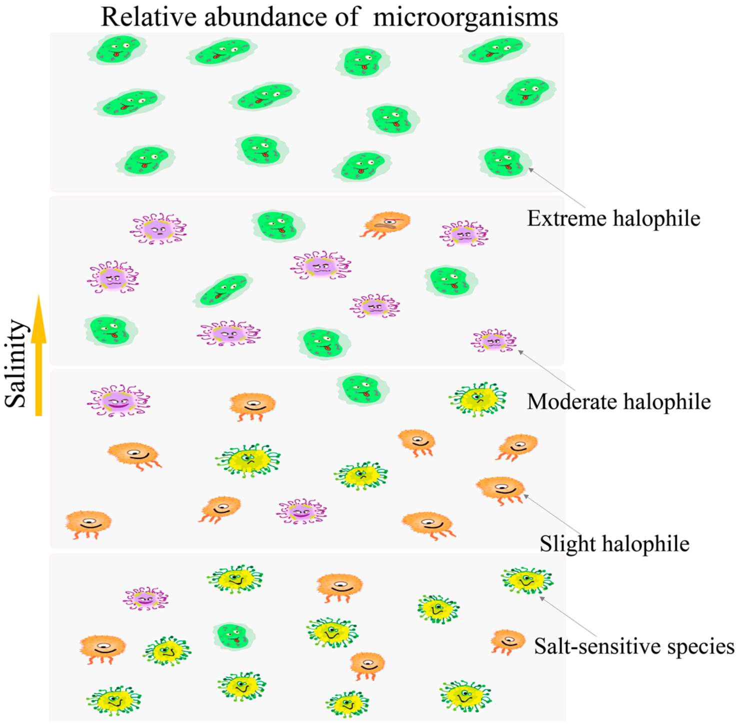

**Figure 16.4** Schematic diagram of the relative abundance of microorganisms with an increase in salinity.

**Table 16.2** List of the typical halophilic microorganisms for saline wastewater treatment.

| Categories | Salinity | Microorganism | Reference |
|---|---|---|---|
| Non-halophilic bacteria | <2% | Common microorganisms and most of freshwater microorganisms (*i.e. Firmicutes*, *Planctomycetes*, *Proteobacteria*) | 43 |
| Slightly halophilic bacteria | 2–5% | Most marine microorganisms (*i.e. Arthrobacter* sp., *Desulfobacter halotolerans*) | 44 |
| Moderately halophilic bacterium | 5–20% | *Vibro costicola*, *Paracoccus halodenitrificans* (*i.e. Pseudomonas putida*, *Staphylococcus* sp.) | 45 |
| Extremely halophilic bacteria | >20% | *Halobacterium salinarium*, *Halococcus morrhuae* | 1 |

### 16.5.2 Halophilic Microorganisms Applied in Wastewater Treatment

It is well known that the biodegradability of organic matter by microorganisms might be decreased under high-salt conditions, but halophilic microorganisms can address these limitations due to their special biological properties. Moreover, halophilic microorganisms exhibit good biodegradability of various pollutants including azo dyes, phenols and hydrocarbons. Tian *et al.*[46] investigated the isolated halophilic bacterium *Halomonas* sp. strain from textile industrial wastewater for the biological treatment of saline dyeing wastewater and found that decolourization of azo dyes could be effectively achieved at a salinity of 10%. However, azoreductase gene expression in *Halomonas* sp. was restrained at high NaCl concentrations. Hasanzadeh *et al.*[33] evaluated the feasibility of using walnut shell as a biocarrier for the immobilization of isolated halophilic microorganisms in an MBR system for the treatment of oilfield-produced water, and found that halophilic microorganisms performed satisfactorily in up to 90 g $L^{-1}$ total dissolved solids. The use of walnut shell as an inexpensive and accessible adsorbent-carrier was conducive to the immobilization of isolated halophilic microorganisms. Although halophilic microorganisms have a strong tolerance to high-salt concentrations, salinity fluctuations can affect their activity of halophilic. Corsino *et al.*[42] compared the performance of contaminant removal between halophilic granular and flocculent sludge in withstanding short- and long-term salinity fluctuations, and found that a significant loss in organic matter removal occurred in bioreactors after drastic and moderate salinity shocks. However, stable performances were still achieved 18 days after the salinity shock in the reactor with the halophilic granular sludge, and after 27 days in the reactor with the halophilic flocculent sludge. In addition to the function of halophilic bacteria to remove organic matter, many halophilic microorganisms have the ability to remove nitrogen. Duan *et al.*[47] isolated a novel halophilic bacterium, *Vibrio diabolicus SF16*, capable of heterotrophic nitrification–aerobic denitrification, and the average removal efficiency of ammonia and nitrate reached 91.8 and 99.7%, respectively. In addition, the performance of halophilic microorganisms in contaminants removal under higher salt stress has been also tested in anaerobic or aerobic conditions: the halophilic microorganisms can grow in both anaerobic and aerobic conditions. Moreover, different halophilic microorganisms have different metabolic pathways for the biodegradation process. Nonetheless, the metabolic mechanism for halophilic microorganisms against high-salt wastewater is not well known. In the future, more studies should be focused on the metabolic mechanisms of halophilic microorganisms.

## 16.6 Summary and Future Prospects

Biological technology is the most widely used wastewater treatment process. However, it is difficult for ordinary microorganisms to adapt to high-salt conditions, which limits the application of biological treatment in high-salt wastewater. Therefore, it is necessary to develop advanced biotechnologies toward the efficient treatment of high-salt wastewater.

Currently, there are many kinds of pretreatment technologies for high-salt wastewater, but they suffer from high cost. In order to achieve high-efficiency and low-cost operation of wastewater treatment, the development of future pretreatment technology should be appropriately combined with biological treatment systems. Future research should focus on assessing the biochemical feasibility of high-salt wastewater after pretreatment, including anaerobic and aerobic systems, due to significant variation in the quality of the wastewater. Although activated sludge can tolerate a certain level of salinity, the performance of biological systems can still be affected by salt concentration and salt species within the wastewater, which means that the analysis of salt components and the real-time monitoring and control of salt concentration are of vital importance in terms of the treatment of different types of high-salt wastewater.

Previous studies have focused on the biological treatment of high-salt wastewater with specific water quality. Considering the complexity and variability of the practical applications, there are still many problems to be solved urgently, so as to further expand the pilot-scale system on the basis of existing experimental results. More in-depth understanding on the degradation mechanism of halophilic bacteria is still a hot topic in the treatment of high-salt wastewater. In addition, the cultivation time of halophilic microorganisms for the treatment of high-salt industrial wastewater by activated sludge processes is also very long. Alternatively, directly screening and isolating halophilic bacteria from a high-salt environment is a fast and effective method to shorten the cultivation time of halophilic bacteria. Moreover, investigation of the functions of complex halophilic microorganisms is of great significance. Along with the development of molecular biology technology, the functions of halophilic bacteria need to be studied in detail, and the relationship between halophilic bacteria and biological system performance should be systematically evaluated, so as to reveal the biodegradation mechanism of high-salt wastewater and provide theoretical guidance for biological treatment of high-salt wastewater. Therefore, the use of these halophilic microorganisms is recommended in the treatment of high-salt wastewater.

## Acknowledgements

This work was supported by the Shanghai Science and Technology Committee (No. 19DZ1204903), the National Natural Science Foundation of China (No. 51909034), and the Ecological Environment Protection and Restoration of Yangtze River in Zhoushan (No. SZGXZS2020068). H.X. thanks the Graduate Student Innovation Fund of Donghua University (CUSF-DH-D-2020071).

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CHAPTER 17

# Mineralization of Recalcitrant Pollutants from Wastewater by Solar Nano-photocatalysis

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## 17.1 Introduction

The present era is notorious for the pollution and devastation of water resources. The effective handling of industrial and domestic wastewater assures economic growth and progress. The effluents of textiles, pharmaceutical, pesticides, fertilizers, paper and pulp industries are the main culprits polluting water bodies all around the world. These pollutants are not only toxic, but also cause aesthetic problems, thus their treatment and removal from wastewaters is critical. The techniques employed for the treatment of wastewater involve their physical and chemical removal *via* coagulation/flocculation, adsorption and membrane processes. However, with these techniques, the risk of toxicity due to the dumping of hazardous waste persists. The significant factors which contribute and influence the remediation of wastewaters include total suspended solids, colouration, turbidity, and most

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

causative non-biodegradable substances. Therefore, there is a critical demand for devising and implementing efficient and cost-effective treatment technologies for improving water quality.[1]

Ever-increasing industrialization and the excessive use of chemicals pose serious environmental threats and also consume a large amount of fossil fuels. These problems have stimulated scientists to carry out extensive, innovative research into alternative energy sources, especially furthering exploiting the potential of solar energy. The extensive use of fossil fuels in various industrial and domestic areas has overburdened the environment and also caused severe environmental pollution and an energy crisis, which are considered major challenges of the present era. Among many available advanced technologies, heterogeneous photocatalysis, using solar light as a radiation source in combination with nanomaterials and semiconductors, is the most advantageous. Regeneration of solar energy and its unlimited availability have made it one of the most promising strategies for resolving environmental issues as well as the energy crisis, thus solar photocatalysis has gained much attention in recent years.[2]

This chapter encompasses the treatment of some selected effluents through photocatalytic approaches. The chapter will proceed from the basic introduction of catalysts and catalysis followed by a detailed account of nano-photocatalysis and its implementation to treat recalcitrant pollutants from various industrial effluents.[3–8]

### 17.1.1 Catalysts and Catalysis

Catalysts facilitate reactions by accelerating the rate of the reaction by lowering the activation energy, and also determine the feasibility of a reaction to take place. The processes in which catalysts are employed to speed up the rate of chemical transformations in a reaction and are recovered afterwards, is called catalysis. Catalysts are classified on the basis of the reaction phase of the reaction mixture, *i.e.* homogeneous (same phase) and heterogeneous (different phase). Catalysis is a critical area in chemistry, playing crucial roles ranging from laboratory-scale processes to industrial level. Berzelius was a pioneer who coined the word "catalysis" in 1836, originating from a Greek word meaning "loosen".[9]

Heterogeneous catalysts are usually classified as conductors of metals and alloys; semiconductors, including sulfides and oxides of various metals; and insulators, including silica and alumina and zeolites. Industrial processes rely on the involvement of the above-mentioned catalysts like oxides of Ti, Zr and Zn, silica phosphoric acid (SPA), polyoxometallates (POMs), hexa-aluminates and many related compounds.[9]

To recapitulate, it could be said that catalysts are the activators of reactions to ascertain absolute transformation of reactants to the desired products. Heterogeneous catalysis plays a pivotal role in different industrial operations, entailing many imperative steps to resolve economic and environmental issues.

### *17.1.1.1 Metal Oxides (MO) as Catalysts*

The most widely used catalysts are the metal oxides and they are comprised of inorganic materials possessing specific attributes and potentials to be used as catalysts. The metal oxides of early 3d transition series have been explored for their catalytic applications in various catalytic processes.[10] There has been phenomenal advancement in MOs in terms of their preparation methodologies and lattice modifications, making them the best substitutes for noble metals in catalytic processes.[11]

The process of heterogeneous oxidation reactions is highly favoured when MOs are used as catalysts owing to their greater stability and surface flexibility under any prevailing reaction conditions without their structure collapsing. The variable oxidation states of the transition metal cations confer on them superlative redox properties on account of their superior electron diffusivity and oxygen anions. The efficiency of MOs depends mainly on how the active sites behave on a crystal surface as $M^{n+}/M^{n+1}$ and these ion pairs serve as an acid–base site. The involvement of the electronic properties of a single MO and mixed metal oxides has led to their successful employment in various catalytic procedures. The importance of redox properties and other related parameters in the fabrication of a mixed MO, the structural attributes of a host MO, and phase co-operation of multi-component catalytic systems and supported catalysts has become very obvious.

The crystal structure of metal oxides shows that the surfaces are terminated by oxide anions ($O^{-2}$) on account of their greater size in comparison to metal cations ($M^{n+}$). This results in the loss of coordination and symmetry of cations and subsequent movement in the bulk of the crystal surface. The unsaturation caused at the surface is compensated for by reaction with water vapour, thus leading to hydroxyl group formation as given in eqn (17.1).

$$\text{Lattice surface } (O^{-2}) + H_2O_{(vap)} \rightarrow \text{Lattice surface } (2OH^{-}) \qquad (17.1)$$

Moreover, there are many defects present at the surface of the MO, including kinks, terraces, steps, *etc.*, which are more prone to environmental exposure, thus they play a seminal role in catalysis. These points of electronic and related extended defects in the structures of MOs can be recognised by their atomic compositions and crystalline phase structures corresponding to electronic probabilities in energy states.[12] The energy zone that indicates if any electronic levels are absent between conduction and valence bands (CB and VB) of atoms or molecules is termedthe band gap. The determination of band gaps in MOs in the most decisive factor to in understanding the catalytic system, especially in determining the position of the top end of the valence band and the bottom end of the conduction band. The catalytic redox properties of electronic levels are directly involved in charge transfer (CT) to or from the catalyst.[13]

### 17.1.1.2 *Intrinsic and Extrinsic Semiconductors*

Intrinsic semiconductors consist of pure MOs without incorporating any dopant or impurity in the lattice. The electrons in the CB are exactly equal to the number of holes present in the VB as given in eqn (17.2).

$$n = n_\mathrm{e} = n_\mathrm{h} = n_0 \exp^{(-\mathrm{EG}/2kT)} \tag{17.2}$$

In the equation, $n_0$ represents a constant; EG stands for the energy gap, also termed the energy of the band gap; $k$ is the Boltzman constant; while $T$ is the temperature.[11] The importance of oxygen vacancies existing at an intrinsic semiconductor surface cannot be taken for granted. They play a credible role in creating active sites, owing to the coordinated bonds of MOs.[14] Since there are large band gaps in most metal oxides, a certain content of impurities is incorporated to generate electronic defects in the semiconductors. This class of MO semiconductors are named extrinsic semiconductors due to their extrinsic defects to generate charge carriers (CC) at localized energy levels to electrically activate the MOs.[15]

A dopant that causes an electronic defect below the CB in the energy level is designated as the donor dopant, due to its ability to provide electrons for the conduction band and increase n-type conductivity. In a donor-doped semiconducting material, the total number of the CC is as shown in eqn (17.3):

$$n_\mathrm{total} = n_\mathrm{e(dopant)} + n_\mathrm{e(intrinsic)} + n_\mathrm{h(intrinsic)} = n_{0\ D}{}^{\exp(-\mathrm{ED}/kT)} + 2n_0{}^{\exp(-\mathrm{EG}/2kT)} \tag{17.3}$$

Unlike the donor dopant, the accepter dopant involves the creation of holes in the VB due to its ability to capture electrons from the VB of MOs, hence, p-type conductivity increases.[11] This fact is illustrated in Figure 17.1.

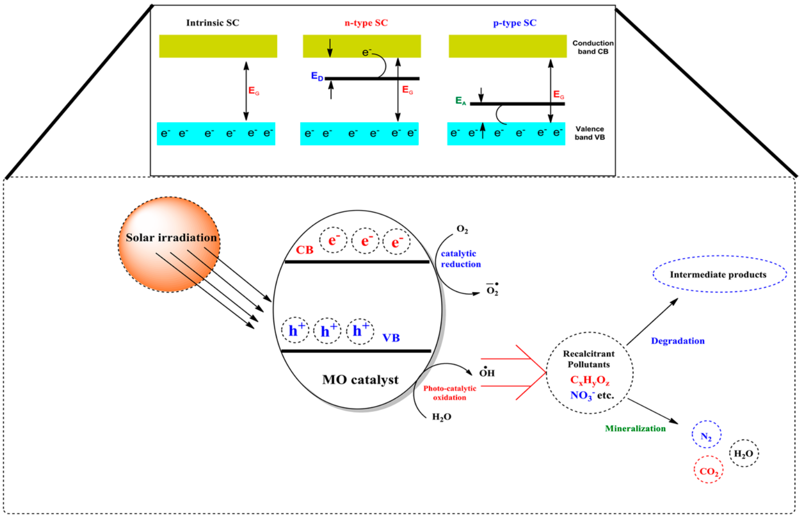


**Figure 17.1** Semiconductors and the mechanism of photocatalysis for mineralization of pollutants.

Heterogeneous catalysis depends on the shape, size and other surface properties of the MO crystals, as it is a surface phenomenon. The density of active sites present on the crystal surface directly depends on the ultimate shapes of catalysts (rods, wires, sheets, discs *etc.*) and crystalline polar faces to impart vital functions in redox reactions. Furthermore, the crystal defects (interstitial atoms, shear planes, vacancies, electronic defects) and the nature of exposed crystal faces are also substantially associated with the efficiency of a catalyst.[16] The solar photocatalytic degradation mechanism of pollutants relies on the number of available active sites on the surface of semiconductor photocatalysts. They render the photocatalyst capable of carrying out oxidation and reduction processes on exposure to solar light.[14]

### 17.1.2 Photocatalysts and Photocatalysis

Photocatalysts are those catalysts capable of catalyzing chemical reactions at ambient conditions of temperature and pressure when irradiated with a stream of suitable energy photons. Therefore, the process that uses light photons and a catalyst in tandem for triggering and speeding up chemical reactions is termed photocatalysis. Thus, it can be defined as a photo-induced reaction that depends on light-driven acceleration of a catalytic process.[17] Photocatalysis belongs to a relatively new science and has gained considerable attention from researchers and environmentalists especially those involved with the principles of green chemistry. Photocatalytic reactions are categorized into two phases (1) homogeneous and (2) heterogeneous.

Photocatalysts have been exploited for numerous applications and have also been employed for the mineralization of the contaminants of wastewater from various sources, owing to their potential for complete degradation of the target pollutants. The contribution of MOs in photocatalysis has been experimentally proven and it depends on surface defects, band gaps and the surface area of polar facets. There are some pre-requisites of an excellent photocatalyst, including its chemical and biological inertness, photo-activity, photo-stability and ability to utilize near UV/visible light, high temperature stability, non-toxicity and cost effectiveness. Oxides of titanium, zinc, zirconium, tungsten, copper, cadmium and cobalt have been explored for their photocatalytic applications and they showed band gap in the UV region $\geq 3.36$ eV ($\lambda = 388$ nm). Such catalysts facilitate and carry out chemical reactions under UV illumination.[18]

Physicochemical reactions involving photocatalysis can be classified generally as follows.

- Transference of pollutants from the bulk phase to the photocatalyst.
- Chemisorption/adsorption of reactants onto the surface of the photocatalyst.
- Adsorbed phase chemical reactions:
  (i) absorption of photons by the photocatalyst
  (ii) generation of photo-induced electrons ($e^-$) and holes ($h^+$)
  (iii) charge transfer (CT) reactions.
- Desorption of the products after degradation reaction.
- Diffusion of final products into the bulk phase.

The mechanism driving photocatalysis actually involves the photo-excitation of electrons ($e^-$) from the VB to the CB of a semiconductor (SC) photocatalyst when irradiated with light (UV; visible or solar radiation). This photo-excitation leaves holes ($h^+$) in the VB (eqn (17.4)). In the presence of photocatalysts in an aqueous medium, holes are trapped by water molecules and generate hydroxyl radicals ($^\bullet OH$) (eqn (17.5) and (17.6)). The probability of photo-generated degradation of organic molecules by $e^-$ either directly (eqn (17.11)) or indirectly by (1) reacting with oxidants ($O_2$), (2) adsorbing on the catalytic surface, or (3) getting dissolved in aqueous medium and reducing it to oxygen superoxide radical anion ($O_2^{-\bullet}$) is given in eqn (17.7).[19] On the other hand, the photo-generated holes oxidize the reacting organic molecules R to $R^{\bullet +}$ (eqn (17.10)). Hydroperoxyl free radicals ($^\bullet HO_2$) are also produced besides other reactive oxidizing species (ROS), which ultimately get converted into hydroxyl free radicals ($^\bullet OH$) when they react with hydride ion ($H^+$) (eqn (17.8)). These $^\bullet OH$ radicals have the ability to reduce or oxidize other organic molecule pollutants through mineralization. After a complete photocatalytic degradation reaction causing mineralization of pollutants, carbon dioxide and water are ultimately produced (eqn (17.9)).

$$SC + h\nu \rightarrow SC\ (e^- + h^+) \tag{17.4}$$

$$SC(h^+) + H_2O \rightarrow SC + H^+ + OH^\bullet \tag{17.5}$$

$$SC(h^+) + OH^- \rightarrow SC + OH^\bullet \tag{17.6}$$

$$SC(e^-) + O_2 \rightarrow SC + O_2^{-\bullet} \tag{17.7}$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \tag{17.8}$$

$$R + OH^\bullet \rightarrow \text{degradation products} \tag{17.9}$$

$$R + h^+_{VB} \rightarrow \text{oxidation products} \tag{17.10}$$

$$R + e^-_{CB} \rightarrow \text{reduction products} \tag{17.11}$$

The majority of organic and inorganic semiconductors have been exploited as efficient photocatalysts in many reactions. The photocatalytic activities of various metal oxide heterogeneous catalysts have gained the limelight in recent years, especially semiconductors with wider band-gaps, such as $TiO_2$, ZnO, $SnO_2$ and $WO_3$. The photon irradiated (sunlight/UV rays) photocatalysts $TiO_2$, ZnO, ZrO and other doped metal oxides and sulfides are proficient at catalyzing gaseous and liquid reactants/pollutants.[10,11,13,14,20,21]

#### 17.1.2.1 Principles of Solar Photocatalysis

The sun is continuously supplying radiation over a wide range of wavelengths and intensities. The electro-magnetic solar radiation impinging on the upper edge of the atmosphere is called extra-terrestrial radiation. The mean integral for the complete spectrum is 1367 W $m^{-2}$ (the solar constant). The various techniques conventionally used for the degradation of colours and natural contaminants are usually costly. As of now, analysts are concentrating on financially effective ways of obtaining energy. The use of solar energy for nano-photo catalysis has gained much attention in recent years due to its easy accessibility and maintainability. Solar light is classified on the basis of energy and 3–5% of it falls in the Ultra Violet range ($\lambda < 400$ nm) and about 47% is in the visible range ($400 > \lambda < 700$ nm). According to a hypothesis, our planet receives about 89300 TW of sunlight each year.[22]

Heterogeneous photocatalytic reactions are preferred over homogenous reactions owing to the separation of reactants and products. Heterogeneous photocatalysis generally involves photo-sensitization, involving the absorption of photonic energy by photo-sensitizing species to conduct a photochemical reaction. The primary photocatalytic reaction involves *in situ* generation of hydroxyl radicals (with standard redox potential +2.8 eV) as a result of formation of electron hole pairs, while the secondary reaction involves catalytic oxidation of organic reactants on adsorption onto the photocatalyst surface. The generalized reaction involved in photocatalytic mineralization of recalcitrant organic pollutants is given below:

$$\text{Organic contaminants} \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \quad \text{(complete mineralization)}$$

Overall, five steps are involved for a heterogeneous catalytic reaction to take place.

(1) *Transfer* of organic pollutant molecules (A) from bulk aqueous phase to the photocatalyst surface.
(2) *Adsorption* of the pollutant molecules at the active sites of the photocatalyst.
(3) *Photocatalytic reaction* occurs at the photocatalyst surface, leading to the breakdown of pollutant molecules (A → B).
(4) *Desorption* of broken-down molecules (B) from the photocatalyst surface occurs.
(5) *Transfer* of the catalyzed molecules (B) from the inner to the outer catalyst surface.

#### 17.1.2.2 Advantages of Photocatalysis

Photocatalytic technology has gained quick and prompt acceptance by the masses due to being a green and effective strategy to remediate environmental pollutants, especially wastewaters. Environmental photocatalysis encompasses purification and remediation of all types of pollutants including air, water, and hazardous wastes in addition to having deodorizing and anti-bacterial effects. In recent years photocatalysts have also attained an eminent position as self-cleaning and anti-fogging agents.[23]

In 1972, Fujishima and Honda, discovered the photocatalytic implementation of $TiO_2$ to cleave water and afterwards many researchers explored the remarkable attributes of other photocatalysts. This was subsequently much studied for numerous environmental applications involving redox processes. The remediation of environmentally hazardous materials from wastewater using different MO-based semiconductors ($TiO_2$, ZnO, $Fe_2O_3$, CdS, $WO_3$ *etc.*) has been demonstrated by numerous scientists and researchers. Photocatalysis has also been employed for air deodorization, degradation of volatile organic compounds (VOCs), and remediation of low molar-mass gaseous compounds. VOCs are degraded by destroying their molecular bonds using hydroxyl radicals to accelerate the degradation process. This treatment converts malignant organic gases into simple benign species.[17,24] The reactive oxygen species (ROS) generate photo-induced charges on the surfaces of the photocatalyst which in turn leads to organic mineralization and inactivation of microbial growth without producing secondary pollutants. These above-mentioned salient features and practically useful attributes have motivated environmentalists and researchers to explore the use of photocatalysts in chemical and biological remediation of wastewaters.[25]

### *17.1.2.3 Solar Nano-photocatalysis*

The use of solar radiation to catalyse chemical reactions has emerged as a very useful tool in the hands of researchers to mineralize pollutants. This technology has been the most studied in current research, increasing the use of the photocatalysts particularly for wastewater treatment. These goals have been achieved by modifying existing semiconductor-based nanomaterials in terms of decreasing their band gap energy from the ultraviolet to the visible region.[26] The band gaps of the metal-based semiconductors are generally diminished by dislocating their light absorption spectra in the visible region on doping MO with metals or/and non-metals to effectively improve their photocatalytic activity. In the doping strategy, recombination of photogenerated electrons and holes is avoided in order to enhance the efficiency and quantum yields of catalytic materials.

The improvements and modifications in the nano-photocatalysts have also been assessed through harvesting visible solar radiation in order to expand their application. There are several methods to modify solar photocatalysts but the most widely practiced methods are dye sensitization of their surface, doping of the metal oxides with anionic and cationic impurities, and narrowing the band gaps in semiconductors by composite formation and hybridization.[27] The process of solar photocatalysis is initiated by incorporating metals or their corresponding anions with photocatalysts or by compositing two or more metal oxides to narrow the band gap. These attributes introduce inter-band energy levels and initiate catalytic reactions on exposure to solar light at longer wavelengths. The electrons are channelized in these catalytic materials due to accelerated photo-excitation on harvesting solar radiation.[28]

In a typical photocatalytic process, electron–hole pairs are generated with specific oxidation and reduction potentials in the conduction band (CB) and valence band (VB) when irradiated with solar light. The radiation provided must have higher energy as compared to the band gap of the semiconductor used. The band gap determines the rate of energy utilization, and the energy values in CB and VB originate oxidation and reduction potentials of the photo-excited holes and electrons. However, considering the practical aspects of the process, photocatalytic performance is governed by two conditions: firstly the energy ($h\nu$) of incident photons should be higher than the energy gap ($E_g$) of the photocatalyst; secondly, the redox potentials of reacting species should lie between the potentials of CB and VB of the semiconductor (shown in Figure 17.2).

In the in case of first condition, the narrower the band gaps the greater the harvesting of solar radiation in the visible region. Whereas the second condition demonstrates the thermodynamic feasibility of the reaction and a higher CB potential facilitates reduction of reactants while a lower VB potential is beneficial for oxidation of reactants. However, one problem associated

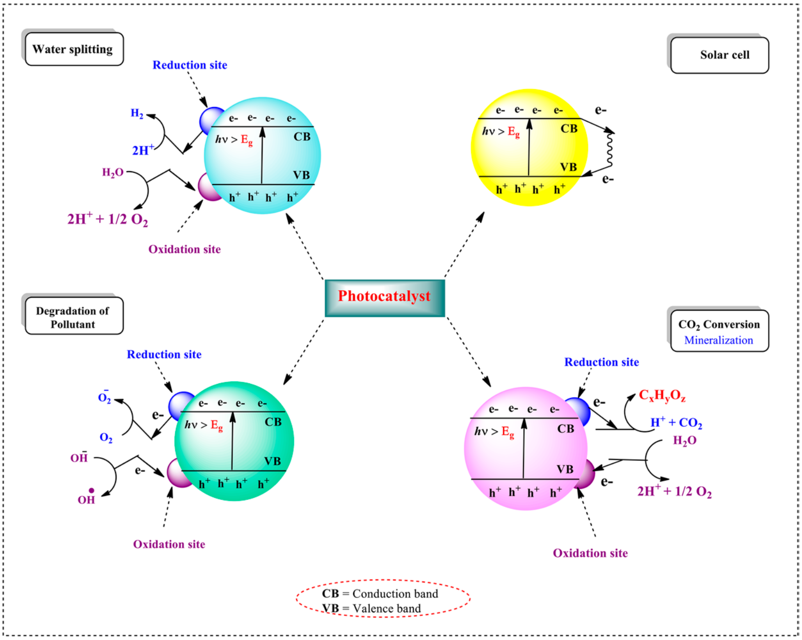


**Figure 17.2** Photocatalytic mechanism involved in water splitting, solar cells, degradation of pollutants, and mineralization by $CO_2$ reduction. Adapted from ref. 29, https://dx.doi.org/10.5772/62206, under the terms of a CC BY 3.0 license https://creativecommons.org/licenses/by/3.0/.

with higher CB and lower VB potentials is that they broaden the band gap of the photocatalyst, which in turn reduces utilization of solar radiation in the visible spectrum, according to first condition. It appears that both the aforementioned conditions are mutually contradictory, but they plays a central role to maintain balance in the design of photocatalysts. A comprehensive photocatalytic mechanism for complete mineralization of recalcitrant organic pollutants is shown in Figure 17.2. The mechanism involves splitting of water, working of a solar cell, degradation of wastewater and other pollutants, and complete mineralization of contaminants and pollutants in a single-step of $CO_2$ reduction *via* photo-excitation.

However, research findings have proved that photocatalysts with single components have difficulty in wide range harvesting of solar radiation to attain strong redox potential. In addition to the structural features of single-component catalysts, there is facile return of electrons generated in the CB which can easily return to the VB, or they get trapped in the doped state and then recombine with respective holes. These problems can be overcome effectively by designing an appropriate heterogeneous photocatalyst.[30,31]

In recent years, researchers have explored the fabrication of vertically oriented nano-structures immobilized onto substrates on account of their recyclability as compared to powdery catalysts.[32] Substantial efforts are dedicated to growing nanostructures of metal oxides using specific methods and substrates to achieve ideal catalytic properties, array density and geometries, to maximize their photocatalytic applications. Some of commonly used substrates immobilize for MOs are aluminium or copper foils, glass, pure metal, fluorine- or indium-doped tin oxides (FTO or ITO), or quartz to degrade recalcitrant pollutants especially textile dyes.[33] The photocatalytic activity of metal oxides can be enhanced or tuned according to the requirements by changing the surface area of the substrates. These functionalized catalysts work very efficiently for degradation of residues of toxic moieties present in effluents.[4]

#### *17.1.2.4. Tailoring of Solar Nano-photocatalysts*

Nano-scaling the particle size of solar photocatalysts renders some very useful features, in particular high surface area/volume ratio and enhanced surface energy for strong agglomeration during the course of reaction.[34] Powdered photocatalysts in particular acquire comparatively superior photocatalytic activities, owing to their small size, great surface area, and increased catalytic activity, facilitating contact with recalcitrant pollutant molecules. However, there is one drawback associated with these powder catalysts, principally the difficulty in their recovery from the reactions after each catalytic cycle, leading to unavoidable loss of catalysts.[6] Moreover, the recovery of photocatalysts following the degradation demands additional resources and time. Thus, tailoring and adjustment have become indispensable to maximize the practical implementation and large-scale application of catalysts; in this regard photocatalysts are immobilized or coated onto the substrates for quick and easy recovery.[35]

In tailoring of photocatalysts, surface area plays a major roles in determining the catalytic activity of such materials. Researchers have made many attempts to not only reduce the size of these materials but also enhance their photocatalytic properties in nano-scale powder forms. They have synthesized solar nano-photocatalysts in diverse shapes, following various experimental methodologies and protocols including hydrolysis; co-precipitation; hydrothermal/solvothermal methods; ionic liquid-assisted fabrication; thermal decomposition and combustion methods; and synthesis through combining hydrothermal and reflex condensation methods. Doping of nanomaterials can cause morphological changes and size reduction, which in turn can decrease the overall surface area.[29]

Some major strategies to enhance photocatalytic efficiency include tailoring of photocatalysts and optimization of some parameters such as particle size and morphology, crystal phases, polar surface area, distribution of –OH groups and charge separation. Increasing charge separation and surface area is achieved by anchoring MO particles onto a substrate with relatively greater surface area. Some of the substrates such as zeolites, mesoporous materials or carbon-based/graphene-based composites are the most promising. The graphene oxide and metal oxide composites have improved electron transport, thus they have great potential for photocatalytic degradation of persistent organic contaminants. The improved electron transport prevents the recombination of charges and enhances the adsorption capacity of recalcitrant pollutants onto the surface of photocatalysts. Thus, innovative nanostructured composites in solar photocatalysts are playing a dominant part in wastewater purification.

In the process of developing photocatalysts exhibiting maximum catalytic reactivity, the visible solar spectral range (>400 nm) is optimally employed. There have been numerous proposals for modifications in MO-based photocatalysts including:

- doping of $MO_x$ with other transition metal-ions
- reduction of $MO_x$ photocatalysts
- doping of MOs with non-metal (B, C, N, P, S, I, F *etc.*)
- fabricating $MO_x$ composites with semiconductors of lower band energies CdS nano-particles *etc.*
- sensitization of $MO_x$ with synthetic dyes (such as thionines and other dyes)
- doping of $MO_x$ with a luminescence agent through an up-conversion method.

Since nano-sized metal oxides (ZnO, $ZrO_2$, $TiO_2$ *etc.*) show chemical and biological inertness, photocatalytic stability, facile synthesis, and low environmental risks, they are extensively researched materials for wastewater treatment from various industries, laboratories and factories, including degradation of textile dyes, paper and pulp wastes, fertilizers and pesticides, pharmaceutical wastewater and materials from antimicrobial studies.

**17.1.2.4.1 Nanomaterials as Photocatalysts.** Nanomaterials having large surface areas and high reactivity, including metals, metal oxides or hydroxides, servie as excellent photocatalysts to degrade and remediate environmental pollutants. Moreover, densely distributed and low-coordinated atoms generally reside at the outer surfaces or edges of nanomaterials, which endow them with high reactivity to adsorb and finally degrade pollutants from water bodies.[21,36] Metal oxide nanomaterials are extensively used to remove recalcitrant and hazardous pollutants from industrial and domestic wastewater. The single metal oxides of titanium ($TiO_2$),[37] ZnO,[38] MgO,[39] and $Fe_2O_3$[40] and doped composites of metal oxides with dendrimers, polymers or other substrates[20,41] are nano-photocatalysts characterized on the basis of their small size, large surface area, low solubility in various reagents, high stability, eco-friendly nature, and high photocatalytic activity.

A wide range of semiconducting photocatalysts ($TiO_2$/ZnO/$WO_3$/$Fe_2O_3$/CdS/CdSe *etc.*) with morphological diversity and modifications has been investigated and developed. The catalytic and optical properties of photocatalysts are significantly influenced by surface area and crystal structure, which subsequently control the reaction kinetics and overall mechanisms.[42] Differential interfacial charge transfer (CT) triggers recombination of charged pairs of holes and electrons, and retards overall photocatalytic activity.[43]

The applications of $TiO_2$ with solar energy as radiation sources were limited in the past due to the large band gap and reduceds quantum efficiency. This drawback was compensated by doping, nano-composites, surface modification, dye sensitization, and deposition of noble and non-noble metals. These considerable efforts extended the photolytic activity and photo-response of $TiO_2$ in the visible region of solar spectrum. ZnO is another alternative to $TiO_2$ which harnesses its photocatalytic potential due to its similar band-gap energy. ZnO exhibits comparatively higher absorption efficiency across the solar spectrum than $TiO_2$. Both of them have been evaluated for photosensitization and photocatalytic degradation of pollutants of diverse chemical nature in wastewater under solar irradiation.

Several literature reviews on photocatalytic mineralization and destruction of organic as well as inorganic recalcitrant pollutants are available using solar light and artificial UV radiation. Solar irradiated photocatalytic oxidation of organic pollutants converts them into relatively harmless end-products.

The basic mechanism involved in photocatalysis initiates with ejection of electrons from the VB of the $TiO_2$ semiconductor to its corresponding CB, thus leaving holes ($h^+$) in the VB. Highly reactive radicals are generated in the second step from the semiconductor surface and there occurs direct oxidation of the polluting species (R). In the final step, the electrons react with the respective acceptor, such as $O_2$, which is already dissolved or adsorbed in water.

Step 1: $TiO_2 + h\nu \rightarrow e^- + h^+$ (ejection of electrons from semiconductor)

Step 2: $h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$ (generation of ${}^{\bullet}OH$)

Step 3: $h^+ + OH^- \rightarrow {}^{\bullet}OH_{ads}$ (absorption of $^{\bullet}OH$)

Step 4: $h^+ + R_{ads} \rightarrow R^+$ (oxidation of polluting species)

Step 5: $e^- + O_2 \rightarrow O_2^{\bullet -}$ (Reaction of electrons with acceptor $O_2$)

#### 17.1.2.4.2 Enhancement of Photocatalytic Activity (PCA).

Several studies have been conducted on the enhancement of PCA in synthesized powdered or immobilized photocatalysts. This mechanism depends on many factors such as particle size, catalyst loading, band gap energies, the concentration of pollutants in effluents, and pH of the medium. Surface modifications are considered to be the most facile methods for improving PCA on irradiation with solar light without disturbing the lattice structure. Modified semiconductors influence the CT behaviour of charge carriers at particle–particle, particle–solution, and particle–air interfaces. Moreover, it is necessary to understand the factors controlling surface-modification properties to comprehend the process involved in photocatalysis.[44] The transfer of charges generated by photo-excitation may follow certain pathways, such as entrapment, recombination, and transfer of defects within the bulk or surface defects to the reservoir phase (*e.g.* graphenes). Nano-particles exhibit various phases and electron transfers between electron acceptors and donors in the media to achieve desirable photocatalytic reactions.

Numerous efforts to enhance the activity of MO photocatalysts have been carried out *via* surface modifications and doping with cationic or anionic dopants. Among all the practically employed and tested techniques for photocatalysts, doping has the most intense impact on extending the optical absorption range when done with appropriate elements. These dopant species function as trapping centres in retarding charge recombination and also extend excitation wavelength to the visible range.[45]

#### 17.1.2.4.3 Advanced Oxidation Processes (AOPs) for Wastewater Treatment.

AOPs are generally defined as oxidation methods based on the action of highly reactive and unselective species (hydroxyl radicals), the second highest known oxidant species ($E_0$ = 2.81 V), which are able to promote organic matter oxidation and mineralization at high reaction rates. Although the treatment of wastewater is the most common area for research and development, AOPs have found also several other applications such as in groundwater treatment, soil remediation, ultrapure water production, treatment of organic volatile compounds, and odour control.

AOPs are among the most used industrial methods to remove pollutants from various effluents. AOPs work with the help of different strong oxidants and are the most frequently used physico-chemical approach for treating industrial wastewater.[46] The AOP approach for wastewater treatment was initially proposed in the early 1980s and implemented for water purification; it received significant attention due to its remarkable success.

Sonolysis is another very versatile technique that degrades organic molecules. Ozonation and other oxidation processes for water treatment are highly effective in degrading microbes, micro-pollutants, and other organic pollutants to purify water.[47] There are four main types of oxidation processes including:

(1) chemical oxidation which is based on peroxide photocatalysis;
(2) biological oxidation based on ozonation;
(3) physico-chemical oxidation during Fenton or Fenton-like processes;
(4) advanced oxidation process (AOP) in the presence of solar irradiated nano-photocatalysts especially metal oxides. This is the most important and widely implemented process.

Combination of ozone ($O_3$) with hydrogen peroxide ($H_2O_2$) has opened new vistas in the remediation, purification, and removal of persistent pollutants from effluents due to effective oxidization of both organic and inorganic materials. There are many compounds which are oxidized with great difficulty by ozonation due to the presence of certain saturated ring systems. This issue was resolved by combining the oxidation potential of ozone with homogeneous/heterogeneous catalyst systems (MOs) to further enhance the oxidation reaction for complete mineralization of pollutants and contaminants (Figure 17.3).[48]

Photochemical AOPs make use of solar radiation sources including UV (B, C) and visible light, either independently or in synergy with nanomaterials and chemicals to degrade pollutants. Solar irradiation for remediation is generally termed photolysis and comes into action at as a tertiary step for removing microbes and degradation of organic compounds.[49] This process advanced further when a combination of solar light and $O_3$ revolutionized oxidation technology. This technique has provoked researchers to extend its applications. The ultraviolet region of solar light on encountering $O_3$ generates free radicals ($OH^{\bullet}$) in aqueous medium.[50]

Recalcitrant moieties, such as persistent organic pollutants (POPs), are basically carbon-based substances with super resistance against degradation treatments and are persistently released into the environment. These persistent pollutants cause severe effects on human beings and wildlife due to their low bio-degradability and carcinogenicity. Advanced technologies play a decisive part in ensuring complete reclamation of water through mineralization processes. The conventionally employed treatment techniques to remove recalcitrant components from wastewater (adsorption, coagulation, membrane separation) merely concentrate these organic pollutants to solid phase. This drawback is overcome by additional treatments to remove these secondary pollutants. These are a few reasons to prefer AOPs for purging wastewaters from recalcitrant pollutants, especially those with poor biodegradability. AOPs proffer numerous advantages: (1) high degradation rates; (2) operate under ambient conditions of temperature and pressure;

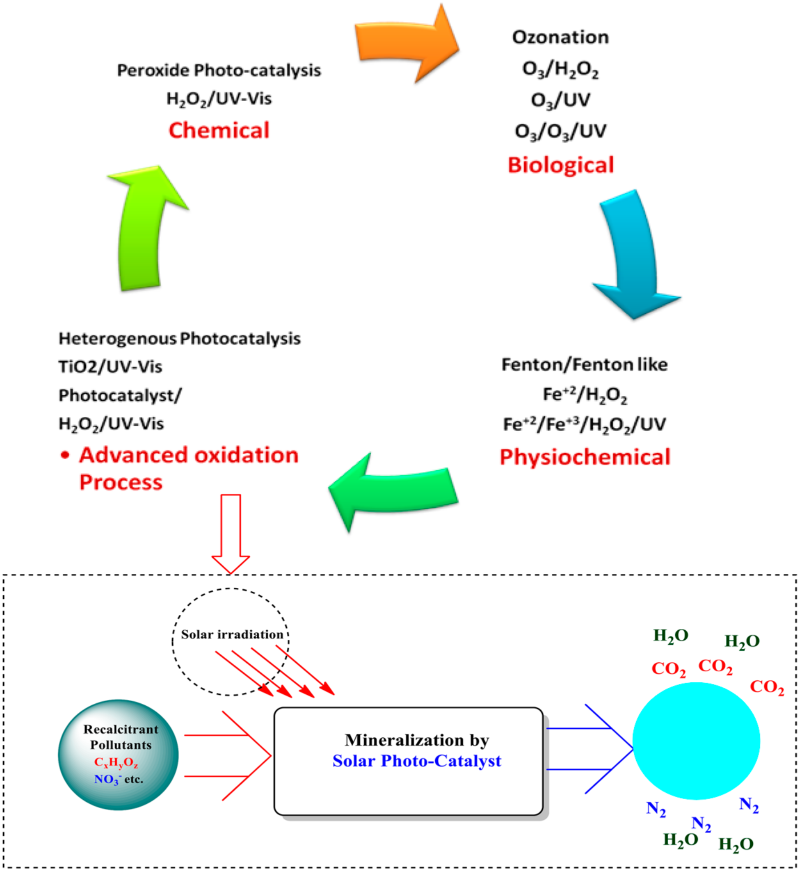


**Figure 17.3** Types of advanced oxidation processes for solar photocatalysis.

(3) reduction of the toxicity of organic compounds, and (4) complete mineralization of recalcitrant organic compounds into green and harmless end-products.[51]

**17.1.2.4.4 Water and Its Pollution.** Water is the most essential natural resource on our planet and it is indispensable to sustain all life forms. Its availability needs to be assured in pure and unpolluted form for not only human beings but also other living creatures. Water is termed the "universal solvent" on account of its physical and chemical properties. In this technologically and scientifically advanced current era, water contamination is, among a range of major problems, the most important for numerous reasons such as inadequate treatment of sewage wastewater, industrial wastes, marine-dumped pollutants, radioactive materials, agricultural runoffs, and many others in a never-ending list.

Pollution and contamination of water has many adverse effects on our environment and it triggers other forms of pollution including air and soil pollution and causes harm to human health. Water contamination and pollution have long-standing adverse impacts for countries from both economic and social perspectives. In a report published by the United Nations it is clearly stated that the availability of water in purified form is getting more and more difficult globally, and in the 21st century the lives of living beings are going to be affected by contaminated water. Water contamination is defined as the addition of harmful and unwanted materials into water reservoirs to render them unsuitable for drinking and other uses. This emerging and continuously growing problem could be overcome by physical, mechanical, and chemical treatment methods. In addition, technologists and researchers are continuously putting efforts into exploring new technologies for improving the quality of water by cost effective, eco-friendly, highly efficient water purification processes to remove recalcitrant pollutants and increase its reusability.

Recently, nanomaterials have taken a central position in the treatment wastewaters due to their nano-size, greater surface area, high reactivity and efficient solution mobility, versatile properties, and diverse applications. Their mechanical strength, dispersibility, hydrophilicity, and hydrophobicity have further enhanced their usefulness as efficient materials for wastewater treatment and purification. There are numerous sources that play leading roles in polluting water and the most serious are effluents of industries laden with heavy metals, metal complexes, and other organic or inorganic pollutants. These pollutants and harmful microorganisms have been reported to be efficiently removed by a combination of nanomaterials and solar catalysis.[52]

Thus the involvement of phenol and phenolic compounds as raw materials during manufacturing various products in pharmaceuticals, fertilizers, pesticide, textiles, and paper industries are major causative agents that highly affect our environment owing to their toxic and carcinogenic nature. Thus their abatement and complete removal from water is much needed to preserve ecosystems and maintain their balance.

**17.1.2.4.5 Photocatalytic Mineralization of Recalcitrant Pollutants.** Different types of pollutants and contaminants are being dumped into water bodies through various sources but the most dangerous and persistent class of harmful materials is called recalcitrant materials. Among the various technologies and processes to degrade pollutants have been employed to date, the photocatalytic degradation of such pollutants is the most explored one as this technique works efficiently to remove these obstinate chemicals from water. The chemical nature of contaminants in industrial effluents, their concentrations, and other parameters provide an initial idea of the degradation process. Studies conducted on photocatalytic degradation of recalcitrant pollutants focused on MO nano-particles, and their rate of reaction depends on the concentration of contaminants in the water. High concentrations of such pollutants saturate the surface of MOs ($TiO_2$, $ZrO_2$, ZnO *etc.*), reducing their photonic efficiency and leading to catalytic deactivation. In addition, there are many other factors that directly influence photocatalytic performance during degradation, such as chemical structure and substitutions on the pollutant molecules. For instance 4-chlorophenol requires prolonged irradiation because it transforms into a number of intermediates, unlike oxalic acid which completely mineralizes to carbon dioxide and water.

Furthermore, the nature of the specific water contaminant depends on its effective adherence to the surface of a photocatalyst, which facilitates the removal of such materials from wastewater solutions. Therefore, the photocatalytic degradation through mineralization of recalcitrant aromatic compounds highly depends on substitution patterns. The presence of electron-withdrawing groups in organic substrates make them adhere strongly to the photocatalyst surface and hence become more susceptible to complete mineralization by direct oxidation in comparison to electron-donating substituent groups.

The AOP involves *in situ* production of oxidizing radicals with the help of various illumination sources such as solar, artificial, or chemical light energy. Hydroxyl radicals ($OH^•$) are capable of transforming persistent and toxic organic species into comparatively less detrimental end-products like $CO_2$ and mineral acids. When solar radiation interacts with a homogenous catalyst such as iron ions ($Fe^{3+}$), or during the photo-Fenton process with a heterogeneous catalyst ($TiO_2$, ZnO) in photocatalysis, the rate of pollutant degradation increases as a result of the photochemical reactions that take place during these processes. These two AOP processes have proved their mineralization efficiency in degrading vast amounts of aqueous organic contaminants such as emerging, recalcitrant, persistent pollutants from various industrial sources.

## 17.2 Solar Nano-photocatalysis for Treatment of Wastewater from Various Industrial Effluents

Nanotechnology is the most widely explored technology in the recent era and is responsible for the nano-scale production of different materials for diverse applications. Nanomaterials whether nano-particles, nano-wires, and any other nanostructures are characterized as single molecules falling in the range 1–100 nm. Nanostructures can be categorized into three groups on the basis of dimensions: zero-, one- and two-dimensional. AOPs play a very important role in treating wastewaters and developing bio-availability of uncontrollable organic pollutants.[8] Thus nanotechnology is becoming a useful tool for scientists in the treatment of wastewater. Improvement in nano-scaling has made the process of treating effluents of industrial sources, very feasible and conceivable. These nano-methods are not only economically plausible but also naturally stable for satisfactory and proficient treatment of wastewaters.[53] Converting the metal-based photocatalysts into nanomaterials increases their novelty and effectiveness owing to the changes their chemical and physical properties. The structural modifications and increased surface-to-volume ratio allow more proficient detection and remediation of the contaminants.[54]

There are various techniques to mineralize or treat wastewaters to degrade colouring components, heavy metals, and synthetic and natural contaminants but they incur high costs. To resolve the issue, researchers and analysts have started focusing on exploring more efficient, reliable, and financially effective forms of energy. This idea got significant attention on its first practical implementation to remove or minimize pollutants from water resources and wastewaters. So, the proposal of utilizing solar-oriented energy amalgamated with nano-photocatalysis has been widely accepted owing to its diverse applications, ease of accessibility, facile maintenance and efficiency.[22]

However, this solar nano-photocatalytic approach needs to be used intelligently to achieve maximum benefit. New methods of wastewater degradation involving sunlight-based irradiation are constantly being discovered.

### 17.2.1 Wastewater and Solar Nano-photocatalysis

During the past decades of continuous ramping up of the global population and economic growth, addressing the environmental concerns around the sustainable supply of water and energy has become a priority issue for humanity. Exponential population growth and intensified agricultural and industrial exploitation has generated a serious demand for freshwater supply.

The ever-increasing demand for a supply of clean water for drinking and the consumption of water by industrial units, coupled with the high disposal of wastewater, is overriding other environmental issues. Wastewater effluents from industry could be treated to degrade pollutants by various treatments, but the traditionally used techniques have not proved to be effective in completely removing or degrading many recalcitrant contaminants. These treatments have to abide by many strict quality standards for water purification to make the water reusable.[28] Conventionally the physical methods employed, such as filtration, sedimentation, flocculation, chemical treatments, and membrane based technologies, are not cost effective. These conventional methods also generate highly toxic secondary pollutants which are ultimately dumped into ecosystems.[55]

Continuous contamination of water bodies by growing industrialization and other anthropogenic factors is currently posing a major challenge with the ever rising demand for water.[56] Large amounts of recalcitrant, non-biodegradable pollutants of organic or inorganic nature are contaminating water reservoirs, and these primary and secondary pollutants are posing serious environmental problems even under ambient conditions. Water is contaminated mostly by POPs, including wastewater from textiles industries (dyes, surfactants, pigments), fertilizers and pesticides industries, paper and pulp production industries, and pharmaceutical industries.[2]

Therefore, a proper treatment of wastewater containing effluents of synthetic dyes, tanneries, food, cosmetic, paper pulp and pharmaceutical industries is in high demand environmentally. In recent years, there is much environmental awareness and stringent legislation regarding the treatment of industrial effluent dumped into natural resources.[57] Solar irradiated photocatalysts mounted on semiconducting surfaces, especially metal oxides, have gained much attraction globally due to their efficiency, environmentally benign nature and cost effective methods of degrading pollutants in water. Development of versatile and effective heterogeneous solar nanophotocatalysts could be achieved either by depositing metals on semiconductor surfaces or by combining semiconductors.

### *17.2.1.1 Solar Photocatalytic Degradation and Mineralization of Effluents of Textile Industries*

The wastewater from textile industries is heterogeneous in nature and laden with persistent and non-biodegradable recalcitrant compounds, making its treatment challenging. These effluents are comprised of acids, alkalis, stabilizers, bleaching agents, hydrogen peroxide, dyes, surfactants, suspended solids, dispersing agents, chlorinated hydrocarbons, scouring agents, heavy metals, and many other organic and inorganic compounds.[7]

The textiles industry generates large quantities of coloured wastewater, regarded as highly toxic, that is difficult to treat by conventional physical, chemical, and microbiological methods. In fact, the existing wastewater treatment technologies suffer several drawbacks, such as incomplete removal of dyes and other chemical residues in addition to toxic sludge generation.[26] Nano-scaled solar photocatalysis has emerged as the most efficient technology for the treatment of effluent from the textile industry. These recalcitrant pollutants are mainly dyes, pigments, surfactants, and auxiliary chemicals.

When these effluents from textile units are mixed with natural sources of clean water, they retard photosynthesis and hence disrupt ecosystems. Moreover, synthetic dyes and pigments belong to very rigid class of recalcitrant pollutants. Since their degradation does not occur by microbes or biological factors, they are categorized as non-biodegradable pollutants. Furthermore, these synthetic dyes have high thermo-stability and high resistance to solar photolysis, thus as a consequence, they accumulate in ecosystems and threaten the environment. Although conventional methods such as coagulation and adsorption have long been practiced to degrade dyes, many secondary pollutants are always generated. Additionally, because of the presence of many hydrophilic groups in the core system of dyes, they show excellent water solubility.[58]

Large quantities of synthetic dyes, pigments, and their auxiliary chemicals with limited biodegradability make them difficult candidates for characterization in wastewater samples. The textile industry is indispensable to fulfill clothing and apparel requirements throughout the world, but the pollutants resulting from the pre-treatment of effluents, usually by flocculation or coagulation, are dumped as wastewater into the drainage system. However, these methods are not very effective as they remove colouring components merely by precipitation and wastewater reusability is limited and insufficient. Nanomaterial-based solar photocatalysis has proved to be the most efficient and suitable approach for complete oxidation of synthetic dyes and pigments, surfactants and other textile effluents not only at laboratory- but also at pilot-scale. The easy and free availability of solar energy is the best feature of solar photocatalysis for the treatment and reprocessing of textiles wastewater, and countries located in the third world have a plentiful supply of sunlight and water.

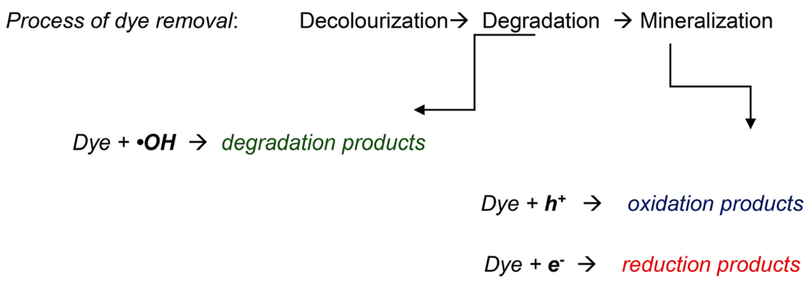
**17.2.1.1.1 Removal of Recalcitrant Dyes from Textiles Wastewater.** Environmental vulnerability, threats, and strict legislation have clearly directed the treatment methods of industrial wastewater to remove coloured, dissolved, or suspended recalcitrant organic pollutants, heavy metals, and inorganic ions (sulfates, phosphates, nitrates). Among several in-practice biological or physio-chemical degradation technologies, solar nano-photocatalysis are currently being employed to remove all types of persistent pollutants.

Textile finishing and dyeing processes produce wastewater in large quantities and these effluents have high concentrations of coloured and organic materials and removal of such persistent compounds by classical methods is very not easy. Apart from creating aesthetic problems, when these effluents are mixed with natural water reservoirs the dye molecules strongly absorb solar light and seriously threaten ecosystems. Reactive azo and other synthetic dyes are non-biodegradable and their removal through biological treatments is not effective. Therefore, it is necessary to find an effective method of wastewater treatment and solar-assisted nano-photocatalysis is serving this purpose very efficiently.[46,57–59]

Dyes are categorized on the basis of their chromophoric nature:

- acridine dyes comprise of derivates of acridine
- anthraquinone dyes consist of anthraquinone derivatives
- arylmethane dyes are mainly diarylmethane dyes and derivates of triphenylmethane
- azo dyes are based on the –N=N– azo bond in the dye structure
- phthalocyanine dyes and its derivatives
- quinone-imine: quinone, azin, eurhodin, Safranin dyes, indamin derivatives
- thiazole dyes
- xanthene dyes
- fluorene and fluorone dyes
- rhodamine dyes

Solar light is available to our planet free of cost and use of this light in photocatalytic degradation is somewhat challenging due to inability of colourless MOs to react with pollutants. MO-based photocatalysts can be tailored to enhance their activity to maximize the use of solar light[59]. The complete removal of dyes from effluents is a three step process as given below.



AOPs comprise treatment procedures especially designed for the degradation and mineralization of organic and inorganic pollutants from wastewater through some sort of chemical or photochemical redox reactions. Pollutants aaret oxidized by oxidants (ozone, oxygen, peroxides, or air) in precise combinations. These oxidants function in combination with some irradiation sources such as solar light in particular. AOPs are very effective at removing synthetic dyes and auxiliary chemicals from wastewater. Oxidation of the chromophoric functional groups responsible for colour in the dyes, most significantly the azo (–N=N–) group and aryl rings, is achieved by the attack of free radicals ($OH^\bullet$). These free radicals are generated by chemical species ($O_3$ and $H_2O_2$). Additionally, when solar light (UV and visible regions) is combined with oxidizing agents, the efficiency of the mineralization or degradation process increases as a result of $O_3/H_2O_2$ photolysis.

AOPs, supported by artificial and solar-assisted photocatalysis are very effective processes for decolourization, degradation, and finally mineralization of synthetic dyes. They are ideally applicable to treat industrial effluents laden with dyes and thus to reduce water and environmental pollution. For the complete mineralization and degradation of notorious synthetic dyes, this sequential strategy is very successful.

In recent years, photocatalytic oxidation processes with ultra violet (UV) radiation and semiconductor photocatalysts like titanium dioxide ($TiO_2$) and zinc oxide (ZnO) have gained immense research interest as an effective wastewater purification method because of their efficacy in decomposing and mineralizing hazardous organic pollutants as well as the opportunity to utilize solar UV and visible spectrum light. A UV-assisted heterogeneous photocatalytic oxidation process was conducted to explore its catalytic mechanism. The immobilization of photocatalysts is an effective method to treat wastewater.

Photocatalytic decomposition using ZnO and $TiO_2$ catalysts is mainly applied for treating organic contaminant dyes in wastewater because of their ability to achieve complete mineralization of the organic contaminants under mild reaction conditions such as ambient pressure and temperature. A total of 187 published papers have been reviewed and summarized with a focus on the photocatalytic oxidation of organic dyes present in wastewater effluent. Most recently, photocatalytic degradation of organic molecules using $TiO_2$ and ZnO has been studied extensively, particularly the degradation of persistent organic pollutants, PAH (polycyclic aromatic hydrocarbon) dyes and other organic chemicals that are known to be endocrine disruptors. Treatment of wastewater in a titanium and zinc dioxide suspended reactor has been widely used due to its simplicity and enhanced photodegradation efficiency.

**17.2.1.1.2 Removal of Surfactants from Textile Wastewater.** Surfactants are amphiphilic carbon-based mixtures having a hydrophilic head group (water loving) and a hydrophobic tail end and are hydrocarbons in nature. In recent years due to their high consumption their removal and treatment have become essential because they cause serious water pollution on accumulation. The surfactants which are extensively used in industries add toxic substances into the water by micellization and solubilization.[60]

Surfactants are among the most widely used chemicals in the textiles industries and also in domestic settings. These surface active agents, although very useful in laundry operations and for cleaning purposes, pose some serious environmental problems when they start accumulating in water bodies over a certain threshold. These anthropogenic contaminants are being dumped into water systems all around the world. Textile industry effluents contain many synthetic chemicals along with surfactants and detergents in large quantities due to their extensive use. Surfactants have a wide range of applications in many industries including pharmaceuticals, food processing, oil recovery units, plant shields, polymer industries, mining, cosmetics, and paper production and are employed in large quantities in the textile and fabric industries.

Degradation of surfactants and their related chemicals have become a global issue and various physiochemical, chemical, and biological methods have been applied for their treatment and removal from wastewaters. However, keeping in mind the non-biodegradable nature of some of surfactants, photocatalytic methods have been used to remove them from effluents. Biodegradation processes are very time consuming, ineffective and involve many pre-treatments, which render them ineffective for mineralizing surfactants. Alternatively, there has been widespread research on oxidation processes and solar photocatalysis due to their super efficiency, reliability and cost-effectiveness, and this technique works very effectively to completely remove surfactants from industrial and domestic wastewaters. These methods also facilitates in reducing the concentration of such toxic substances in aquatic systems.

Photo-assisted catalytic and electrochemical oxidation processes have been explored in investigations for getting rid of up-and-coming organic, recalcitrant, inorganic pollutants, among many other types of compounds present in commercial surfactants. Based on available information, solar irradiated photo-assisted electro-chemical oxidation is the most reliable and viable alternative to reclaim wastewater loaded with surfactants and other organic pollutants. This technology is important for avoiding pollution and prevention of contamination in water resources.

#### *17.2.1.2 Degradation and Mineralization of Wastewater from the Paper and Pulp Industry*

Every day we use paper products for different purposes and it is very hard to imagine life without paper and its products. The paper and pulp industry plays a major part in polluting aquatic and soil environments as it dumps and discharge significant amounts of hazardous materials especially chlorinated compounds. Starting from the raw materials, the production of pulp and finally paper involves several steps, and from the original mass almost 40–45% forms pulp, whereas the remaining materials are released as effluents. The effluent is comprised mainly of cellulose, hemicellulose, resin acids, tannins, chlorophenols, and most hazardous chloro-lignin which is the generated as a result of bleaching of pulps.[5,61,62]

In paper and pulp industries there is high consumption of water for processing, which generates various environmental concerns. In recent years, solar-triggered photocatalytic degradation of the resultant recalcitrant pollutants by mineralization and through AOPs has been widely explored considering the demands for effective wastewater recycling and reusability. In solar-illuminated processes using nano-composites of metal oxides and AOPs, strong oxidizing agents are generated which are very effective for complete destruction of recalcitrant pollutants in wastewaters. There are wider applications of heterogeneous photocatalytic degradation using illumination of solar or UV light, focused on semiconducting surfaces, and this makes advanced oxidation very attractive for wastewater treatment.

Many efforts have been made to attempt degradation and mineralization of pollutants from paper industry effluents, in particular using zero-liquid effluent technology. In this technology water is continuously recycled in close circuits to remove recalcitrant and persistent chemicals. However, in implementation of these techniques, a major drawback is encountered in that closure of circuits results in the accumulation of the pollutants; hence, the overall quality of the water is decreased. These techniques were abandoned owing to their limited effectiveness for further purification of water.

The pollutants released from paper industries are categorized in three major groups:

(1) products of starch degradation, mainly saccharides or/and carboxylic acids;
(2) phenolic compounds from wood lignin;
(3) Auxiliary chemicals add some other pollutants originating from the fresh water such as detergents and surfactants.

The presence of organic pollutants in paper manufacturing industry effluents during papermaking processes make it highly biodegradable; however these pollutants cannot be degraded completely by conventional biological processes. To resolve this issue, a combination sequential anaerobic and aerobic process was subsequently employed. However, disappointingly this caused accumulation of non-biodegradable organic compounds in the water.

Solar photocatalysis is an AOP that has been an effective and efficient treatment for mineralization and degradation of paper industry wastewaters. This mechanism uses solar light as the illumination source and then the generation of highly oxidizing species facilitates the conversion of organic pollutants into harmless end-products by mineralization and degradation. Thus catalysts play a central role in this process, and metal oxide catalysts are widely employed. The degradation process is usually accelerated by solar irradiation of the wastewater solution; the UV-range is most commonly used for irradiation. Solar light is used in particular because of its economic and environmental advantages. The mechanism of solar photocatalysis still needs to be fully established but the generally reported mode of action depends on the holes ($h^+$) to initiate the process of oxidation of substrates to generate corresponding radical cations. Alternatively, this process generates hydroxyl radicals from water molecules.[5,61]

#### 17.2.1.2.1 Degradation and Mineralization of Chlorolignin-containing Compounds from Paper Wastewater.

Paper processing and manufacturing units use numerous chemicals to decolourize the colouring components in paper. In developing countries chlorine or chlorinated bleaching agents are still in use to remove colour from pulp. This bleaching process generates a number of chlorinated species such as organochlorines, which are collectively termed adsorbable organic halides (AOX).

According to many survey reports >300 kinds of organochlorines are found in chlorine-bleached industrial effluents and the majority of these chemicals are toxic, carcinogenic, or mutagenic to living cells. These recalcitrant compounds are not degraded by microbial degradation due to their high toxicity. Hence, developed countries have banned chlorinated bleaching processes, which are being replaced with as total chlorine free (TCF) and elemental chlorine free (ECF) bleaching processes. The lower economic feasibility of the pulp and paper industries in developing countries makes its difficult to implement in permissible limits.

As the best solution for the degradation and complete mineralization of chlorinated chemicals, solar nano-photocatalysis is now actively employed for effluent treatment. Solar radiation with wavelength <380 nm (UV fraction) are absorbed by $TiO_2$ during this process. Metal oxide based photocatalysts have been exploited as substitutes for chlorinated bleaching agents to bleach the black effluents produced during the kraft process.[5]

#### 17.2.1.2.2 Degradation of Endocrine-disrupting Compounds.

During the last few decades many chemical compounds including bisphenols have been reported and recognized for causing endocrine disruption. Bisphenol A/F are used as raw material for manufacturing many important chemical products especially polymers, epoxy resins and polycarbonate plastics. The release of BPA and related compounds into the environment during manufacturing and their leaching from other products causes serious contamination.[63] Some of the common endocrine disrupting compounds belong to following chemical classes:

- xenoestrogens (alkylphenols)
- bisphenol S (BPS) and bisphenol F (BPF)
- dichlorodiphenyltrichloroethane (DDT)
- polychlorinated biphenyls
- polybrominated diphenyl ethers
- phthalates
- perfluorooctanoic acids

There have been many reports and studies about the presence and prevalence of BPA in various reservoirs and in environmental matrices and effluents because of its incomplete removal during conventional wastewater treatments. Hence, removal of such hazardous materials from the environment to reduce their ubiquity in water bodies and matrices is much needed to sustain the environment, and the development of technologies to resolve related issues is required. The use of oxidation processes especially AOPs has become an excellent alternative for treatment of wastewaters and removal of persistent and recalcitrant compounds. The use of semiconductor-based heterogeneous photocatalysis triggered by solar energy for irradiation is among the most used technologies. Heterogeneous photocatalytic processes are of special interest since the illumination source, *i.e.* sunlight, is an easily and freely available radiation source.

Many metals and metal oxides are being employed as heterogeneous photocatalysts and among all the MO-based catalysts $TiO_2$ has the strongest photo-induced oxidation power. Many investigations have been reported to have extended the photo-activity of $TiO_2$ from the UV region to the visible light region of the solar spectrum. This tailoring has expanded the range of practical photocatalytic applications using solar radiation. Doping strategies have been mostly employed for $TiO_2$-based catalytic materials with transition metals and non-metallic elements. Key to efficient utilization of solar light is to enhance the photocatalytic activity of catalysts for the degradation of a wide range of micro-pollutants and contaminants.

The degradation and mineralization of endocrine disruptors such as xenoestrogens, BPS and BPF, DDT, polychlorinated biphenyls, polybrominated diphenyl ethers, phthalates, and perfluorooctanoic acid has been made possible by solar energy. The photocatalytic activity depends on various parameters such as kinetic constant, catalytic conversion, and percent mineralization. The endocrine disrupting reaction intermediates formed during the process of wastewater treatment are also affected by photocatalysts.

The oestrogenic effect of intermediates formed during degradation of endocrine disrupting compounds is usually measured by yeast oestrogen screening. Photocatalytic degradation and mineralization of hazardous intermediates is extensively employed these days. To detect and offset the oestrogenic effect of persistent and harmful intermediates, solar catalysed AOPs are now commonly used.[61,64,65]

### *17.2.1.3 Degradation of Pharmaceutical Industry Wastewater*

Pharmaceutical products have been in use over a vast time period in history. During the last few decades, the high demand and use of pharmaceuticals has increased greatly and as a result environmental pollution and concerns have been on the rise due to the persistence and recalcitrant nature of these chemicals. These pollutants show long- or short-term toxicity because of their bioactivity.[66]

Pharmaceutical industries are providing a great and continuous service to sustain life, and their products (medicines and formulations) are widely consumed for controlling diseases and improving the health of humans, animals, and other ecosystems. Amongst various pharmaceutical products, the most widely and highly consumed are antibiotics due to their effectiveness and potent action against pathogens and harmful microbes. But these industries are also contributing to high risks of water, soil and air pollution when exposed to the environment. Water pollution has reached an alarming level, which is a major concern especially in industrialized countries.

The hazardous wastes released by pharmaceutical industries are categorized into three main types (1) chemical, (2) elemental, and (3) radioactive. These waste materials require approximately similar management strategies and practices and the major differences are due to their different characteristics.[67–70]

The most important chemical species contaminating the effluents of pharmaceutical processing and manufacturing units belong to some already established and some emerging contaminant groups and are listed below, and many more such compounds are found in wastewater samples:

- acetaminophen
- antipyrine
- atrazine
- caffeine
- carbamazepine
- diclofenac
- flumequine,
- hydroxybiphenyl
- ibuprofen
- isoproturon
- ketorolac

- ofloxacin
- progesterone
- sulfamethoxazoles
- triclosan

Declining quality of water reservoirs is linked to rapidly growing populations all around the globe. Among many strategies of water reclamation, solar-driven semiconductor catalysis is most effective for the degradation of pharmaceutical effluents.

Pharmaceutical products found in wastewater are categorized depending on their origin, chemical structure, or their therapeutic applications. Some of the broad classes and most extensively used chemical compounds in pharmaceuticals are:

- alkaloids which are plant-derived pharmaceuticals (cocaine, quinine, morphine)
- antibiotics
- lipid regulators
- non-steroidals
- anti-inflammatories
- antidepressants
- anticonvulsants
- anti-neoplastics
- beta blockers

The pharmaceutical residues are released into the aquatic systems *via* various routes. It has been reported that, compared with other organic pollutants, there are some factors which aggravate the potency and bioaccumulation of even the lowest concentrations of pharmaceuticals in ecosystems. These factors lead to high health risks for organisms.[67]

**17.2.1.3.1 Nanotechnology for Pharmaceutical Waste Treatment.** Conventional treatment technologies and methods achieve only partial removal of pollutants, while AOPs actually degrade and mineralize the pollutants into less hazardous and eco-friendly products and also improve the percentage degradation of the target chemicals. The most suitable method for removing pharmaceutical products from wastewater is solar-driven heterogeneous photocatalysis.

The use of nanomaterials such as MOs for photo-degradation of pharmaceutical effluent like tetracycline, cloxacillin, amoxicillin, ampicillin, atenolol, benzotriazole, clarithromycin, sulfamethoxazole, methylbenzotriazole, metformin, primidone, metoprolol, and gabapentin has been reported in studies using various solar irradiating AOPs. The semiconductor-based nanophotocatalytic AOPs shows high efficacy to degrade pollutants and adsorb them on active sites of MO semiconductor photocatalysts in the presence of solar light. Nano-photocatalysts have some remarkable and unique photophysical and photocatalytic attributes owing to their nano-size as compared to bulk materials.

### *17.2.1.4 Degradation of Fertilizer and Pesticides Wastewater*

Fertilizers are supplements that are added to the soil to enhance plant growth and also prevent unnecessary chemicals being taken up by plants. Fertilizers penetrate into the soil and ultimately mix with water reservoirs to cause detrimental effects. Pesticides are those additives which are added to soils and crops to prevent, destroy, or control any pests. Pesticides include all those chemicals used as plant growth regulators, desiccants, defoliants, and fruit-thinning agents, and these substances are supplied to crops either before or after harvesting to avert deterioration while in storage or transport. Pesticides are categorized into many sub-classes such as: insecticides, herbicides, fungicides, nematicides, rodenticides, plant growth regulators, and many related chemical compounds. Pesticide products have active moieties to kill, repel, or control pests, in addition to inert ingredients to ensure usability and performance of products (Table 17.1).

**Table 17.1** Nano-photocatalytic degradation of various recalcitrant pollutants.[71]

| Pollutant | Light source | Photocatalyst |
|---|---|---|
| Phosphamidon | UV | $TiO_2$ |
| Acephate | UV | $TiO_2$ |
| Diphenamid | UV | $TiO_2$ |
| Carbofuran | UV | $TiO_2$ |
| Thiram | Solar | $TiO_2$ |
| Indole-3-acetic acid | UV | $TiO_2$ |
| Indole-3-buteric acid | UV | $TiO_2$ |
| Lindane | Visible | N–$TiO_2$ |
| Dimethoate | UV | $TiO_2$ |
| Isoproturon | Solar | $TiO_2$ |
| Triclopyr | UV | $TiO_2$ |
| Daminozid | UV | $TiO_2$ |
| Methamidophos | UV | Re–$TiO_2$ |
| 2-Chlorophenol | UV | Co–$TiO_2$ |
| Erioglaucine | UV | $TiO_2$ |
| Bentazon | UV | $TiO_2$ |
| Propham | UV | $TiO_2$ |
| Prophachlor | UV | $TiO_2$ |
| Tebuthioron | UV | $TiO_2$ |
| **ZnO photocatalysis** | | |
| 2,4-Dinitrophenol | UV | ZnO |
| Diazinon | UV | ZnO |
| Resorcinol | Solar | ZnO |
| Phenol | Solar | ZnO |

### 17.2.1.5 Abatement of Fertilizers and Pesticides

Fertilizers and pesticides are continuously released into soil and aquatic environments by anthropogenic activities in pursuit of increasing plant growth and pest control. These chemicals belong to a specific class of chemicals and their detection in wastewater effluents pose an impediment in water purification and recycling. Moreover, their diverse variety, high toxicity, persistence, and accumulation are threatening to life through pollution of surface and ground water resources. Thus the frequent occurrence and persistence of fertilizers and pesticides in agriculture runoff that adds to surface and ground water pollution has triggered environmentalists to search for suitable technologies to degrade them. Conventional methods of treating wastewaters such as biological methods, coagulation or adsorption have not fulfilled the ever-increasing demands. These methods were merely concentrating recalcitrant chemicals but there was no mineralization.[49,71,72]

To resolve this issue, solar-irradiated nanomaterial-based photocatalysis came into action, as this method not only removes these chemicals from water but also converts them into environmentally safe chemicals. The discharge of wastewater from fertilizer and pesticide manufacturing industries is aggravating these environmental issues, due to the presence of biocides and recalcitrant pollutants. Thus the removal of these toxic chemicals from polluted surface, waste and ground water is part of long-standing strategies for improving water quality before returning water to its natural cycle. Therefore, the solar photocatalysis is the most economical, effective, and robust technique to decontaminate wastewater. The role of "solar chemistry" is now considered central, especially the photo-chemical processes involving absorption of photons by substrates and/or catalysts to trigger chemical reactions. In recent years, interest in AOPs has grown vastly for the removal of fertilizer and pesticide residues due to their potential to abate pollutants by complete mineralization.

Photocatalytic oxidation processes employing heterogeneous catalysts ($TiO_2$, ZnO *etc.*) and solar irradiation have demonstrated promising degradation of recalcitrant and persistent organic pollutants and their mineralization to less toxic and innocuous products such as $CO_2$ and $H_2O$. In this process, semiconductor photocatalysts work synergistically with energetic solar radiation and oxidizing agents to govern the degradation and finally mineralization of recalcitrant organic compounds. Photocatalytic degradation and complete removal of fertilizers, pesticides, and phenolics from water resources have been widely investigated. This process depends on many factors such as type of catalyst, pH of the solution, composition and concentration, nature of organic pollutants, solar light intensity, ionic components in wastewater, catalyst loading, solvents, concentration of oxidants, calcination temperature, and many others.

Recent advances in the technology of $TiO_2$- and ZnO-based photocatalysts doped with metals, non-metals or ions has made them popular for the degradation of fertilizers, pesticides and phenolics from industrial effluents and agriculture runoffs. This solar driven nano-photocatalysis facilitates the removal of a vast variety of recalcitrant toxic pollutants which are polluting aquatic systems due to their carcinogenicity, bio-accumulation, and non-biodegradability. These chemicals persist and remain in the environment and cause harmful effects to aquatic life and other ecosystems. The chemical nature of pesticides causes contamination in water sources due to their direct application on plants/crops and industrial discharge.

### 17.2.2 Future Perspectives of Solar Nano-photocatalysis

Extensive research is being conducted into the application of nanomaterials in the field of solar nano-photocatalysis which is revolutionizing water purification technology. Although the development and expansion in nano-photocatalytic materials has already began, still there remain important issues to be addressed, particularly related to the morphological and functional attributes of nano-photocatalysts. The flaws in the intensification process remain a major challenge along with limitations in mass transfer and consumption of photons.

Moreover, the fabrication and tailoring of nanostructures such as rods, spheres, flowers, flakes, and cones with enhanced structural and functional properties require particular care. In future research, more areas of nano-photocatalysis should be investigated to bring new photocatalysts into action. When synthesizing novel nano-photocatalysts, efficiency, inexpensiveness, eco-friendly aspects, and stability should be carefully considered.

Moreover, practical implementation of solar-driven nano-photocatalysis for wastewater effluents from various industrial sources is required in synergy with several related technologies, such as electrocatalysis, adsorption, thermodynamics, and other processes, to expand applications. Preparation of more nano-composites with improved properties other than metal oxide nanoparticles, such as carbonaceous materials, polymers, and ceramics, to enhance catalytic functionality and broaden their range of applications, is required.

## 17.3 Conclusions

This chapter described the use of solar radiation to accomplish redox reactions to mineralize recalcitrant water pollutants from various industrial sources. In the past few decades water purity has become a major concern, so water reclamation and recycling are being implemented rapidly worldwide to offset anthropogenic effects and avoid water scarcity. Climate change and poor management of water resources has aggravated this problem and caused imbalance in the availability and consumption of water resources. One of the best and attractive solutions is to avoid water pollution in the reclamation of wastewater in order to ensure sustainable development and management of water resources. The major concerns of water pollution arise from the involvement of persistent or recalcitrant organic pollutants even in water treated by conventional technologies. Environmentalists are engaged in a search for of non-toxic, cost-effective, environmentally friendly, and multifaceted new materials to remediate pollutants from all eco-systems. In terms of irradiation sources, there are some other issues that need to be dealt with appropriately, especially the generation of renewable energy. The sustainability of the environment needs to be ensured and production of innovatively effective nanomaterials, and modifications to already existing materials, is required in the future.

Heterogeneous photocatalysis using solar illumination is a promising technology to remove toxic and recalcitrant organic and inorganic materials from water *via* complete mineralization. Practically, the photocatalytic process becomes cost effective due to exploitation of solar light as a renewable energy source. Nanomaterials-based photocatalytic degradation of pollutants and contaminants using solar radiation has become very economical and eco-friendly as compared to artificial UV radiation which requires substantial electrical power input to carry out photolysis. To enhance the catalytic activity of nano-photocatalysts, they are tailored to increase their surface area and other morphological features. Morphological engineering and tuning of band-gaps in nano-photocatalysts are the indispensable factors required to prepare solar active nanomaterials for remediation.

In the recent years, effective wastewater treatment is supported by AOPs to meet ever the increasing demand for clean water. In AOPs, powerful oxidizing agents ($O_3$, $H_2O_2$ *etc.*) generate hydroxyl radicals for complete destruction of recalcitrant pollutants from wastewater. Heterogeneous photocatalysis through solar illumination on the surface of semiconductors is a smart approach for the use of oxidation processes for wastewater treatment applications.

Solar-driven photocatalysis (photo-Fenton and $TiO_2$-based photocatalysis) is an attractive environmentally friendly alternative, as the participation of sunlight curtails the use of electricity. Total mineralization of organic pollutants is achieved by solar photocatalysis. Mineralization of organic contaminants in asolar-driven process depends on a number of factors, such as the nature and initial concentration of contaminants, pH of solution, nature and amount of catalysts *etc.* Thus, to ensure a high mineralization rate, photocatalytic processes require optimal operational conditions. However, to take maximal advantage of solar radiation in photocatalytic technologies, the photo-reactors and technologies need to be carefully designed.

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CHAPTER 18

# Comparison of Biological and Physicochemical Techniques for Treatment of Coffee Wastewater – A Comprehensive Review

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## 18.1 Introduction

Water is of the greatest importance for all living organisms. The massive increase in the human population, rapid industrialization and urbanization have led to contamination of ground and surface water globally, and owing to this the world faces a great scarcity of fresh water.[1] Thus, it is essential to develop novel methods, with green chemistry and minimization of waste in mind, to overcome the drawbacks of conventional treatment technologies.[2] There are different methods to achieve removal of caffeine from effluent and treatment strategies for caffeine effluents, such as physical, chemical, electrochemical and biological treatment processes along with several alternate methods for caffeine elimination from wastewater. In this chapter, an overview of the opportunities and challenges of the various processes are elucidated.

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Chemistry in the Environment Series No. 5
Biological Treatment of Industrial Wastewater
Edited by Maulin P. Shah

Published by the Royal Society of Chemistry, www.rsc.org

### 18.1.1 Sources and Routes of Pollutants

The primary sources of water pollution are from agricultural, industrial and domestic activities, and global changes. More challenging is the unsafe level of various pollutants discharged into the surrounding environment directly or indirectly. Water sources, specifically freshwater bodies, are affected and natural water resources may be rendered unsuitable for practical use.[1,3]

As pollutants from industries are composed of acids, organic matter, detergents, silt, agricultural chemicals deposition, oil spillage, and are often high in temperature, industrial effluents have high total dissolved solids (TDS), total suspended solids (TSS), toxic metals, chemical oxygen demand (COD), biological oxygen demand (BOD), *etc.*[4] When discharged into surrounding water bodies, changes occur in the physio-chemical properties of water making it unsuitable for aquatic life, irrigation and drinking purposes (see Figure 18.1). Consequently, the pollutants cause damage to human health, living organisms and ecosystems, and modifications to climate. Global demand for quality water has increased, necessitating stringent standards in wastewater treatment and reuse to improve and preserve water quality. To combat the scarcity of water and increase water availability for use in agricultural production, treated

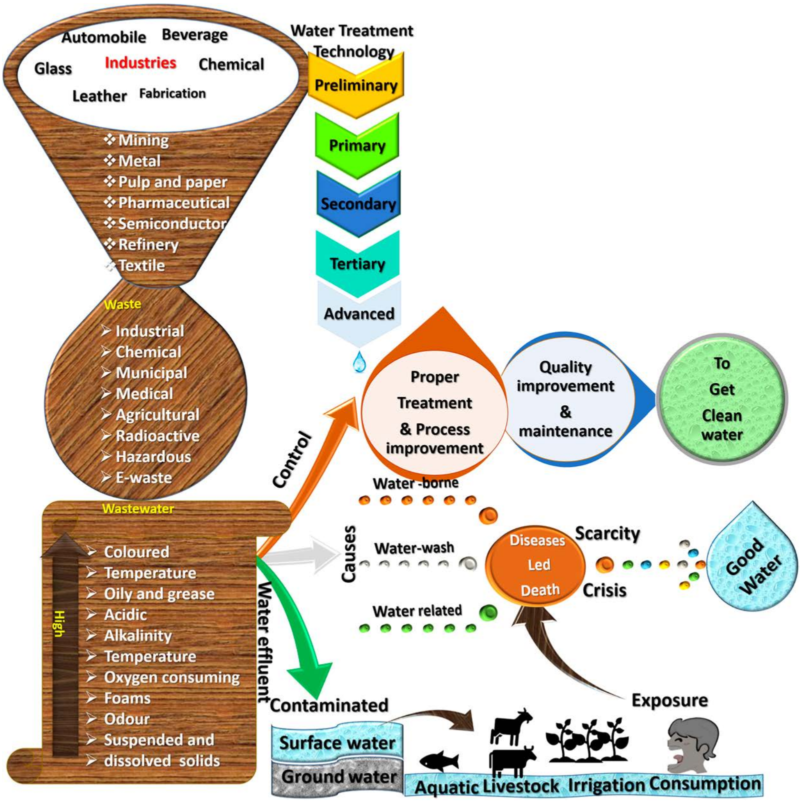

**Figure 18.1** Causes and effects of water pollutants from various industries as well as relevant waste water treatment methods and management systems.

wastewater is an authentic alternative for irrigation. Qiuguo *et al.*, reported that the reuse of treated wastewater carries several societal and economic advantages both for agricultural and environmental sustainability.[5] Nevertheless, treated wastewater releases several pharmaceuticals and personal care products (PPCPs) into agri-foods and water sources leading to contamination, causing numerous risks to human health and the environment.

### 18.1.2 Emerging Contaminants in Wastewater

The key emerging water pollutants are pharmaceuticals and PPCPs, disinfection by-products, endocrine disrupting chemicals (EDCs), flame-retardants, fuel additives, priority pollutants, plasticizers and other industrial organic products.[6] Currently, PPCPs have gained attention as emerging micropollutants and a threat to the marine environment and human health.[3] Several PPCPs and metabolites of toxic compounds have entered into the ecosystems mainly from effluents of wastewater treatment plants and social activities.[3] It has been reported that PPCP micropollutants are not completely removed by conventional wastewater treatment methods in sewage treatment plants. This is attributed to the contaminants' physicochemical properties, such as adsorption capacity on sludge, half-life, hydrophobicity, water-solubility, a tendency to hydrolysis, volatilization and biodegradability.[7] Pharmaceutical wastewater coming out from treatment plants contains different kinds of compounds and in various concentrations; thus, a novel method is required to remove this diverse group and large volume of contaminants.[2] Different types of PPCPs found in the environment include human drugs, veterinary drugs, illicit drugs and their consequent metabolites and conjugates including antibiotics, anticonvulsants, antihypertensives antidepressants, hormones, nonsteroidal anti-inflammatory drugs and lipid regulators.[8] The key root of PPCPs in the environment can be ascribed with anthropogenic activities. As a result, the physicochemical and biological characteristics of natural, surface, ground and drinking water have been altered (see Figure 18.2). Recently, among the

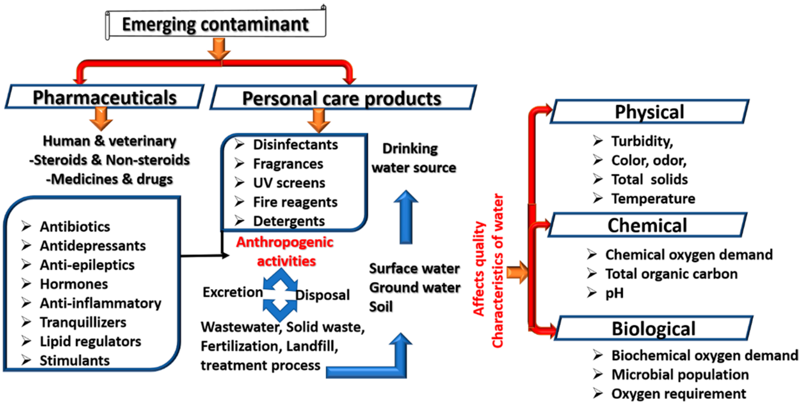

**Figure 18.2** Overview of emerging pollutants and the effect of human activities on the physicochemical and biological characteristics of water.

pollutants, caffeine, a psychostimulant from coffee wastewater, has attracted attention due to its persistence in water and effects on human health and the environment. Also, caffeine is considered a chemical marker for wastewater contaminants.[9,10]

### 18.1.3 Coffee Wastewater: Caffeine

Coffee is the second-largest exported product next to petroleum worldwide. According to coffee market reports of the International Coffee Organisation, the world coffee production is estimated to reach 10 million tonnes in the financial year of 2019–2020. Coffee wastewater has high amounts of COD and BOD, with the highest being reported as ~20 000 and 40 000 mg $L^{-1}$, respectively. On average, ≈200 MT of water is used for every tonne of coffee cherry during wet processing, and up to 80% of the harvested coffee cherry will go as organic waste.[11] The wastewater from coffee processing consists of noxious chemicals and compounds such as tannins, caffeine and polyphenols.[12] It also contains minerals, protein, sugars and high-water contents. Coffee wastes and its by-products are considered the source of severe pollution and cause a serious ecological problem. The literature has documented that the PPCP compound with the highest estimated concentration was caffeine. Current information on caffeine consumption suggests that it is primarily used as a stimulant all around the world. Caffeine, an alkaloid, is a constituent of several beverages such as coffee, tea and soft drinks.[13,14]

Caffeine is a psychoactive substance widely consumed either for beverages or PPCPs. It is predominant over other organic compounds in the coffee bean and is a well-known neurological stimulant. Other potencies of caffeine include its functions as a pain reliever and blood pressure regulator. It shows promising results in the treatment of bronchopulmonary asthma and apnoea in new born children. Derivatives of caffeine, theobromine and theophylline, are used as diuretics, vasodilators and myocardial stimulants. These methylxanthines have a higher half-life and less affinity towards adenosine receptors than caffeine.[15] Hence, they can serve as effective alternatives to caffeine with less neurological activity. Products of caffeine metabolism can be converted into caffeine by chemical derivatization. Xanthine finds its pharmaceutical application in drugs for the treatment of asthma.

Caffeine possesses excellent biocontrol and pharmacological applications. Chlorogenic acid present in the silver skin of the coffee bean has anti-fungal properties. Extract from silver skin inhibits the growth of saprophytic bacteria, and hence, it can be used asa wood preservative.[16] Nevertheless, the high loading rate (>75 L $m^{-2}$) of untreated wastewater significantly decreases the population of insects.[17] The effluent produced from the treatment plants contains several macromolecules such as polyphenols, mainly melanoidins. It also comprises ligand groups such as tannins, polysaccharides and caffeine.[6] These macromolecules and their dark brown colour are hard to remove and degrade by conventional treatment methods. Caffeine has been detected in surface water worldwide and is used as a chemical marker for surface water pollution.[12]

### *18.1.3.1 Caffeine's Adverse Effect on the Environment and Human Health*

When caffeine-rich effluent is released into the environment, it affects the microbial community residing there. It significantly hinders the beneficial growth of bacteria and seed germination.[18] Many researchers reported that >5 mM caffeine concentration causes harmful effects to fish by emerging toxicities at early developmental stages affecting embryos and causing hair cell damage and, abnormal branching.[10] Caffeine is non-toxic to human beings, but intense use of caffeine in the long-term may cause irritability, mutation effects such as adrenal stimulation, cardiac arrhythmias, inhibition of DNA, irregular muscular activity, osteoporosis, and so on.[19] It was reported that caffeine, consumption, as a thermogenic drug, ≈1.2–1.5 g per day, can blur eye vision and causes loss of consciousness and violent muscle contractions. Intake of 10–50 g of caffeine powder can lead to death. As caffeine is similar to adenosine in structure, it can block the adenosine receptor. It has been speculated that deaths owing to the consumption of caffeine are mostly associated with ventricular arrhythmia.[9]

Likewise, numerous studies reported that caffeine is a source of energy for the growth of several microbes. However, high concentrations and long-tern exposure to caffeine were toxic for bacteria and inhibited protein synthesis and DNA repair in bacteria and yeast. Also, it is not rare to find bacterial strains resistant to caffeine.[20] Additionally, it is well-known that caffeine is toxic to germinating seeds. Hence, extreme attention must be taken to degrade caffeine from industrial effluents and human waste products before they enter the environment. In recent years, numerous studies have reported caffeine degradation of up to 1 g initial concentration, but traditional wastewater treatment system cannot mediate complete removal of caffeine.[9] Conversely, caffeine consumption is expected to increase with the increase in the population. Thus, wastewater treatment plants require upgrading with better technology to degrade the caffeine and other PPCPs during wastewater treatment. In the next sections, various methods studied for caffeine treatment and their limitations and removal efficiencies will be presented.[21]

This chapter aims to present the current methods of caffeine degradation and their challenges, pros and cons. Also, suitable and alternate methods for caffeine removal from wastewater are discussed in the sections below.

## 18.2 Caffeine Degradation Methods

Currently, the numerous methods used for the treatment and disposal of wastes from industry can be divided into the following three classes and subclasses[2] *viz.* physical, biological and chemical methods. Physical treatments comprise of adsorption, dialysis, electrodialysis, evaporation, filtration, flocculation, sedimentation and others. Chemical processes include ion-exchange, neutralization, oxidation, reduction and precipitation. Anaerobic digestion, aerated lagoons, activated sludge and waste stabilization ponds are the commonly used biological wastewater treatment methods.[6] Still, discovery of new and novel treatment techniques that are affordable and provide achievable treatment and waste removal are necessary. In the sections below, physiochemical and biological processes of caffeine degradation in wastewater are elucidated.

## 18.2.1 Physiochemical Treatment Process

### *18.2.1.1 Adsorption*

Physicochemical treatment approaches have the ability to degrade multifaceted pollutants in wastewater in a short time. In this regard, adsorption, is one of the most commonly used technique for the effective removal of different micro-pollutants that do not biodegrade simply, like the emerging pollutant caffeine.[12] Adsorption is a simple process to execute and has a high removal rate. Rigueto *et al.* reviewed and listed various adsorbent materials for the degradation of caffeine, such as activated carbon, carbon nanofibre, charcoal, graphene oxide-based composites, and metals like Ni- and Cu-modified inorganic and organic pillared clays.[21]

Among the carbonaceous materials, activated carbon is one of the most commonly used absorbents for wastewater treatment. It has a good number of polar groups with hydrophilic behaviour, so adsorption of caffeine can happen easily by dipole–dipole interactions. However, it was reported recently that carbon adsorption and coagulation are considered as a pre-treatment, and tertiary treatment methods (like ultrafiltration) are required for complete removal of caffeine.[21] Recently, zero-valent iron (ZVI) has been used to treat all types of pollutants; ZVI is less toxic, is plentiful and is readily recovered by magnetism. However, since ZVI particulate matter is not easily restored, this makes ZVI-mediated methods economically unfeasible because ZVI materials need to be changed after each treatment process.[12]

Recently, layered double hydroxide (LDH) composite nanomaterials have been extensively used for wastewater treatment as adsorbents because they have several desirable physical traits, such as large interlayer spacing, and wide and specific compositions. Among the composite nanomaterials LDH/graphene is an efficient adsorbent material for removal of organic pollutants like caffeine from effluents. However, LDH nanomaterials have instability, deficiency of functional groups on the material surface, and crystalline structure limitations that minimize their efficient removal and hinder their application and large-scale production.[21] If this adsorbent material can be modified to have the required features, such as high surface area, less toxicity, easy recovery, recyclability and selectivity, then the LDH material can be used as a caffeine adsorbent. In the future researchers needs to address and overcome these issues and develop applications with these materials as the adsorbents.

### *18.2.1.2 Advanced Oxidative Processes*

Advanced oxidation processes (AOPs) are an alternative method for the degradation of hazardous, stubborn and non-biodegradable organic pollutant constituents in wastewater. AOPs consists of various processes such as the instantaneous usage of more than one oxidation process and include enhanced creation of the extremely reactive hydroxyl free radical.[1,22] This free radical mineralizes and oxidizes organic molecules to $CO_2$ and ions as the end-products, hence AOPs are considered as a good choice. The radicals are formed on site, interact with organics substance in the effluent and degrade the toxic molecules by hydrogenation or dehydrogenation.[9] AOPs have been classified into two phases: homogenous and heterogeneous. Radicals can be generated by non-photochemical and photochemical methods as well.

### *18.2.1.3 Non-photochemical Methods*

Non-photochemical methods include ozonation, Fenton reaction, sonalysis, wet air oxidation *etc.* In these processes, OH radicals are generated without light energy.[23] Electro-oxidation, where a stable anode is used to decrease the concentration of pollutant after pre-treatment with chemical flocculation or coagulation, has been described by several researchers in coffee wastewater treatment. Likewise, ozonation can be successfully applied in the rapid degradation of caffeine, but mineralisation is not quick.[12]It has been reported that 5.0 mg $L^{-1}$ of caffeine was degraded by 95.5% using a 1.0 g $L^{-1}$ $CeO_2$ catalyst *via* a sonocatalytic process.[10] However, the mechanism described for the sonochemical method is generally based on the generation of short-lived radical species formed in violent cavitation actions.[1]

A heterogeneous Fenton oxidation process using zeolite-incorporated iron nano-particles (NPs) has been used for the degradation of caffeine. The results indicated that the treatment cost of the heterogeneous process employed was more economical than the Fenton process.[24] The prepared catalyst was found to be stable, and reaction heterogeneity was maintained, as evidenced by tiny iron loss from the surface of the catalyst. However, mineralization of caffeine had not occurred in a significant reaction time.[25] Due to incomplete degradation of pollutants there is the risk of generation of metabolites more injurious than the parent compound. The above drawback can be overcome by light irradiation, *i.e.* photochemical methods.[9]

### *18.2.1.4 Photochemical Methods*

**18.2.1.4.1 Photo-Fenton Method.** Currently, several AOP methods have been used for the treatment of coffee effluents, including photo-catalysis with $H_2O_2$ and $Fe^{2+}$, with a semiconductor metal oxide. These methods degrade the toxic pollutants by producing hydroxyl radicals *via* the catalytic reaction between $H_2O_2$ and ferrous ions in solution. This process has been shown to decolourize coffee effluent by up to 93% in 250 min with various dosages of $H_2O_2$ and UV light. Likewise, researchers reported using a photo-Fenton process and 200 mg $L^{-1}$ of magnetic $FeO_2$ nanomaterials to achieve caffeine degradation of 5.0 mg $L^{-1}$.[10] The photo-Fenton reaction is more efficient for coffee effluent decolourization when $H_2O_2$ is added during the process. The main drawback of the process is that it is difficult maintain optimum pH (acidic) for this reaction at large scale.[12]

**18.2.1.4.2 Ultraviolet Radiation Catalysis (with Ozone).** Ozonation is a better choice as compared other photochemical process since ozone is a good oxidizer of several toxic organic pollutants. Low mineralization of pollutants by ozonation has been reported to be the main disadvantage of this process. This can be resolved and improved by use of UV or $H_2O_2$.[22] It was reported that COD reduction of 87% was achieved for pre-treated coffee wastewater by a photo-oxidation technique using UV/$H_2O_2$. Reports indicate that UV catalysis alone cannot be used as an effective method for wastewater treatment.[12]

**18.2.1.4.3 Photocatalysis.** At present, photocatalysis has been largely used for the degradation of organic contaminants owing to its better performance, ease of handling and its reasonable cost. Photocatalysis by green-mediated semiconductors and their ability to utilize a solar energy source makes it an efficient technology for wastewater treatment. Nano-scale semiconductor photocatalysis is considered an efficient system as it is largely available, cheap, less toxic and solar-energy harvesting.[21]

Similarly, caffeine degradation using numerous photocatalytic nanomaterials like Mg–ZnO–$Al_2O_3$, Mg-doped ZnO–$Al_2O_3$, $TiO_2$ powder, $TiO_2$ NPs, vanadium-doped $TiO_2$, ZnO NPs, ZnO–$ZnAl_2O_4$ *etc.*, have been reported in various studies and are listed in Table 18.1. As seen from the table, the photocatalytic degradation method showed the highest efficiency compared to other methods reported in the literature.[3] Earlier, the photocatalytic process faced issues with separation of catalyst from the treated wastewater. However, nanocomposites such as photocatalytic $AgFeO_2$ and FeZnO have superior catalytic activity, magnetic properties, lower toxicity, high stability and excellent recycling capacity traits. Due to these properties they can be easily separated from the water. Thus, nano-photocatalyst mediated processes are believed to be economical, effective as well as eco-friendly methods for caffeine wastewater treatment. Also, Lara-Ramos *et al.* reported that coupling of photocatalysis and the ozone process was more efficient for caffeine degradation in synthetic and real wastewater compared with other processes.[26]

## 18.2.2 Biological Treatment Process

Coffee wastewater has high amounts of caffeine and phenolic compounds, both of which are resilient. However, natural selection helps microbes to sustain and grow in such a toxic environment. Microbial treatment is a widely used wastewater treatment strategy due to its capacity to degrade a wide range of contaminants. Microbial techniques are economical as they

**Table 18.1** Comparison of various NPs and processes used for degradation of caffeine. Reproduced from ref. 10 with permission from Elsevier, Copyright 2020.

| No. | NPs | Catalyst load (g $L^{-1}$) | Process | Initial caffeine concentration (mg $L^{-1}$) | Degradation (%) | Time (min) | Reference |
|---|---|---|---|---|---|---|---|
| 1 | Zero-valent iron/copper | 0.2 | Adsorption | 5 | 86 | 45 | 10 and 26 |
| 2 | ZnO and ammonium persulfate | 0.7 | Photo-catalytic | 6 | 95.5 | 140 | |
| 3 | Mg doped ZnO–$Al_2O_3$ | 0.3 | Photo-catalytic | 20 | 98.9 | 70 | |
| 4 | ZnO–$ZnAl_2O_4$ | 0.3 | Photo-catalytic | 20 | 97.3 | 90 | |
| 5 | Bio-based substances-iron oxide magnetic NPs hybrid and hydrogen peroxide | 0.2 | Photo-Fenton | 5 | 99 | 180 | |
| 6 | $CeO_2$ | 1.0 | Sono-catalytic | 5 | 95.5 | 150 | |
| 7 | TiO2 Degussa P-25 | 0.25 | Ozone and photo-catalysis | 10 | 100 | 120 | |
| 8 | CdS@($Er^{3+}$ : $Y_3$ $Al_5$ $O_{12}$/$ZrO_2$) | 1.0 | Sono catalytic | 5.00 | 94.0 | 180 | |
| 9 | TiO2 Degussa P-25 | 0.3 | Coupling of $TiO_2/O_3/H_2O_2$/UV | 15.0 | 100 | 20 | |
| 10 | $TiO_2$ powder | 2 | Photo-catalytic | 2 | 100 | 360 | |
| 11 | Vanadium-doped $TiO_2$ | 3 | Photo-catalytic | 25 | 96 | 360 | |
| 12 | ZnO and $TiO_2$ | 1 | Photo-catalytic | 30 | 100 | 240 | |
| 13 | $AgFeO_2$ | 0.05 | Photo-catalytic | 50 | 100 | 900 | |

require fewer resources with lower operational cost compared to conventional physio-chemical methods. The ability of microbes to degrade such persistent compounds lies in the enzymes they harbour.

### *18.2.2.1 Enzymes Degrading Toxic Compounds in Coffee Wastewater*

**18.2.2.1.1 Caffeine Oxidases.** Caffeine oxidases belong to the enzyme class of oxidoreductases and these enzymes oxidise caffeine at the C8 position to produce 1,3,7-trimethyluric acid. It is the first characterized enzyme in the C8-oxidation pathway studied in a caffeine degrading mixed culture of *Rhodococcus* and *Klebsiella*. The purified caffeine oxidase is an 85 kDa single-subunit enzyme with higher specificity towards caffeine than other methylxanthines. Monomeric caffeine oxidase purified from *Alcaligenes* is smaller in size measuring 65 kDa. Spectral analysis of the enzyme showed the presence of a flavin group and non-haem iron. Biochemical studies further discovered serine and sulfhydryl groups in the active site, similar to xanthine oxidases. Although its characteristics were the same as xanthine oxidases, xanthine oxidase inhibitors did not affect caffeine oxidase activity. The flavin group helps in the transfer of an electron from donor to non-haem iron, which acts as a catalytic site for caffeine oxidation.[27]

**18.2.2.1.2 Caffeine Dehydrogenase.** In the C8-oxidation pathway of *Pseudomonas putida* CBB1, Yu *et al.* discovered a novel enzyme, caffeine dehydrogenase (*Cdh*), which is a multi-subunit enzyme, unlike caffeine oxidase. It belongs to the oxidoreductase family that oxidizes caffeine to trimethyluric acid (TMU). Its native form is 158 kDa with subunits CdhA, CdhB and CdhC with apparent molecular masses of 90, 40 and 20 kDa, respectively. Cdh has a non-haem molybdenum active site, FAD as a coenzyme and iron–sulfur clusters in subunit CdhA. Though it has similarities to several trimeric xanthine dehydrogenases and even a trimeric xanthine oxidase, none showed caffeine specificity.[28] For both caffeine oxidase and dehydrogenase, NAD and NADP are not suitable electron acceptors. The enzyme uses oxygen from water instead of activating molecular oxygen for catalysis. Further catalysis of TMU is aided by TMU monooxygenase (TmuM), producing 1,3,7-trimethyl-5-hydro xyisourate (TMU-HIU). Later, this is converted into 3,6,8-trimethylallantonin by either a hydrolase or rapid decomposition.[29] It enters into the purine catabolic pathway for complete mineralization.

**18.2.2.1.3 Caffeine Demethylases.** The major caffeine metabolic pathway in all mammals follows demethylation by cytochrome p450. Around 80% of caffeine degradation by microbes is *via* the demethylation pathway. It was first discovered in *P. putida*, where a cell-free extract of the strain catalyzed the conversion of caffeine into methylxanthines. Further investigation revealed that the reaction involves hydrolytic demethylation of caffeine into the respective methylxanthines. The hydrolytic cleavage of a methyl group from caffeine results in the formation of methanol as a by-product. Another strain of *P. putida* followed oxidative demethylation where formaldehyde is produced as a by-product. The demethylases produced are inducible in nature and degrade caffeine sequentially to xanthine through dimethyl and monomethyl xanthines. In the bacterial demethylation pathway, the major dimethylxanthines produced are theobromine and paraxanthine. 7-Methylxanthine was found to be prevalent over other mono-methylxanthines. Formaldehyde dehydrogenase and formate dehydrogenase found in microbes suggest formaldehyde conversion into $CO_2$.

Methanol dehydrogenase, which degrades caffeine by hydrolytic demethylation, is present in microbes. It converts methanol into formaldehyde, which is further acted on by formaldehyde dehydrogenase and formate dehydrogenase. Both types of demethylation need NAD(P)H as an electron donor for each demethylation step.[30] Previous studies on the caffeine-degrading microbes showed that all demethylases are inducible. Two-component oxidoreductases, oxygenase and reductase, carry out each demethylation step. Molecular studies revealed that five genes are involved in caffeine demethylation: ndmA, ndmB, ndmC, ndmD and ndmE. Oxygenase (NdmA, NdmB or NdmC) has a loosely bound non-haem Fe in the active site. The reductase component (NdmD) has a flavin group and a Rieske domain, which transfers the electron from the donor to the oxygenase component. The Rieske domain has a rhombic 2Fe–2S cluster, which helps in retaining and transferring electrons from NAD(P)H to the catalytic site. The enzyme sequentially demethylates caffeine to theobromine, 7-methylxanthine and xanthine by NdmA, NdmB and NdmC, respectively. NdmC lacks the Rieske domain, but it is present in the other two oxygenases, and requires NdmE for stabilization and activity. The function of NdmE is unknown but it has high sequence similarity to glutathione-*S*-transferase. Molecular studies on NdmD reveal that the presence of an additional Rieske domain has no role in reductase and demethylase activity.[31]

**18.2.2.1.4 Peroxidase and Laccases.** White-rot fungi, which degrade lignin, produce extracellular peroxidase and laccase predominantly. Also, these enzymes reduced phenol levels in a synthetic medium as well as in real effluent. Peroxidases are hydrolytic enzymes that break down complex organic compounds by oxidation. Immobilized soybean hull peroxidase was found to efficiently remove ≈20% of phenolic and caffeic acid from coffee wastewater.[32] Laccases are copper-containing enzymes that fall under the superfamily of oxidoreductases. An enzyme purified from the white-rot fungus *Trametes pubescens* degrades various phenolics present in a wide range of agro-industrial waste, including coffee wastewater.[33]

### *18.2.2.2 Bioreactors in Coffee Wastewater Treatment*

Reactors provide controlled conditions for the bioconversion or degradation of contaminants present in wastewater. Different reactors have been studied to evaluate their performance in coffee wastewater treatment. Most of the reactors studied were anaerobic, which aims for biogas production as a by-product of treatment. Coffee-processing residues have high mucilage content, which enhances the accumulation of methanogens under anaerobic conditions, thereby facilitating the process.[34] Thermophilic sludge used in a continuous stirred tank reactor (CSTR) increases the stability of the operation at high organic loading rate (OLR) and produces methane at a lower hydraulic retention time (HRT).[35] It has been shown that the higher organic loading rate and the thermophilic temperature were suitable for the evolution of methanogens like *Methanosarcina* to *Methanothermobacter.*[36] An anaerobic membrane bioreactor (AnMBR) operated at a mesophilic temperature with a HRT of 15 days yielded an average of 0.29 L $CH_4$ per gram of COD.[37] The introduction of exhausted coffee waste into a continuous anaerobic reactor increased methane yield 3-fold due to its high C/N ratio.[38]

An anaerobic environment favours the production of organic acids, methane and $H_2$. $H_2$ gas production can be carried out by inactivating the methanogens present in the inoculum by heat pre-treatment of 90 °C for 2 hours. This leaves the spore-producing *Clostridium* sp., which produces $H_2$ gas from carbohydrate present in wastewater.[39]

Wastewater has high carbon and nitrogen content and attracts plenty of microorganisms based on storage and exposed environment. Simulated wet-processing of coffee beans under laboratory conditions accumulated three predominant bacterial communities, namely *Clostridium*, *Lactobacillus* and *Acetobacter* sp. The distribution ratio of bacteria in coffee wastewater can be tuned by adjusting the pH, temperature, COD and aeration, which in turn alters the levels of $H_2$, alcohols and organic acids production.[40] Details of anaerobic reactor studies on coffee wastewater treatment so far are given in Table 18.2.

**18.2.2.2.1 Upward Anaerobic Sludge Blanket Reactor.** Upward flow Anaerobic Sludge Blanket reactors (UASBs) are widely studied reactor systems for coffee wastewater treatment that have a high benefit to cost ratio. They have been explored extensively in treating coffee wastewater, which focuses on by-product production from wastewater COD reduction. The sludge collected from anaerobic reactors under mesophilic conditions is used as seed for the UASB. Experiments conducted under mesophilic (35 °C) and thermophilic (55 °C) conditions significantly reduced the COD level. The efficiency of COD removal varies with inoculum, HRT and microbes present in wastewater. The performance of the reactor was found to be effective under mesophilic conditions, with 78% COD reduction at a HRT of 21 days.[40] The total volatile fatty acids can be efficiently removed under thermophilic condition upon pre-acidification of wastewater.[45] Chen *et al.* investigated the caffeine degradation potential of an AnMBR in coffee effluent and at a HRT of 5 days: up to 87.5% of externally added caffeine was degraded.[46] A UASB combined with a photocatalytic reactor increases the treatment efficiency in terms of COD and polyphenol removal in retting-pond wastewater.[47] Further integration of a photocatalytic reactor with the Fenton process increased COD and polyphenol removal up to 97.5 and 98.4%, respectively.[48]

**Table 18.2** Reactor studies for coffee wastewater treatment.

| No | Inoculum | Reactor type[a] | Temperature (°C) | COD removal (%) | BOD removal (%) | TDS removal (%) | HRT (days) | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | Sludge from anaerobic coffee treatment | UASB | 55 | 70 | — | — | 21 | 41 |
| | | | 35 | 78 | | | | |
| 2 | Cow dung enriched with coffee waste | UAHB | RT | 61 | 56 | 68 | 0.75 | 42 |
| 3 | Methanogen-inactivated sludge from an anaerobic digestor | Two stage UASB | 35 ± 1 | 98 | — | — | 2 | 39 |
| 4 | Waste-activated sludge | AnMBR | 55 | 82.4 | — | — | 10 | 37 |
| 5 | Sludge from food waste treatment | AnMBR | 55 ± 1 | 90 | — | — | 3 | 36 |
| 6 | Mesophilic UASB sludge | Anaerobic chamber | 37 ± 2 | 74 | 47 | 69 | 32 | 43 |
| 7 | Soil microbes | IMBR | 28 ± 2 | 99 | | 76 | 15 | 44 |

[a] UASB, upward anaerobic sludge blanket reactor; UAHB, upward anaerobic hybrid bioreactor; AnMBR, anaerobic membrane bioreactor; IMBR, integrated membrane bioreactor.

Aeration favours reduction of COD, BOD, TSS and conductivity of biomethanated wastewater and makes water suitable for environmental release. A steady increase in the removal percentage of contaminant markers was observed upon increasing the aeration interval. Integrating UASB with aeration and a constructed wetland system was found to be highly efficient by removing 97% COD, 98% BOD and 90% TDS.[42]

**18.2.2.2.2 Integrated Membrane Bioreactor.** An integrated membrane bioreactor (IMBR) is an integration of a membrane bioreactor, reverse osmosis and ultrafiltration. In an IMBR, microbial consortia are allowed to attach to the membrane for 15 days with aeration. The MBR acclimatized with anaerobic sludge reduced COD by up to 40%. Colour reduction and turbidity was reduced by up to 50%. After 15 days, the treated water was filtered through high flux ultra-filtration (HF-UF) followed by reverse osmosis, resulting in a 100% reduction in colour, odour and turbidity, with 99% COD reduction.[44]

**18.2.2.2.3 Extractive Membrane Bioreactor.** An extractive membrane bioreactor is a combination of an extraction and a membrane bioreactor. The set-up had a cross-flow hollow fibre membrane when used with phenol-rich wastewater, and the inner surface of the membrane was immobilized with phenol-acclimatized sludge. The hollow fibre membranes were prepared by coating layers of polydimethylsiloxane over polyetherimide. A hollow fibre membrane made of polypropylene impregnated with trioctyl phosphine oxide decreased substrate inhibition of *P. putida*. The resultant extractive membrane bioreactor degraded 2 g $L^{-1}$ of phenol entirely in 36 h.[49]

### *18.2.2.3 Constructed Wetlands*

Constructed wetlands are a common treatment strategy employed in all stages of treatment depending on the influent characteristics. Aerated constructed wetlands increase the removal of COD, N, P and phenolic compounds present in coffee wastewater, and introducing plants into the system further enhances the removal efficiency. Also, the treatment was affected by the type of plantation in the wetland. Plantation helps in the efficient removal of TDS when compared to non-planted wetlands. Plants with phytoremediation potential seem to be effective in the reduction of contaminant indicators. However, studies conducted with these combinations so far are restricted to natural habitats. Constructed wetlands with two-stage constructed wetlands in sequence having two types of plants in each, removed 95% COD with 94% TSS removal.[50]

### *18.2.2.4 Other Treatment Processes*

Torres-Valenzuela investigated the usee of long-chain fatty acids and alcohol for the treatment of coffee wastewater. Hexanol or decanoic acid rearranges itself as hexagonally inverted aggregates spontaneously in wastewater, and the resultant aggregated solvent is called supramolecular solvents (SUPRAS).

SUPRASs help in recovering caffeine and anti-oxidants and thereby reducing the COD level. BOD, TSS and conductivity were reduced by 89, 50 and 67% for hexanol-based SUPRAS, whereas decanoic acid-based SUPRASs were found to be best for COD removal.[51] A membrane-filtration technique has been successfully used for the treatment of industrial wastewater. The main disadvantage is membrane clogging and fouling. In addition, the membrane only filters and separates the caffeine compound; it does not degrade the compound in the wastewater. Other treatment processes such as chemical coagulation and flocculation, electrochemical, spray irrigation and ionization irradiation using gamma radiation have also been used for wastewater treatment in various studies. However, these methods have been unable to achieve complete removal of toxic compounds found in coffee wastewater. Thus, for exceedingly contaminated effluent such as coffee wastewater an advanced treatment method may be required.

## 18.3 Alternative Methods for Caffeine Removal from Wastewater

Currently available methods of caffeine degradation, although robust and well-studied, have several shortcomings when it comes to application in treating a complex effluents such as those from coffee processing units. Several other alternate methods have been studied and their advantages over the currently used methods have been discussed in recent reports.

The use of ion-exchange resins has been advocated to be effective for caffeine-containing wastewater in one report. Ion-exchange resins have been successfully used in reducing COD, colour and complex chemistries in various kinds of contaminated water.[12] Studies using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy have demonstrated that strongly hydrated anions desolvate the caffeine molecule and increase aggregation,[52] and this may form the basis for the use of an appropriate ion-exchange resin coupled with adsorption to decaffeinate coffee wastewater. Another novel system which combines chemically enhanced primary sedimentation of sewage with acidogenic fermentation of sludge in tandem has been shown to effectively remove trace emerging chemical contaminants from wastewater in a more cost-effective manner compared with conventional wastewater treatment systems.[53] This strategy can be studied for decaffeination of coffee effluent.

Biological decaffeination by use of enzymes and microbes is one of the best strategies for caffeine removal. Considering the solubility and biodegradability of caffeine, novel methods have been developed as an alternative to physical and chemical methods. Keeping in mind the various biochemical steps involved in caffeine degradation, combination of more than one enzyme or the combination of microbe and enzyme may also be very effective in removing caffeine and its metabolites from effluent. Along with the enzymes discussed in the previous sections, other enzymes such as glucose oxidase have also been shown to be effective in reducing caffeine content in effluents. A combination of glucose oxidase, laccase and peroxidise was found to effectively reduce caffeine by 41%, which was further enhanced to 46% in the presence of co-substrates such as glucose and manganese sulfate.[54] Apart from enzymes, immobilized whole cells of caffeine degrading strains have been shown to be very efficient in decaffeination and this can be extended to treatment of caffeine-containing wastewater. Induced whole cells of *Pseudomonas* sp. immobilized in agar–agar beads degrade caffeine at 10 g $L^{-1}$ initial concentration and this is mediated by mass transfer of substrate, which is ideal for waste water treatment.[55] In another study on coffee processing industrial effluent, up to 80% caffeine removal was mediated by alginate-immobilized cells and biofilm of the yeast *Trichosporon asahii* formed on gravels over a period of 48 h in batch mode.[56] Such strategies can be used in combination with existing biofilm-based water treatment methods such as fixed-bed reactors (FBRs) and mixed-bed bioreactors (MBBRs).

## 18.4 An Overview of Opportunities and Challenges

The consumption of caffeinated beverages and food products has seen a considerable increase in the recent past owing to the fast-paced lifestyle. This in turn has led to an increase in the production capacity of coffee processing units, which generate more effluent. Due to the constant modifications in processing aids and chemicals, the chemical nature of effluent has also become more complex, making it recalcitrant and resistant to the currently available effluent treatment methods. Caffeine in particular is quite resistant to the natural environmental micro flora of an effluent treatment plant, hence it is deemed necessary to incorporate the treatment processes described in the effluent treatment systems of coffee processing units and also municipal sewage treatment plants. There is immense scope for development of a biological method for caffeine removal in effluents, which might be enzymatic or microbial or a combination of both. Also, the shortcomings of physical and chemical methods to remove caffeine in effluents, in terms of high running costs, could be overcome by a hybrid technique consisting of a suitable biological method in combination with a physico-chemical method. Significantly low caffeine concentration in wastewater, often in the range of ng $L^{-1}$ or μg $L^{-1}$, makes it difficult to selectively remove caffeine from effluent, and this is one of the challenges in this field. Apart from that, caffeine effluents have a large number of diverse compounds, which makes quantification and characterization of each constituent difficult and hinders effective decaffeination. Most described physico-chemical methods are slow and not suitable for an industrial set-up. Enzymes in the caffeine degradation pathway have yet to be studied and most of them have been found to be unstable or very poorly expressed. More research is required in this field to develop a better and robust method of caffeine removal from wastewater.

## 18.5 Conclusions and Future Perspectives

Wet processing of coffee produces considerable amounts of caffeine-containing effluent which enters the environment and has several detrimental effects on aquatic and soil microflora and animal life. Caffeine from surface and ground water can be ingested by humans and over a period of time caffeine bio-accumulates in tissues and may harm health. The various methods described for removing caffeine from wastewater have their pros and cons. In this aspect, efficiency and cost of operation play major roles in the acceptance of a method at large scale, such as for a coffee processing unit or sewage treatment plant. Of the various methods described in this review, biological methods are more specific and economical along with being environmentally friendly. However, research on scale-up and commercial development of a biological method for caffeine degradation in effluent is still at the laboratory scale. An integrated approach of physico-chemical and biological methods may prove to be most efficient for removing caffeine from wastewater.

## Acknowledgements

The authors would like to acknowledge IIT Madras for the research facilities. M.K.S. would like to thank MHRD and IIT Madras for a fellowship. H.M. acknowledges SERB-DST for a National Post-Doctoral Fellowship (SO. No: PDF/2018/000795).

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