Engineering Materials

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Magnetic Nanomaterials

Synthesis, Characterization and Applications

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Engineering Materials

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To our families: past, present, and future.

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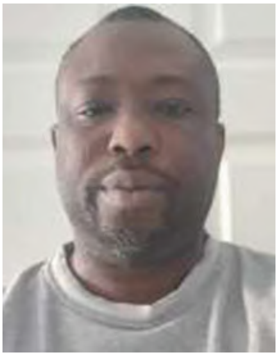

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An Overview of Magnetic Nanomaterials

Kingsley Eghonghon Ukhurebor, Uyiosa Osagie Aigbe, Robert Birundu Onyancha, Vincent Aizebeoje Balogun, Osikemekha Anthony Anani, Kenneth Kennedy Adama, Kaushik Pal, Heri Septya Kusuma, and Handoko Darmokoesoemo

Abstract Like every other nanomaterial (NM) or nanoparticles (NPs), magnetic nanomaterials (MNMs) or magnetic nanoparticles (MNPs), utilize bionanomaterials (BNMs), nanosized materials composed of various biological entities. MNMs are advanced materials that, once synthesized and characterized, can be used in solar cells, theragnostic nanomedicine, drug and gene delivery agents, tissue engineering,

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biosafety and bioregulation aspects, pathogen combat, wastewater treatment, soil decontamination, detection, sensing, and monitoring of heavy metals, dyes, toxic gases, and so on. Several MNMs or MNPs have been utilized for applications in biomedical, agriculture, and environmental (atmospheric, aquatic, and terrestrial) fields. Hence, this introductory chapter presents a summarized highlight of the various synthesis and characterization techniques of MNMs, along with the various applications and potentialities of MNMs both in the biomedical, agricultural, and environmental fields, as well as catalytic processes which is the major aim of this book. Also, some outstanding prospects of MNMs or MNPs in biomedical, agricultural, and environmental applications are highlighted in the conclusion section.

Keywords Agriculture · Biomedical · Environment · Nanomaterials · Nanotechnology · Magnetic nanomaterials

1 Introduction

Exciting scientific and technological advancement is one of the utmost gains to humanity [1, 2]. Its potentiality to manoeuvre innovative materials of various dimensions has generated an evolution in the scientific and technological fields that has improved the lives of human beings, and nanotechnology (NTech) remains one of the major contributors to this evolution [3, 4]. Contemporary advances in the field of NTech have helped to advance and revolutionize a variety of industries. The number of advantages and uses for NTech is expanding quickly and have advanced scientific and technological field, and it has been considered one of the best technologies for studying the properties, synthesis, characterization, and applications of nanosized constituents [3]. They differ from their parent bulky materials in that they are small particles with an average dimension range of between 1.00 and 100.00 nm, which makes them suitable for a variety of applications [3, 5].

Among these, magnetic nanoparticles (MNPs) or magnetic nanomaterials (MNMs), a nanoscale substance with exceptional magnetic features, have found extensive use in a variety of industries, including biomedical, engineering, energy, and environmental applications. Due to their distinct and distinctive features, which could make them valuable in biomedical, agriculture, environmental (atmospheric, aquatic, and terrestrial) fields and catalysis processes [6]. MNMs have recently become the focus of intense investigation [6]. Hence, Researchers' interest in the possibility of increasing a material's potential at the nanoscale has led to success on a worldwide scale in practically all fields [7].

Due to the potential, they present, MNMs or MNPs are a type of materials that have drawn interest from the research community. Their capacity to alter their morphology and particle size has resulted in the modification of their spin alignment [8]. For a variety of uses, the tuning of the spin alignment can be gathered. For soft magnet applications, for instance, the saturation magnetism seen in ferromagnetic nanomaterials (NMs) or nanoparticles (NPs) is essential because it makes scaling up and shrinking simple [6]. Modern industries have undergone significant change as a result of numerous NM applications [3]. MNMs or MNPs have engrossed study attention lately owing to their environmental, agricultural, biomedical and industrial applications [6, 9].

Evidently, several MNMs have been utilized for applications in biomedical, agriculture, and environmental (atmospheric, aquatic, and terrestrial) fields, and these synthesized and characterized MNMs are used in solar cells, theragnostic nanomedicine, drug and gene delivery agents, tissue engineering, biosafety and bioregulation aspects, pathogen combat, wastewater treatment, soil decontamination, detection, sensing, and monitoring of heavy metals (HMs), dyes, toxic gases, etc. Hence, this chapter, which is an overview of MNMs and is the introductory part of this book titled "MNMs-synthesis, characterization, and applications", will briefly highlight the various synthesis and characterization techniques of MNMs, along with an overview on MNM's basic applications/utility in biomedical, agriculture, and environmental (atmospheric, aquatic, and terrestrial), as well as catalytic processes along with the prospects and topical tendencies. A diagrammatic illustration of this introductory chapter is shown in Figs. 1 and 2 illustrates the various chapters contained in this book.

Additionally, this book attempts to emphasize the synthesis and characterization of MNMs in Chap. 2. Chapter 3 deals with the utility of MNMs for theragnostic nanomedicine, while Chap. 4 is on MNMs for HMs detection, and Chap. 5 discusses MNMs for dye sensing. MNMs' applications in solar cells are discussed in Chap. 6 and the applications of MNMs for wastewater treatment are discussed in Chap. 7.

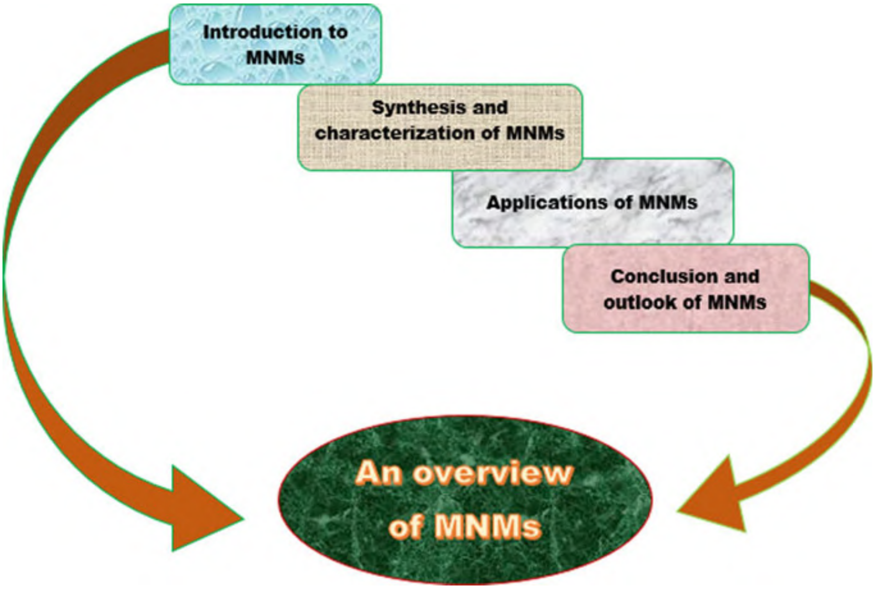

Fig. 1 A diagrammatic illustration of this introductory chapter (MNMs: magnetic nanomaterials)

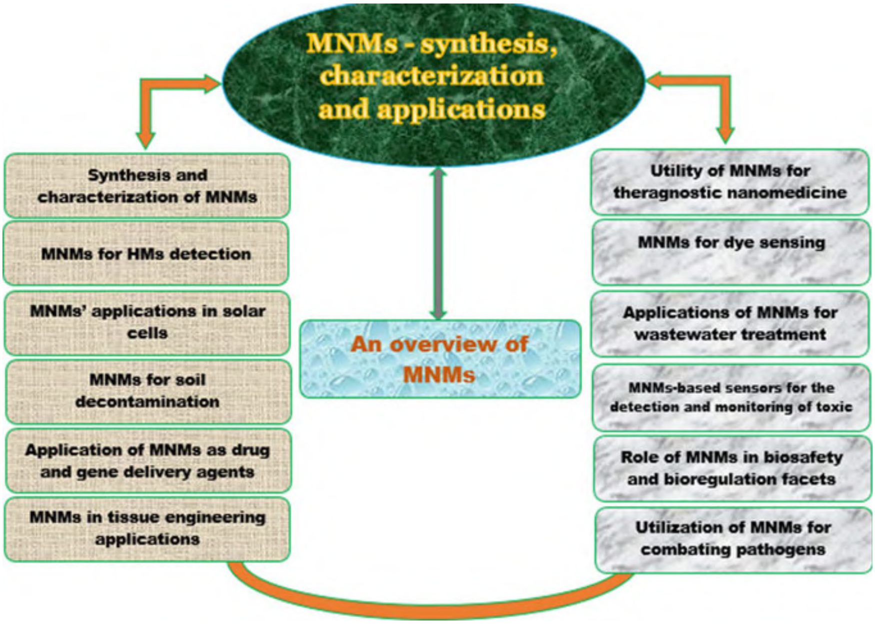

Fig. 2 An illustration of the various chapters contained in this book (MNMs: magnetic nanomaterials)

Chapter 8 covers MNMs for soil decontamination, and Chap. 9 is on MNMs-based sensors for the detection and monitoring of toxic gases. Chapter 10 will deal with the application of MNMs as drug and gene delivery agents, followed by Chap. 11, which deals with the role of MNMs in biosafety and bioregulation facets. The potentialities of MNMs in tissue engineering applications are discussed in Chap. 12, while Chap. 13, which is the last chapter of this book, will deal with the utilization of MNMs for combating pathogens.

2 Synthesis and Characterization of MNMs

This section briefly highlights the various synthesis techniques and characterization techniques of MNMs.

2.1 Synthesis Techniques of MNMs

The development of various methods for the synthesis of MNMs or MNPs has been the focus of intense research during the last few years. Several synthetic techniques

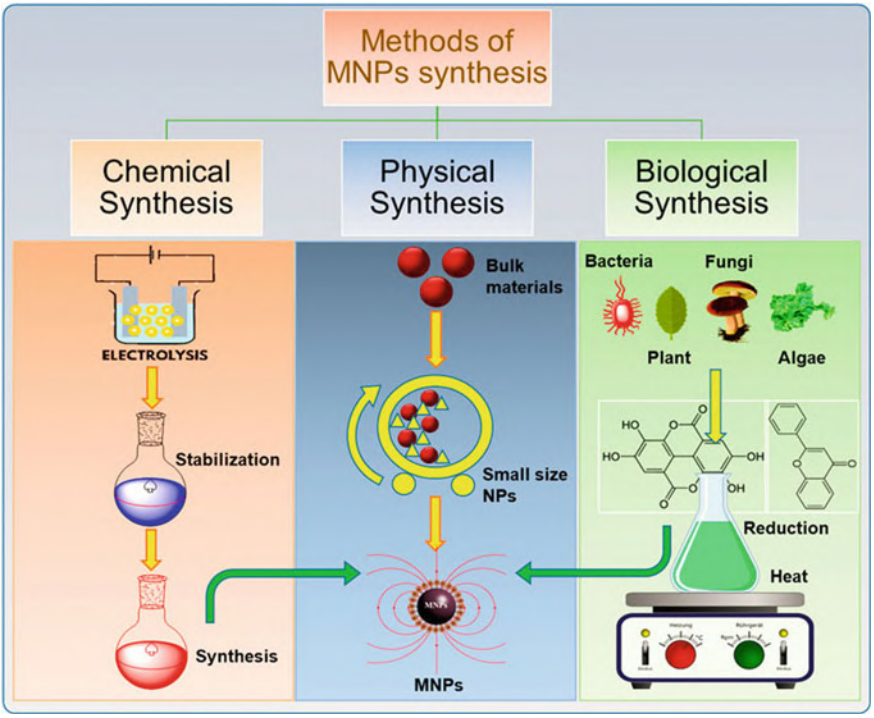

Fig. 3 Pictorial diagram of the synthesis of MNMs or MNPs prepared through various biological, chemical, and physical techniques. Adapted from Ali et al. [9]; Copyright, Frontiers publishers, 2019. Reprinted with permission from Frontiers publishers from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY). (MNPs: magnetic nanoparticles, NPs: nanoparticles)

are utilized to produce MNMs with the necessary size (dimension), shape, stability, and biocompatibility. The most popular techniques for synthesizing MNMs are; "ball milling, thermal decomposition, coprecipitation, sol–gel, hydrothermal, microemulsion, and biological techniques". Figure 3 contains a schematic/pictorial illustration/diagram of the synthesis of MNMs prepared through various biological, chemical, and physical techniques as adopted by Ali et al. [9].

2.1.1 Physical Techniques

The physical techniques use both top-down and bottom-up strategies. Through high intensity ball milling, the bulk constituents are reduced to nanoparticle size in the top-down method. It is challenging to produce NPs through mechanical crushing that are the required form and size [10]. In contrast to the top-down strategy, the bottom-up method can produce fine, well-dispersed nanoparticles. A bottom-up strategy example is laser evaporation [11]. MNPs are also created using different physical techniques such as the wire explosion technique and the inert-gas condensation technique. Some of the commonly used physical techniques are mechanical/ball milling technique [12], wire explosion technique [13, 14], and laser evaporation technique [11].

2.1.2 Chemical Techniques

The various bottom-up processes used in chemical synthesis are diverse. In a recent review publication by Ali et al. [9], several popular techniques that are frequently employed in synthesizing MNMs are comprehensively described. These commonly used chemical techniques are coprecipitation technique [15–18], thermal decomposition technique [19–22], microemulsion synthesis technique [18, 23, 24], hydrothermal synthesis technique [24–27], and sol–gel technique [12, 28, 29].

2.1.3 Biological Techniques

Biological synthesis is one of the well-known techniques for synthesizing MNMs [9], which involves employing living things like plants and microorganisms (such as actinomycetes, fungi, bacteria, and viruses) [30]. This approach creates MNMs that are comparably biocompatible and have practical uses in the biomedical industry. This approach has advantages in terms of effectiveness, environmental friendliness, and clean procedure. The drawback is the NMs' ineffective dispersion [31]. Researchers are now very interested in the production of NMs employing the tissues, extracts, exudates, and other components of plants [32]. For instance, ferromagnetic magnetite particles with an average size of 60 nm have reportedly been produced naturally [33]. The use of microorganisms and plants (biological) to produce NMs is one of the potential methods that have just come to light for the synthesis of MNMs, although the mechanism by which this occurs is still poorly understood [31, 34]. For instance, some research offered potential processes for metal NM mycosynthesis [9].

Nitrate reductase activity, shuttle electron quinones, and a mixed process are the three proposed mechanisms [9]. However, the process of acknowledging MNM preparation is not particularly clear [31]. The Suzuki–Miyaura reaction and photocatalysis were both carried out using biologically produced Fe_3O_4 magnetic material as a catalyst [27]. This approach has some drawbacks that need more research, such as yield and MNM dispersion [34, 35].

However, utilizing magnetism to help separate biosorbents from the solution and increase efficiency is a relatively recent development that is now clearly attracting attention. This entails using external magnetic fields and employing magnetic biosorbents during the biosorption process [6, 36].

2.2 Characterization Techniques of MNMs

To evaluate the physicochemical characteristics of MNMs, they are characterized using a variety of equipment [37–43]. The display of many physicochemical features of NMs depends significantly on their size. Their characteristics can be altered by even a slight change in their nanoscale dimension [9]. The following are some of the most commonly used tools for the characterization of MNMs: "Atomic Force Microscopy (AFM), Energy Dispersive X-ray Diffraction (EDXD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FT-IR) Spectroscopy, UV Spectrophotometer, Transmission Electron Microscopy (TEM), and Mossbauer Spectroscopy (MS) are a few of the tools used for the characterization of MNMs" [9, 44].

3 Applications in of MNMS

The MNMs have attracted lots of consideration in the last few years owing to their promising outcomes in a variety of sectors [9]. MNMs' applicability is made more promising by their super/exceptional-magnetic characteristics, distinctive dimensions and form, high surface area and volume ratio, and biocompatibility [6]. These characteristics have drawn researchers from various fields to it [9]. In this section of this introductory chapter, we have briefly discussed the endowed applications of MNMs in a number of well-known fields, such as the biomedical, agricultural, and environmental domains, as well as catalytic processes.

3.1 Biomedical Applications of MNMs

As a result of their numerous physicochemical characteristics, simplicity in synthesis, biocompatibility, and stability, MNMs have recently been widely used in numerous biological applications [1, 9, 45]. External magnetic fields can affect MNMs. Magnetic resonance imaging can be improved by MNMs since they can change the magnetic fields nearby (MRI) [9, 46]. The translation, rotation, and energy dissipation that the externally applied magnetic field causes and creates in dipoles occur from several types of force and torque. Numerous applications of these phenomena exist, such as cell separation and biomarker transfer, magnetic drug administration, magneto-mechanical activation of cell surface receptors, biomedical imaging, bacterial theragnostic, drug release triggering, and hyperthermia. Depending on their use in various applications, several materials with different physical and magnetic properties make up the formulation of MNMs. However, in biomedical research, their potential biocompatibility or toxicity must be taken into account as the most crucial element [9, 47]. The following are some of the recognized biomedical applications of MNMs: cancer theranostics [48, 49], bacterial theranostics [25, 50–56], and biosensing [57, 58].

3.2 Agricultural Applications of MNMs

Numerous studies have been completed that demonstrate how well metallic nanoparticles can be used for soil quality improvement, plant protection, and seed germination effective application of metallic NMs in plant safety, seed germination, and enhancing soil quality [59, 60]. Iron (Fe) oxide MNMs, for instance, can be utilized as nutrients of the soil to boost production with the fewest adverse effects [61]. Fe is a very important element that is involved in many physiological processes, including respiration, biosynthesis, the production of chlorophyll, and redox reactions [62].

A number of plants, including peanuts, lack Fe. Numerous studies have been done in this field to use Fe NMs to treat the deficit and increase Fe consumption [63–66]. The majority of the time, NMs are used as nano-fertilizers in hydroponic systems rather than in the field. Fe is thought to be the soil nutrient that is most prevalent for plants. Its accessibility is still a problem for plants. Therefore, using analytical methods, functionalized Fe oxide NMs can circumvent this issue and overcome obstacles and uptake by plants [9].

Ju et al. [67], created water-soluble Fe oxide NMs (IONP-EDTA) by synthesising Fe oxide NMs through thermal decomposition and oleic acid capation (IONP-OA), followed by a ligand exchange method with N-(trimethoxysilylpropyl) EDTA to track Fe absorption and transport in plants. They developed a technique to use magnetic particle spectroscopy to track the absorption and distribution of various chelating Fe NMs (10 and 20 nm). The authors demonstrate that there were more Fe ions produced by the larger IONP20-EDTA NMs than the smaller IONP10-EDTA. Regarding IONP20-EDTA treatment, there is a rise in the production of biomass and chlorophyll. Neither the size nor the shape of the constituent parts produced from the IONP10-EDTA or IONP20-EDTA samples exhibit any appreciable changes in the TEM images. The location of the Fe oxide NM build-up, which demonstrates the plant's uptake route through roots. The dual paths for the uptake and translocation of the Fe oxide NMs into the upper components of the plants are also shown, along with the uptake of Fe via the root via various oxidation states (apoplastic and symplastic pathways).

The use of MNMs in disease management is still evolving, despite the fact that many MNMs have been employed as antimicrobial agents in biomedical studies to treat innumerable types of plant diseases [68, 69]. For targeted delivery to certain sections of the plant, MNMs can be useful. Tracking the internal MNM movement is particularly useful for the focused treatment of particular plant areas [70]. It has been claimed that MNMs can be used for the transmission of biomolecules (BMs) into plant cells and that their magnetic properties can be used to direct conveyance and localization.

For instance, a study described treating plant diseases with carbon-coated magnetic Fe NMs and in vitro culturing of *Cucurbita pepo*. Using confocal, optical, and electron microscopy, the localisation was detected [71]. In intelligent delivery systems, the conjugation of MNMs with other BMs like nucleic acids, drugs, and enzymes is highly helpful. It is very effectively used to transfer a gene and have it expressed in the host cell. At present, three different categories of carrier systems—viruses, electroporation using nucleic acid, and transfection—are used to convey genes. For many medical issues, the transfection approach holds a very significant solution. Kudr et al. [21], use MNMs to coat cultivated cells to increase their transfection efficiency. The usage of NMs can increase cell toxicity, which limits their utility in certain in vivo and in vitro research studies.

3.3 Environmental Applications of MNMs

As a result of the increased release of hazardous and deadly chemicals and composites because of the anthropogenic activities, the degradation and contamination of the water (aquatic environment), soil (terrestrial environmental), and the air (atmospheric environment) are emerging as major environmental issues [72, 73]. Pharmaceuticals, pesticides, industrial wastes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons are only a few examples of the numerous organic pollutants that are permanently present in the environment [9, 74–76].

Groundwater, ocean, sewage effluents, and drinking water all include various types of organic contaminants. When such types of persistent organic contaminants enter the food chain, humans may experience major health issues [77, 78]. It's crucial to plan and create efficient technologies in order to improve water quality. NTech has recently become one of the most advantageous and dependable alternatives to the conventional treatments' techniques. For the treatment of water and air, metal oxides, carbon, and NMs have been reported. Direct injection of Fe NMs under pressure into the subsoil has shown to decompose the chlorinated composite (trichloroethylene), into environmentally benign composites. Similarly, this technique has been used to treat the immobilization of radionuclides and HMs [79–81]. It's interesting to note that using MNMs to remove organic species, target bacteria, and degrade dye has been found to purify water.

Fe_3O_4@amino acid for the magnetic separation of pollutants from effluent (wastewater) is one of the greatest examples. Three distinct amino acids, including arginine, lysine, and Poly-L-lysine, were added to the surface of Fe_3O_4 NMs to modify and functionalize them, creating Fe_3O_4@Arinine, Fe_3O_4@Lysine, and Fe_3O_4@Poly-L-lysine. Both gram-positive and gram-negative bacteria, such as *Escherichia coli* and *Bacillus subtilis*, were better captured by the functionalized Fe_3O_4@AA. All three types of Fe_3O_4@AA were used to collect and eliminate approximately 97% of the germs [77]. Fe oxide's magnetic feature makes it an efficient and simple separation method from aqueous solutions owing to the fact that they aggregate quickly when exposed to an external magnetic field [82].

At present, magneto-catalysis is thought to be the most efficient approach for destroying persistent contaminants or dyes when used in stimulus–response systems. The underlying process is the catalytic breakdown of organic pollutants by magnetoelectricity (ME), which produces free radicals that combine with parent molecules to transform them into low-risk compounds [9].

Rhodamine B (RhB) and an alternating magnetic field have been used to test the MNMs' ability to breakdown organic contaminants. For instance, Pane's team designed "cobalt ferrite-bismuth ferrite (CFO-BFO) core–shell NMs" having ME properties to catalytically breakdown RhB, a model organic contaminant, and other pharmaceutical composites [83]. Without the use of catalytic chemicals, they created a ME system that uses a mixture of magnetostrictive CFO and multiferroic BFO to cleanse water by means of oxidation reactions under wireless or radio magnetic fields. The multiferroic shell $BiFO_3$ (BFO) was made using the sol–gel technique, while the magnetostrictive $CoFe_2O_4$ (CFO) NMs were made using a hydrothermal approach. Their research shows that as- synthesized NMs by ME induction produce hydroxyl and superoxide radicals, which catalytically breakdown (degrade) RhB with removal efficiency (RE) of 97.00% RE and a combination of pharmaceutical micropollutants with RE of 85.00% (see Fig. 4 as adapted from Mushtaq et al. [83]; Copyright, John Wiley & Sons, Inc. 2019). An important issue is the environment's microbial pollution.

Agricultural and industrial waste releases harmful ions and a wide variety of microbes into water bodies [72, 73, 84, 85]. The MNMs are used to kill and separate microbes, degrade dyes, and purify wastewater by removing organic and inorganic contaminants [6, 9].

Prior research has shown that MNNs with catalytic and photocatalytic properties can breakdown chemical pollutants such as pesticides and antibiotics through oxidation and reduction reactions [86]. Because of their stability, reduced aggregation, and significant surface area with reusing or recycling potential, MNM surfaces can be functionalized with stabilizers [87, 88]. Superparamagnetic Fe oxide NPs (SPIONPs) and their NPs have been used to remove organic contaminants [89].

NPs have been used to remove a variety of micropollutants [84], including harmful dyes [84, 90–92], and HMs [3, 84, 93]. According to a study, amine-functionalized magnetite Fe_3O_4-SiO_2-NH_2 NMs have been created to remove germs and viruses from water. These brand-new MNM types feature well-proven architectures and strong magnetic characteristics in both the core and shell. Pathogens of all kinds, including bacteriophages, the *poliovirus-1*, and bacteria like *P. aeruginosa*, *Salmonella*, and *B. subtilis*, are very drawn to the amine group in MNMs [94]. The transport and availability of Fe NMs in the atmosphere are poorly understood [9]. Because they are colloidal, pure Fe NMs have a limited ability to be transported and moved. According to reports, the migration of Fe NMs at the injection point is only a few feet [95]. Additionally, the speed/movement of NMs depends on the size, speed, pH, ion strength, the soil or groundwater composition, etc. [9, 96].

It should be highlighted that the most important factors, like toxicity and bioaccumulation, need to be considered. To assure the biosafety and stability of NMs, it is crucial to look at the toxicity mechanism [96]. To address the issues of water and

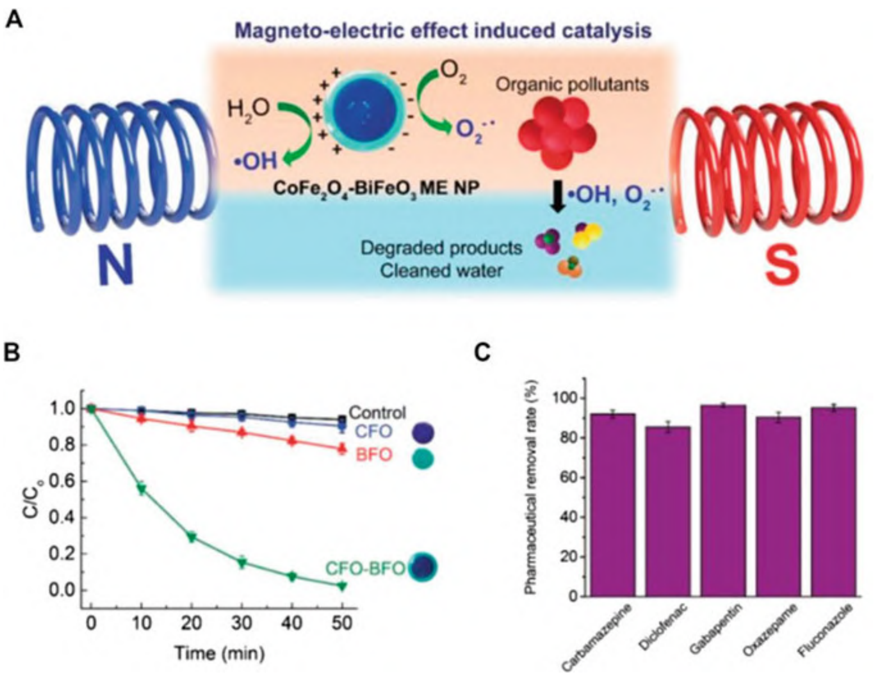

Fig. 4 **A** An outline of the magnetoelectricity effect induced catalytic breakdown (degradation) of organic pollutants employing core–shell CFO–BFO NPs under magnetic fields. **B** The catalytic breakdown (degradation) curves gotten for the model organic dye, RhB, under 15 mT and 1 kHz magnetic fields (n = 5). **C** The RE of a cocktail of five common pharmaceuticals employing the core–shell NPs (n = 4). (BFO: bismuth ferrite, CFO: cobalt ferrite, ME: magnetoelectric/ magnetoelectricity, NPs: nanoparticles)

soil quality, these research gaps must be fully filled. Compared to traditional techniques, wastewater treatment with nanotechnology has a huge potential to improve environmental quality. These techniques for water purification can decrease the need for chemicals, energy, and residual wastes. Consequently, using MNMs might significantly reduce the dangers connected to water cleaning procedures. With previously unheard-of opportunities to improve water and environmental quality, NTech has immense potential [97].

3.4 Catalytic Applications of MNMs

Different catalytic systems and procedures have been developed up to this point for the transformation of reactants into products [98]. The difficulty in separating homogenous catalysts from the reactions is one of their drawbacks. Utilizing catalysts assisted by MNMs, the heterogeneous catalysis constraint has recently been mitigated and eliminated [9]. When such catalysts are separated, the benefits of great dispersion and reactivity are combined with the ability of the MNMs to give a high surface area to assist active sites for reactants to be easily transformed into products [99].

Magnetic constituents with good repeatability in heterogeneous catalytic processes have been described [100–102]. The photocatalytic system has recently come into prominence as an effective and dependable technique for pollutant degradation in the presence of daylight. Sunlight is used in this system as an exterior stimulus source to turn on the system and produce free radicals, which then interact with contaminants to cause deterioration [9].

To this end, Xing's team created "light-responsive magnetic hierarchical porous cadmium (Cd^{2+}) imprinted photocatalytic nanoreactors (MHP-Cd)", which have an outstanding capacity for adsorption for the breakdown of tetracycline [103]. Their research shows that by storing Cu^{2+}, Fe^{3+}, and Zn^{2+} outside the cavities, the homogeneous dispersion of MHP-Cd in Cd^{+2} solution enabled selective adsorption of Cd^{+2} there. The Cds absorbed the light after being added to the tetracycline solution with MHP-Cd and then exposed to sunshine, where they excited free electrons (e^{-}) and heat energy (h^{+}). The transition of Fe_3O_4 is aided by the creation of one e in the Cds. O_2 used another e^{-} to produce hydroxyl (OH) and superoxide (O_2) radicals. A large quantity of tetracycline entered the mesoporous channels at the Cds surface due to the drug's high affinity and was converted into carbon dioxide (CO_2), water (H_2O), and smaller molecules (as shown in Fig. 5 as adapted from Lu et al. [103]). Additionally, it is necessary to create and implement appropriate strategies to regulate and fine-tune the particle size and form using various synthetic techniques. Designing and establishing extremely stable and reliable MNMs for industrial applications is still common practice. For such NMs to impede the reaction settings in heterogeneous processes, they must be sufficiently scalable and affordable [104].

4 Conclusion and Outlook of MNMs

MNMs are a novel class of nanoscale materials composed of biological components such as antibodies, nucleic acids, proteins, etc. NTech's advent has successfully sparked a scientific and technological evolution, and it has found use in a wide range of fields, including biomedical, agricultural, and environmental fields. MNMs are used in numerous industries, including biomedicine, the environment, agriculture, as well as catalytic processes. In this introductory part of this book, we have outlined recent developments in the synthesis, characterization, and prospective uses of MNMs. Different MNM types with potential features are being created utilizing various synthetic techniques. These techniques include; "sol–gel, ball milling, thermal decomposition, hydrothermal synthesis, microemulsion synthesis, thermal decomposition", etc.

Large-scale MNM synthesis is being done using physical techniques like ball milling. The milling jars and balls present a contamination risk with this technique. On the other hand, monodisperse MNMs are created via the thermal decomposition,

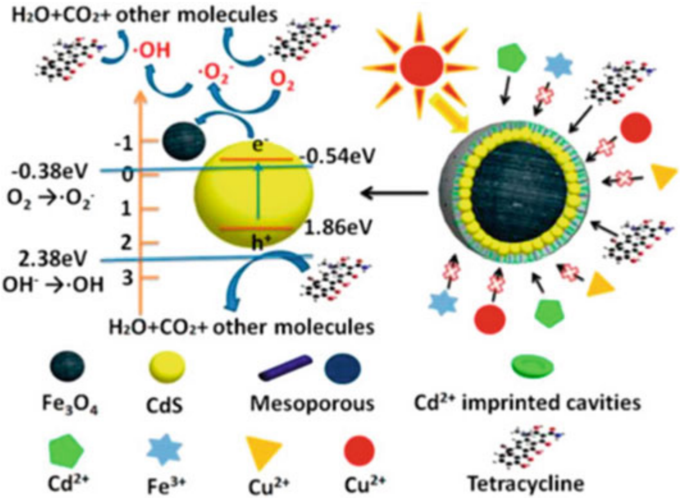

Fig. 5 A prototype photocatalytic and selective device of the MHP-Cd. As adapted from Lu et al. [103]; Copyright, ACS Publisher, 2019. Reprinted with permission from ACS Publisher

or pyrolysis, approach. The ease and superior control over MNM size of the pyrolysis process make it advantageous. At low processing temperatures, MNMs with uniform size distribution and enhanced stoichiometric control are created using the sol–gel synthesis technique. The approaches stated above suggest different MNM types for significant biological and biomedical applications. Numerous issues, such as cancer, pollution, agricultural practices, and others, have impeded human advancement. Different types of functionalized NMs have been created over the years to solve these issues. In order to treat cancer more effectively and safely, nanotechnology-based cancer therapy mostly relies on the effective and clever design of NMs. Due to their distinctive qualities, MNMs have recently contributed more to nanomedicines. Clinical research on various MNM modalities for cancer cell imaging and treatments has been conducted.

Critical biological barriers that the synthesis and formulations of MNMs must overcome include localization at the target site, efficient drug administration to the cross-physiological communication, target site, and other methodological challenges unique to tumour. Clearance, endosomal escape, off-target locations, and drug efflux are some more types of obstacles. In both industrialized and developing nations, widespread bacterial resistance to antibiotics has emerged as a significant public health issue. The emergence and non-availability of new antibiotics will pose a severe concern because of the numerous types of multidrug-resistant bacteria. Strategies based on MNMs have been developed in the last ten years to effectively cure infections brought on by pathogenic bacteria and remove biofilms. MNMs play a significant function in targeted drug delivery and are often used. MNMs-based drug administration can lower drug doses compared to conventional drug delivery, which in turn lowers side effects.

The MNMs also possess innate antibacterial action. They have synergistic therapeutic benefits when these antimicrobial compounds are combined with them, which increases the potency of antimicrobial medications. Similar to this, MNMs are used to purify wastewater, including the elimination of organic and inorganic contaminants, colour degradation, and the killing or isolation of bacteria. The MNPs can be used to control plant diseases and as soil fertilizers to boost yields. Research makes extensive use of the conjugation of MNMs with diverse BMs, including enzymes nucleic acids, and chemicals. In this way, a gene's delivery and expression within the host cell are effectively utilized. In addition to other application disciplines, heterogeneous catalysis is one area where MNMs exhibit exceptional potential. In many forms of catalysis and clean energy, magnetic NMs have been employed to coat catalysts. For the conversion of the reactants into products, the MNMs can offer a large number of active sites.

Designing and manufacturing MNMs for a variety of applications in many fields requires critical and productive research to overcome obstacles. Building regulatory structures for the safe and efficient use of nanotechnology must be taken into consideration as it advances and multidisciplinary approaches are made. In order to establish precise guidelines and platforms for advancing clinical trials and in vivo preclinical studies, there needs to be a regular method for communication between institutions and researchers. MNMs must overcome numerous obstacles before they can be used in the real world to cure cancer and stop drug resistance. It is necessary to discuss the proportion of MNMs to catalysts. The biocompatibility and long-term toxicity of the MNMs are two of the major difficulties. A highly thorough and in-depth investigation is required to examine the composition, morphology, size, form, structure, and side effects of MNMs. The research and synthesis/production of MNMs for a better future require the scientific community to handle such tremendous problems and conduct hassle-free clinical trials.

The need for food is growing due to population growth and globalization, but there is a concomitant decline in the amount of agricultural land available. As a result, it is urgent to develop and modernize traditional agricultural practices. The agriculture sector is one of the largest sources of raw materials for the food and feed industries. The introduction of NTech has greatly expanded the agricultural industry as cutting-edge methods to boost crop output and nutrient content have been put into practice. In the realm of agriculture, NTech uses BNMs such as those formed from carbon, silica, etc. The development of chemical-free nano-fertilizers, nano-pesticides, and nano-insecticides frequently makes use of BNMs.

Additionally, BNMs are employed in the creation of nano-biosensors (NBSs) for the detection of contaminants and nutrient concentrations in soil. The moisture content of the soil may now be accurately predicted by a novel wireless NBSs that uses BNMs. The safety and rules for creating nano-fertilizers are highly significant and need to be further investigated, despite the fact that the agriculture sector requires a lot of care and precision due to the direct impact it has on human health.

The removal of HMs, inorganic and organic pollutants, along with the detection of contaminants in water, soil, and air are just a few of the diverse uses of BNMs in the environmental field. Numerous publications have solely concentrated on the environmentally friendly synthesis of various metals and their applications in diverse fields. Innovative alternative methods to control pollution are now required due to the rise in both global warming and pollution. BNMs have made it feasible to produce solar cells to harness solar energy, bioremediation materials that can quickly deteriorate contaminants found in water and soil, and the creation of NBSs to identify pollutants. These BNMs are crucial in the treatment of wastewater that contaminates freshwater sources. Modernization and globalization have drawbacks that must be addressed as soon as possible. BNMs exhibit the ability to overcome these drawbacks and have a promising future.

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Magnetic Nanomaterials: Synthesis and Characterization

David O. Idisi, Chinedu C. Ahia, and Edson L. Meyer

Abstract Magnetic nanomaterials (MN) have gained popularity recently, due to their versatility in different applications in biomedicine and water splitting. Because of the ease of magnetic response to the applied field and manipulation of the itinerant magnetic moments, MN offers seamless opportunities in different science and technology. In this chapter, different MNs are examined with a focus on their syntheses and characterization. This chapter provides insight into the previously reported characterization techniques for morphology, microstructure electronic and magnetic properties examination.

1 Introduction

Magnetic nanomaterials are an interesting subject to the research community due to the possibilities they offer. The ability to manipulate their morphology and particle size has led to the tuning of their spin alignment [1, 2]. The tuning of the spin alignment can be harvested for different applications. For instance, the saturation magnetism observed in ferromagnetic nanomaterials is crucial for soft magnet applications, allowing for ease of upscaling and miniaturization [3].

High coercivity and remanence of an MMO classify the material as a permanent or soft magnetic material. Because of the ability of the permanent magnets to distribute magnetic flux within the air gap of magnetic circuits [4], they have been prevalent in sensors, motors, actuator applications [5]. Low coercivity, and remanence forms soft magnetic materials, possessing single domain superparamagnetic materials. The control of the remanence and coercivity can be used in the manipulation of the rate of relaxation of magnetic imaging resonance (MRI) applications [6]. The control of the rate of relaxation enables the tuning of spin relaxation times emanating from lattice-spins (T1) and (T2) spin–spin interactions, which are applicable in image contrast control in MRIs [7].

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2 Type of Magnetic Nanomaterials

Depending on the nature of the nanomaterials, they can be classified as metallic oxide nanomaterials, metal alloy nanostructures and graphene oxide/metal nanocomposites. The synthesis process allows for control over the magnetic characteristics of the nanomaterials. This chapter will look at previously described synthesis methods and characterization methods for several magnetic nanomaterials. Firstly, each class of nanomaterials will be discussed. The process of the synthesis method for most of the classes of magnetic nanomaterials are similar, hence a general synthesis section will be considered. Since the characterization is common to most of the materials, a generic characterization section will be presented for all the magnetic nanomaterials.

2.1 Metallic Magnetic Oxides

Metallic magnetic oxides (MMO) are a class of metallic materials with a high magnetic response (coercivity, remanence and saturation) and are chemically stable. However, their high reactivity results in their easy oxidation in air and water. For instance, iron nanoparticles (Fe-NP) easily oxidizes leading to the formation of iron oxide [8]. Although the degree of oxidation can result in decreased magnetic response and application limitations, additional metals can be introduced into the structure of Fe_2O_4 to increase the chemical stability and magnetic response [9]. Among the numerous available metals, Co, Mn and Fe have been used, which results in improved magnetic properties. Enhanced magnetization and chemical stability are usually attributed to uncompensated surface spins and interface interactions between Fe and the metallic ions [10].

2.2 Metal Alloy Magnetic Nanostructures

Magnetic metallic alloy nanostructures (MAN) involve the combination of two magnetic monometallic nanomaterials with the aim of improving their combined magnetic properties. MAN, which is represented by FePd and FePt nanomaterials, is chemically stable and highly magneto-crystalline [11]. The enhanced magnetization can be attributed to the exchange interaction between the valence orbital state. Previous reports [12] have attributed enhanced blocking temperature and coercivity to the degree of stoichiometric tuning of each mono-metallic nanoparticle. The ease of control of the particle size of the bimetallic nanomaterials can result in manipulating the magnetic features. For instance, Hou et al. [13] were able to obtain FePd nanoparticles in the size range of 11–16 nm, which exhibit superparamagnetic properties. Based on the enhanced magnetic features of the MAN nanomaterials, they have found opportunities in different applications such as tissue imaging, drug delivery, and imaging-guided photothermal therapy [14].

2.3 Graphene Oxide/Metal Nanocomposites

A derivative of graphene, which is referred to as graphene oxide (GO) has oxygen functional groups at its edges and basal planes [15]. The presence of the oxygen functional group allows easy attachment of metals to its matrix [16]. Pristine graphene is intrinsically nonmagnetic without localized magnetic moment resulting from the absence of unpaired spins [17]. However, the oxidation and reduction of the carbon atoms create hydroxyl and epoxy doping, resulting in the introduction of magnetic moments [18]. Meanwhile, the magnetization of GO has been widely enhanced with the GO-based nanocomposite and has shown enhanced ferromagnetic [19] and superparamagnetic properties [20], which could find potential in memory device and tissue imaging applications. Additionally, iron-based MMO nanoparticles have been incorporated into GO to enhance its magnetic properties. The coupling of the large surface area and enhanced magnetic properties of GO: Fe_3O_4 nanocomposite has shown enormous potential for biomedical applications [21, 22].

3 Method of Synthesis

The effectiveness in synthesizing the magnetic nanomaterials is crucial for obtaining high throughput nanomaterials. The methods can be used to manipulate nanomaterials' size, shape, and chemical stability, which are crucial for achieving the desired qualities. The following section is focused on previously reported syntheses for MMOs.

3.1 Sol–Gel Method

The sol–gel method involves the use of solution-based chemistry, where precipitate precursors are mixed with reagents/solutions in desired proportions to obtain high-yield precipitates [23]. The process of separation, nucleation and growth of nanomaterials can be easily observed and monitored during the synthesis process. Figure 1 shows the typical steps involved in the synthesis of metallic magnetic nanomaterials. Iron oxide MMO is typically prepared by adding a base solution to ferrous salt under anaerobic circumstances at room temperature. This results in the production of Fe (II) and Fe (III) precipitates. The control of the shape, particles, and composition is usually manipulated using ferrous salt ratio, reaction temperature, medium pH and ionic strength of the solution [24].

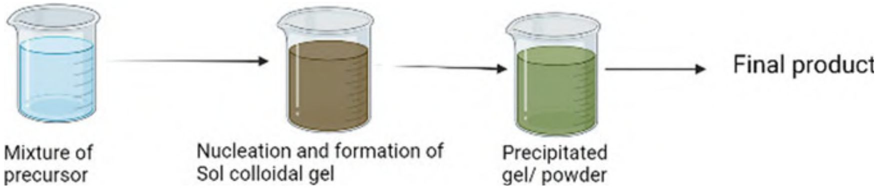

Fig. 1 Schematics representing the process of sol–gel synthesis of magnetic nanomaterials

The case of the use of sol–gel method for the preparation of $CoFe_2O_4$ involves a process similar to that of Fe_2O_3. However, Cobalt(II) acetate tetrahydrate is added to the ferrous salt to create a Co: Fe atomic ratio to produce the desired precipitate [25]. Similarly, the main distinction for the case of $MnFe_2O_4$ involves the use of manganese- (II) benzoyl acetonate as Mn precursor, which is mixed with a ferrous salt precursor in adequate proportion [26]. The effectiveness of the sol–gel method in preparing homogenous precipitate has been proven and is still widely used in the current era. Among the numerous study that has been devoted to the synthesis of magnetic nanomaterials using the sol–gel method, few articles have been considered. The early work of Deheri et al. [27] outlined the synthesis of $Nd_2Fe_{14}B$-based magnetic nanomaterials. The synthesis process followed a typical mixture of the material precursor in deoxidized water with a final yield of random dispersed 100 nm nanoparticles. The resulting composites are shown in Fig. 2. Additionally, Masthoff et al. [28] attempted a modification of the sol–gel method by implementing a non-aqueous approach. The distinction of their approach employed a Polyclave reactor and benzyl alcohol as solvent, which enabled the monitoring of the reaction process. Their results led to formation of faceted shaped magnetic nanoparticles. In general, the sol–gel technique is efficiency and can be modified with precursor to obtain desired shape and morphology of the nanomaterials.

3.2 Thermal Decomposition

Organometallic precursors are broken down in organic solvents during the thermal decomposition process. To achieve high MMO throughput, capping agent surfactants are introduced into the surfactant under anaerobic conditions [29]. For controlling the particle size and form, reaction factors like temperature, reaction time, and ageing are essential [30]. Meanwhile, the use of the thermal decomposition method for the preparation of highly magneto-crystalline MANs has been widely explored [31, 32]. A previous report by Patsula et al. demonstrated the synthesis of Fe_3O_4-based MMO nanomaterials by decomposing Fe(III) glucuronate [33]. Temperature variation and reagent concentration were used to obtain stable nanosized superparamagnetic nanomaterial. In the process, the temperature, concentration of the stabilization agent

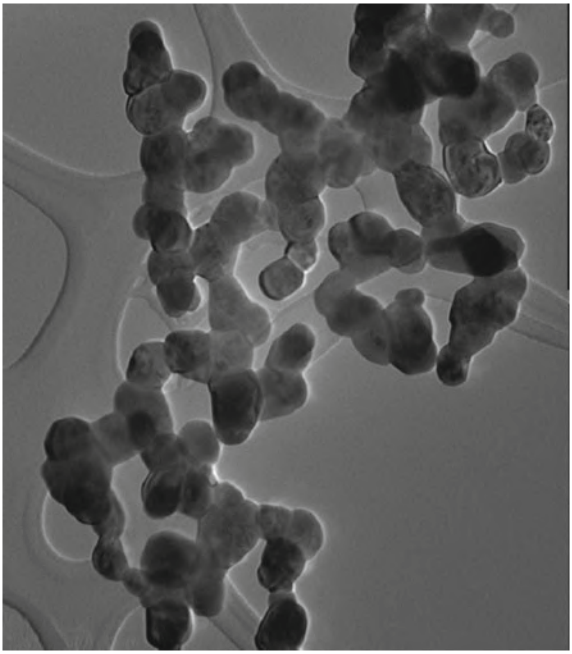

Fig. 2 TEM image of $Nd_2Fe_{14}B$-based magnetic nanomaterials, indicating randomly dispersion nanoparticles. Image adapted from Deheri et al. [27]; Copyright, ACS Publisher, 2010

(poly(3-Omethacryloyl-α-D-glucopyranose)) and high-boiling point solvent, polydispersed and nanosized particles were varied to produce the Fe_3O4 nanoparticles. Figure 3 shows the monodispersed Fe_3O_4 nanoparticles using the thermal decomposition method. Meanwhile, Sun et al. [34] used the thermal decomposition method to prepare monodispersed Fe-Pt nanoparticles. The process of synthesis is similar to MMO preparation, however, octyl ether is used as the capping agent. The process results in 12nm-sized particles, which can exhibit superparamagnetic properties.

While the thermal decomposition method is efficient for preparing monodispersed nanosized magnetic nanomaterials, it suffers some setbacks. For instance, toxic CO gases are generated during the preparation of $Fe(CO)_5$-based precursors [35].

The setbacks cause difficulty in nanomaterial synthesis. Hence, other precursors are either used or other methods are adopted. It is based on this issue; that thermal decomposition is becoming less popular for bimetallic nanostructural synthesis.

3.3 Hydrothermal Method

The hydrothermal method of magnetic nanomaterial synthesis is a solvothermal method, which involves a heterogeneous reaction of inorganic precursors in solutions above room temperature (125–250 °C) and pressure (0.3–4 MPa) [36]. The reaction time and precursor concentration play a key role in regulating the nanomaterial's

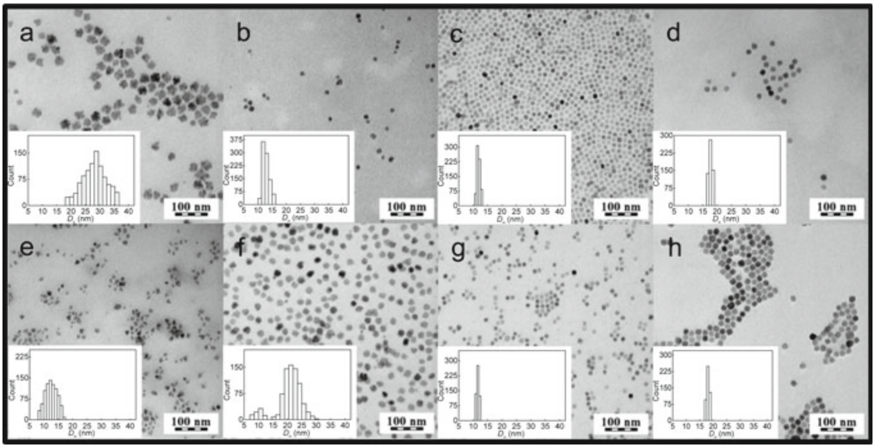

Fig. 3 The morphology of the obtained Fe_3O_4 nanoparticles using the thermal decomposition method. Image reproduced from Patsula et al. [33]; Copyright, ACS Publications, 2016

particle size distribution and shape [37, 38]. In order to create MMOs and graphene oxide/metal nanocomposites, the hydrothermal approach has been extensively used.

For iron oxide based MMO nanomaterial preparation, ferrous chloride tetrahydrate precursor is used in the presence of ammonia hydroxide solution [39]. The vigorous stirring of the mixture leads to a formation of an oxidized iron II oxide precipitate. The iron oxide precipitate is transferred to an autoclave and heated at desired temperatures (120–150 °C) and pressure (2 bar). The case of graphene oxide/metal composite involves a two-step process as in the case of iron oxide based magnetic nanomaterials. The graphene content is prepared from the reduction of Modified Hummer's synthesized graphene oxide [40]. The mixture of the synthesized and ferric chloride or nitride is transferred to a Teflon autoclave for the hydrothermal heating process. The heating and reaction process is similar to MMO-based nanomaterials with similar monodispersed nanoparticles [41, 42]. Numerous research (see Table 1) on the hydrothermal synthesis of magnetic nanomaterials has been reported. However, for sake of simplicity, few reports have been considered in this section. The recent report of Makinose [43] explored ammonia-treated Fe-oleate precursor for hydrothermal synthesis of iron oxide nanoparticles. The impact of the ammonia-treated Fe-oleate precursor resulted in the production of high dispersive iron oxide nanoparticles. The effect of the Fe-oleate precursor suggests the ease of manipulating the structure and morphology of magnetic nanomaterials using the hydrothermal method.

Table 1 Summary of selected reports on the various magnetic nan

Synthesis method	Class of magnetic nanomaterial	References
Sol–gel	Metallic magnetic oxide, magnetic alloy nanostructure and graphene oxide/metal nanocomposites	[19, 20, 29, 54–59]
Thermal decomposition	Metallic magnetic oxide and magnetic alloy nanostructure	[33, 60–64]
Hydrothermal	Metallic magnetic oxide and graphene oxide/metal nanocomposites	[41, 65–69]
Other methods	Metallic magnetic oxide and magnetic alloy nanostructures	[70–74]

3.4 Other Methods

The afore-discussed methods have been widely used for the synthesis of magnetic nanomaterials. However, other methods have been used in recent times, which are efficient in the preparation of high-yield magnetic nanomaterials. Other effective methods include polyol, microemulsion and green synthesis.

The polyol method is a liquid-phase process used for extracting fine metals from oxides, salts and hydroxides using high-boiling and multivalent alcohols [44]. Due to the water-comparable and ionic bonding nature of the polyols class, nucleic coordinated magnetic materials can be synthesized [23]. Due to the nuclei's surface and protective agent, which alters the crystal's characteristics and allows for particle growth of related anisotropic particles, particle size and dispersion are also possible [45]. The polyol technique has been extensively investigated for the synthesis of high yield MANs and MMOs due to the simplicity of removing the glycol residues during post-synthesis. Recent studies of the method being used for the preparation of MANs and MMOs are indicated in Table 1.

The microemulsion method is based on the formation of isotropic-thermodynamically stable dispersion from two–three immiscible solvents. The resulting dispersion produces an interfacial layer with molecular surfactants [46]. Immiscible mixtures have an effect that causes hydrophilic head solubility in water and hydrophobic tail solubility in oil solutions, which are the factors that cause the monolayer interface to form [47]. When tiny droplets of water are continually dispersed in the hydrocarbon phase while being encompassed by monolayers of molecular surfactants, a water-in-oil combination is formed [48]. As a result, when two identical water-in-oil microemulsions are combined with the required reagents, the resulting microdroplets continuously collide, agglomerate, and degrade to form micelles precipitates. To remove the precipitate, the product is filtered or centrifuged in acetone or ethanol [49]. The microemulsion method allows the control of the particle size, shape and crystallinity by tuning the synthesis conditions Selected previous reports on the microemulsion prepared magnetic nanomaterials are given in Table 1.

Green synthesis of magnetic nanomaterials involves the use of green chemistry in preparing the nanomaterials. Green chemistry has gained prominence mainly because of the call for a reduction in environmental toxicity. Increased research activity in nanomaterials synthesis for different applications has resulted in toxic waste by products, which are eventually dumped in the environment. The aftermath of the waste has led to different environmental hazards, which are harmful to both human and plant lives [50]. Magnetic nanoparticles are produced with the aid of plants as part of the green synthesis. Instead of actual chemical reagents, plant extracts are used as sources for citric acid, ascorbic acid, flavones, basic enzymes such dehydrogenases and reductases, and extracellular electron carriers [51, 52]. A typical green synthesis process involves mixing plant extracts with the desired solvent medium, reducing agent and capping agent for the reduction of agglomeration of nanomaterials [53]. Although green synthesis can help reduce toxicity in nanomaterial synthesis, it has not been popular among researchers due to some setbacks. For instance, the poor yield of naturally occurring plant proteins makes it difficult to attain desired particle size, shape, and crystallinity [23]. A summary of the synthesis method for the preparation of magnetic nanomaterials indicating some selected reports is depicted in Table 1.

4 Characterization of Magnetic Nanomaterials

The characterization of magnetic nanomaterials gives insight into the inherent properties of the materials. Characterization of nanomaterials can enable possible optimization and enhancement of the properties as desired. This section of the chapter focuses on the characterization techniques used to probe the microstructure, morphology, and electronic magnetic properties of magnetic nanomaterials. The following details the different techniques used for probing the properties.

4.1 X-ray Diffraction

The study of nanomaterials' structural characteristics, including size, crystal defect, crystallinity, and strain, is made possible through X-ray diffraction (XRD). These characteristics can be utilized to comprehend the behavior of a nanomaterial that has been observed [75]. The XRD technique is based on Bragg's Law of diffraction. The basis of the principle depends on the reflection/scattering of X-rays when a sample of crystal blueprint is bombarded with X-rays with precise wavelength at the incident angle. The reflected/scattered X-rays can be either constructive or destructive. The travelling wave's path differences for constructive wave interference are integer multiples of the wavelength. When constructive interference occurs, a diffracted set of beam X-rays at an angle equal to that of the incident beam create a distinct blueprint of the targeted material [75].

The pattern obtained from the XRD diffraction experiment can be used to extrapolate much information about the magnetic nanomaterial. For instance, the XRD technique can be used to identify the crystal structure of magnetic nanomaterials. For graphene-Fe nanocomposite based magnetic nanomaterials, face centred cubic (FCC) structure can be easily identified from the reflection planes [76] obtained from XRD patterns. Furthermore, the interplanar spacing (d-spacing), which is unique to the desired nanomaterial, can be easily identified. The d-spacing between the lattice planes inherent in the atoms of the desired magnetic nanomaterial, which is responsible for the constructive interference, is indicated by the solution of Bragg's equation. In general, nanomaterials with high symmetry have fewer atomic planes than those with low symmetry, which have more structural atomic planes [77]. One of the numerous reports on the XRD technique was performed by Liu et al. [31], where the focus was made on characterizing NiFe-based magnetic nanomaterial. The XRD characterization of the NiFe-based (see Fig. 4) nanomaterial indicated a face-centered cubic (fcc) type and spinel structure, which is consistent with typical fcc-type NiFe nanoparticles. Other selected reports regarding XRD characterization are indicated in Table 2

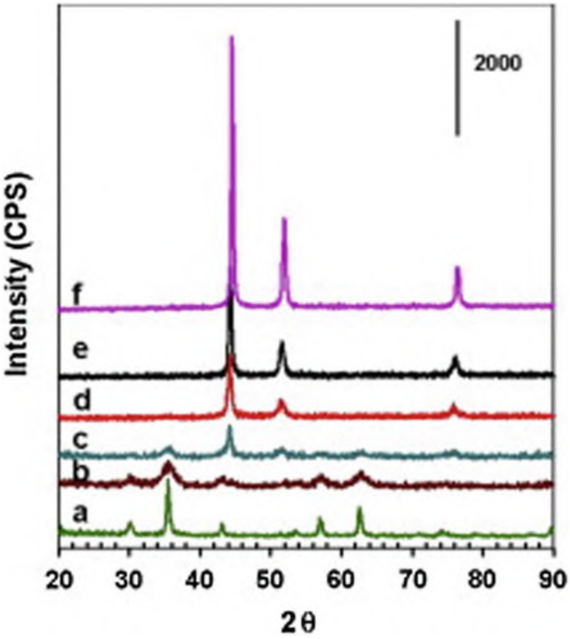

Fig. 4 XRD characterization of NiFe magnetic nanomaterials, showing the microstructure and phase of its electronic structure. Image reproduced from Liu et al. [31]; Copyright, Elsevier Publishers, 2014

Table 2 Summary of selected previous reports on the different characterization techniques for magnetic nanomaterials

Class of magnetic nanomaterial	Characterization technique	References
Metallic magnetic oxide	XRD, SEM, TEM, Raman spectroscopy, TGA, XPS, UPS, XANES, SQUID, VSM	[31, 104–107]
Magnetic alloy nanostructure	XRD, SEM, TEM, Raman spectroscopy, TGA, XPS, UPS, XANES, SQUID, VSM	[11–13, 34, 108–110]
Graphene oxide/ metal nanocomposites	XRD, SEM, TEM, Raman spectroscopy, TGA, XPS, UPS, XANES, SQUID, VSM	[19, 20, 111–114]

4.2 Scanning and Transmission Electron Microscopy

Scanning electron microscopy (SEM) is a widely used technique for probing the morphology (particle size, shape, and texture), of nanomaterials at high resolution. The SEM technique uses an electron beam to scan the sample in a cross-sectionally manner. Under high vacuum conditions, signals and images of the scanned sample are generated and displayed on a cathode ray tube screen [78]. The high resolution of the technique enables the probing of up to 1nm with a high level of accuracy and resolution. SEM can be used with other peripherals such as laser diffractions, to probe particle agglomeration, which is crucial for understanding the behavior of the composites [79]. Furthermore, with the help of various advanced software, the generated images can be analyzed to obtain a histogram of particle grain sizes.

Magnetic nanomaterials' morphology and grain size boundaries have been extensively studied using the SEM technique [80, 81]. Meanwhile, this SEM technique has some disadvantages. For instance, the sample preparation for SEM measurements is time consuming. Furthermore, while it is easy to extrapolate grain size, particle size generation is challenging as the visual image does not provide quantitative information. The non-quantitative limitation is mainly due to the restricted area view that can be probed per time [79].

Transmission electron microscopy (TEM) on the hand is similar to SEM with the electron beams generated from an electron gun. The main distinction of TEM over SEM is the high resolution, which enables the probing of the inner structure of a sample. When the generated electron beams interact with a sample, the beams diffract in accordance with Bragg's second law [82]. The diffracted beams are refocused by a magnetic lens, which results in the formation of an image. The generated image passes through a fluorescent screen where polychromatic images are recorded. Additionally, the image quality can be improved by considering the thickness of the sample layer. For instance, sample layers, which are approximately generated dark contrast images, whereas less thick sample layers result in bright images [83]. The SEM and TEM technique has been the main morphology characterization approach for studying the morphology of nanomaterials. Among the numerous morphology focused research,

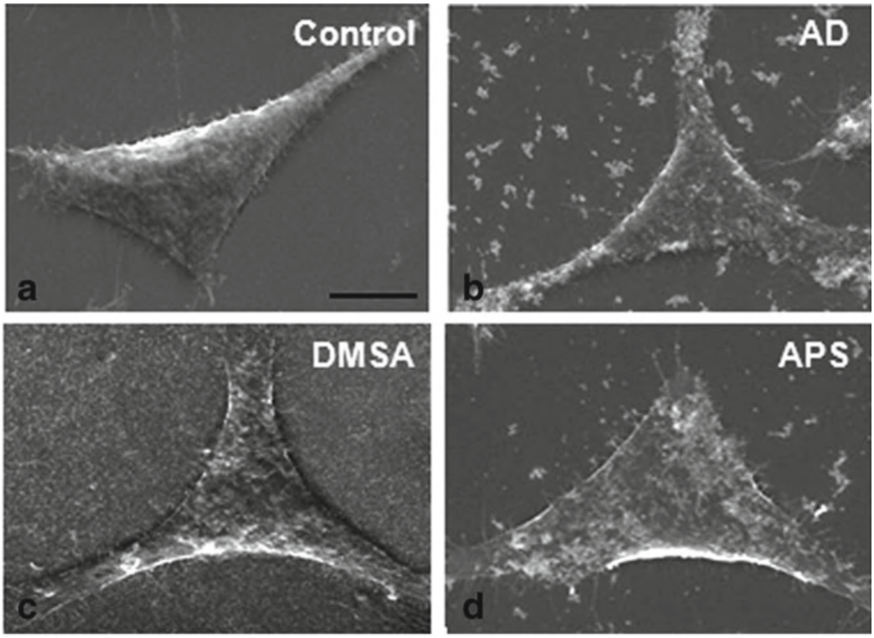

Fig. 5 Morphology of cell coated iron oxide using SEM analysis. Image reproduced from Calero et al. [84]; Copyright, Elsevier Publishers, 2014

Calero et al. [84] studied the morphology of cell coated iron oxide using SEM analysis as indicated in Fig. 5. Their result revealed incubated cells within the iron oxide cell surface adherence to the iron oxide nanoparticles.

Their report suggests the invaluable efficiency in studying the morphology of magnetic nanoparticles in the field of biomedicine. Meanwhile, Mohammadali et al. [85] in their report focused their study on the correlation of particle size of superparamagnetic iron oxide on different biomedical applications using TEM analysis. Figure 6 shows the TEM images and the corresponding particle analysis of the magnetic nanoparticles. Their results were able to show the significance of TEM in showing the morphology of magnetic nanomaterials as well as mean particle distribution within the nanomaterial. Other previous reports are summarized in Table 2.

4.3 Raman Spectroscopy

The impact of doping or functionalizing nanomaterials is studied using Raman spectroscopy, as well as the bonding structure in molecules or solids. When incident light interacts with the desired sample, light is scattered, which is the basis of the Raman technique [86]. The inelastically scattered photons with wavelengths unequal to the incident light depict a blueprint of the chemical bonding of the sample. The detected

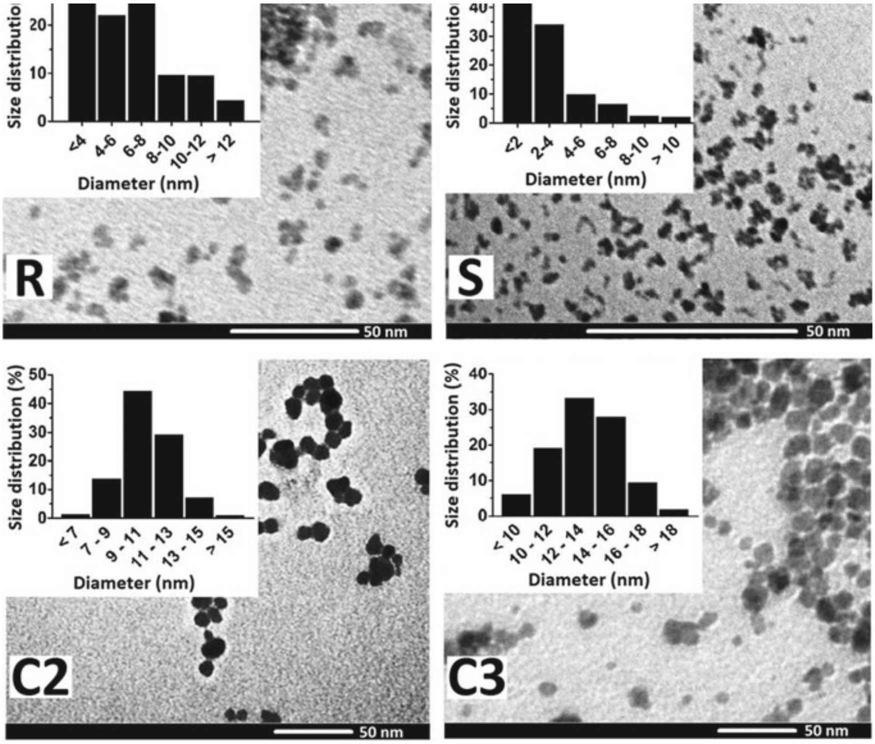

Fig. 6 TEM images and particle size analysis of superparamagnetic iron oxide. Image reproduced from Mohammadali et al.; Copyright, Springer Publishers, 2020

signal from the scattered light is used to form a spectrum with a Raman shift peak and intensity, which is unique to the desired sample.

The Raman spectra give two characteristics peaks at approximately 1585 and 2950cm^{-1} (G and 2D) for a carbon-based nanomaterial. However, a defect peak (D peak) at approximately 1350cm^{-1} appears for a defect carbon nanomaterial, which could be due to oxidation, doping or functionalization [87]. The effect of doping/functionalization changes the frequency of the vibration of the phonons, which leads to either a blue or redshift of the photon vibrations [87]. Additionally, iron oxide-based nanomaterials show Raman peaks between 200 and 1330 cm^{-1} depending on the nature of the magnetic iron oxides. For instance, hematite features peaks at approximately 225, 245, 291, 411, 500, 611 and 1321cm^{-1} [88], whereas, magnetite shows blueprint peaks at the range 661 and 676cm^{-1} depending the power and wavelength of the laser source [88]. The Raman technique has been widely used for characterizing magnetic nanomaterials and has been widely reported. One of such studies was our recent report [89] on SiO_2 decorated multiwalled carbon nanotubes (MWCNT). In the report, we were able to quantify the impact defects resulting from the concentration of SiO_2 nanoparticles on MWCNTs and its corresponding effect

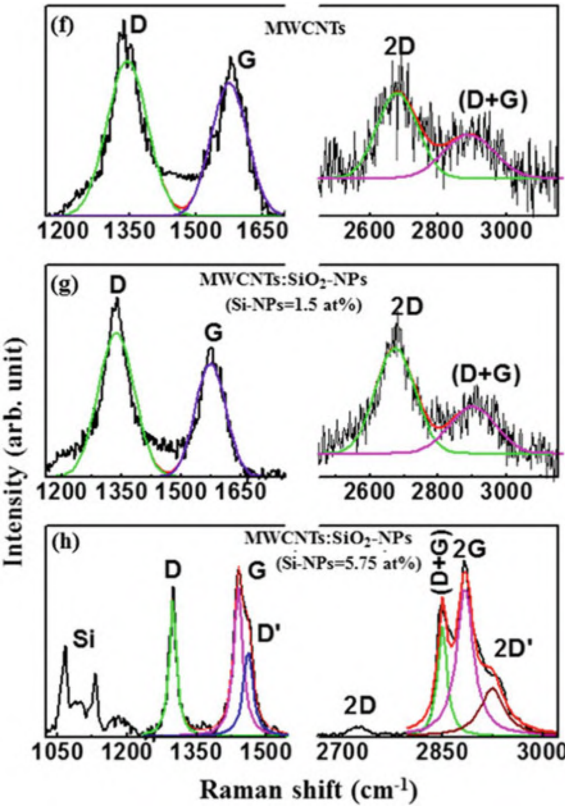

Fig. 7 Raman spectroscopy of SiO_2 nanoparticles decorated MWCNTs. Image reproduced from Oke et al.[89]; Copyright, ACS Publishers, 2019

on the magnetic properties. Figure 7 shows the Raman spectra of SiO_2 nanoparticles decorated MWCNTs. Additional reports in the Raman characterization of magnetic nanomaterials are summarized in Table 2.

4.4 Thermal Stability Properties

The process of nucleation resulting from the functionalization and oxidation of elemental components in magnetic nanomaterials can lead to clustering/agglomeration of the particles. The effect of agglomeration in nanomaterials results in weakened nanoparticles, which makes the nanomaterials less effective for desired applications. A way of controlling the process of agglomeration is using thermal stability studies, where the volatile component and weight changes of the nanocomposites can be easily monitored. Additionally, thermal stability studies are crucial for magnetic nanomaterials for biomedical studies to monitor the impact of temperature and degradation of the magnetic nanocomposite resulting from the nanoparticles.

Meanwhile, thermogravimetric analysis (TGA) has been the standard method for analysing the thermal stability of magnetic nanomaterials. The TGA technique is based on the enthalpy change in a thermodynamic system (nanocomposite), which relies on changing the temperature and mass of the entire system. In the TGA process, the mass of the nanocomposite is continuously monitored as the temperature is linearly increased over a range of 25–1200 °C. The setup includes a programmed furnace that records the experiment, and the spectra that were produced were used for data analysis of factors like absorption, adsorption, desorption, vaporization, sublimation, degradation, oxidation, and reduction. Based on the efficiency of the TGA technique in magnetic nanomaterial characterization, numerous reports have been devoted to the subject. For instance, Sivakumar et al. [90] studied the Nickel ferrite ($NiFe_2O_4$) using TGA to establish the decomposition process. In their study, they found three decomposition regions (see Fig. 8), which gives insight into the adsorption activity of H_2O, CO_2 and NOx in the $NiFe_2O_4$ composite.

Additional information is indicated in the summarized selected previous reports on the use of TGA for thermal stability of magnetic nanomaterials are indicated in Table 2.

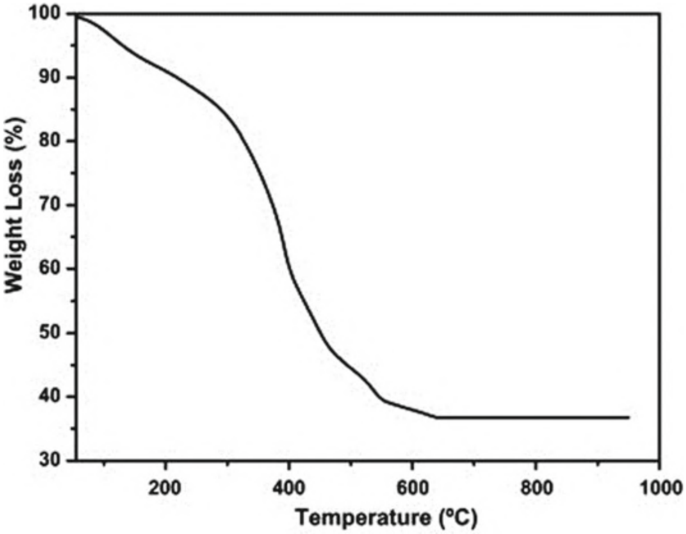

Fig. 8 TG analysis of $NiFe_2O_4$ composite showing the three decompositions at 50–150, 150–480 and 480–640 °C. Image adapted from Sivakumar et al. [90]; Copyright, Elsevier Publishers, 2011

4.5 X-ray Photoelectron Spectroscopy

An enhanced method for analyzing the electronic chemical content, quantity, and bonding structure of materials is called X-ray photoelectron spectroscopy. The photoelectric effect provides a framework for the XPS method. Electrons are released from a sample's surface when it is irradiated with a photon of a particular energy, often Mg K (1253.6eV with a line width of 0.85eV) or Al K (1486.6eV with a line width of 0.85eV) [91]. The signal detected from the population of the emitted electrons from the surface is recorded and used to form a spectrum with varying binding energies. The peak intensities and positions represent the elemental concentration and chemical composition of the material being analyzed. The chemical composition identification from the binding energy is based on a unique energy region where each electron is emitted from the surface [92]. The binding energy regions can be used to identify each element present in a sample. For instance, a spectrum showing peaks at a binding energy of 285.03 eV is attributed to carbon (C1s), 103.29 eV to silicon (Si2p), 83.98 and 87.7 eV are attributed to gold (Au $4f_{7/2}$ and Au $4f_{5/2}$, respectively), and 532.68 eV to oxygen functional groups (O1s) [93]. Additionally, the impact of oxidation and functionalization of the material results in the splitting and broadening of the peaks.

The ability to evaluate the orbital and spin angular momentum of the material's electronic structural configuration makes the XPS technique effective at investigating the electronic structure of nanomaterials [94]. A typical electronic state comprises electrons with orbital and spin angular momentum. When an electron is emitted from the initial state through the absorption of a photon, the electron emerges with a kinetic energy of the final state with electronic subshell and unpaired electrons. Based on the nomenclature of the electronic state, the emerging electrons obey the quantum mechanics principle in accordance with nlj, which are the quantum number, angular momentum quantum number and combined spin, respectively. Hence, spin orbit coupling and splitting are observed in some elemental compositions such as Au 4f and Fe 2p, which possess a doublet state [95].

In summary, XPS has been widely used for in depth profiling of magnetic materials. The result of its use is reflected in the enormous number of research publications. For instance, our recent report [19] indicated a blue and red shift in peak positions of C–C, C-O, C-Au in C 1s and O 1s of rGO functionalized gold nanoparticles (see Fig. 9). The bond interactions suggest the possible attachment of Au atoms on the surface of rGO, which has a corresponding effect on the enhancement of the magnetic properties of rGO. Other significant contributions to XPS characterization of magnetic nanomaterials are indicated in Table 2.

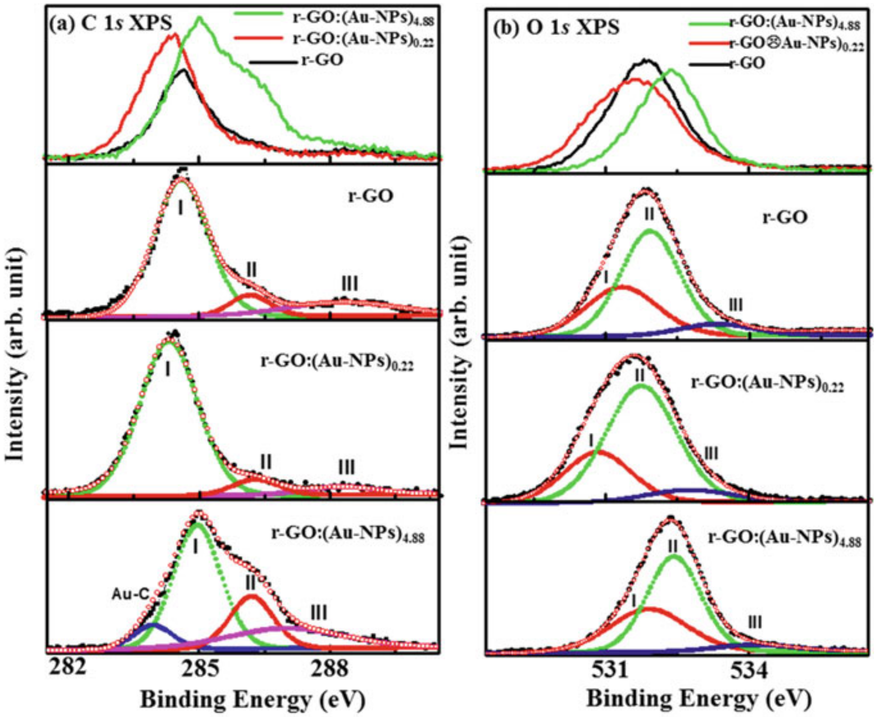

Fig. 9 XPS spectra analysis for gold functionalized rGO showing C 1s and O 1s. Image adapted from Idisi et al. [19] Copyright, Elsevier, 2019

4.6 Ultraviolet Photoelectron Spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) is a complementary technique to XPS, which involves the emission of electrons from an occupied orbital when illuminated with a photon source. The UPS technique comprises two helium photons with excitation energies of (He I = 21.2eV and He II 40.8eV). The helium sources enable the in depth probing of the different electronic transitions and states, which is inaccessible by the XPS technique.

The obtained spectra from UPS can be easily assigned based on the available orbital state in a material. For a typical GO-based magnetic nanomaterial, the orbital states are in the range of 3−15 eV. For instance, the ranges 3−4 eV are assigned to $2p - \pi$, 5−7 eV are assigned to $2p - (\sigma + \pi)$, 8−11 eV are assigned to $2p - \sigma$ and 13−15 eV are assigned to the $2s - \sigma$ state. The effect of reduction, doping and functionalization induce defect levels in the precursor materials. The resulting induced defects lead to an alteration in the electronic structure of magnetic nanomaterials. For instance, a typical reduced or functionalized GO-based nanomaterials will lead to either red or blue shift in the peak positions of the orbital states. The degree of the red or blue shift in the peak positions depends on the degree of reduction and the concentration of the functionalizing agent [20]. Sutar and co-workers have extensively studied the effect of the reduction of GO on the orbital states using the UPS characterization technique.

Additionally, the UPS technique may be utilized to investigate a material's work function characteristics, which is essential for comprehending the electrical structure and chemical make-up of nanomaterials. By measuring the difference between the Fermi Level and the cut-off energy at the lower kinetic energy end of the spectrum and estimating the difference from the incident photon energy, the electronic work function may be retrieved from the UPS spectra [96]. Meanwhile, the process of probing the work function of a magnetic nanomaterial can be extended to the valence band maximum examination. The behaviour of the VBM provides an insight into the defect induced transport properties and valence state of constituent elements of materials. in magnetic nanomaterials. The VBM has been widely used to examine the active orbital states, which are responsible for the magnetic moment interaction in nanomaterials. Menzel and co-workers [97] used the UPS technique to elucidate the effect of Co on the magnetic properties of single crystalline $Fe_{1-x}Co_xSi$. Their result (see Fig. 10) showed a shift of valence band maximum towards the Fermi energy when the concentration of Co is increased. Other previous reports on the use of the UPS technique for probing work function and VBM are indicated in Table 2.

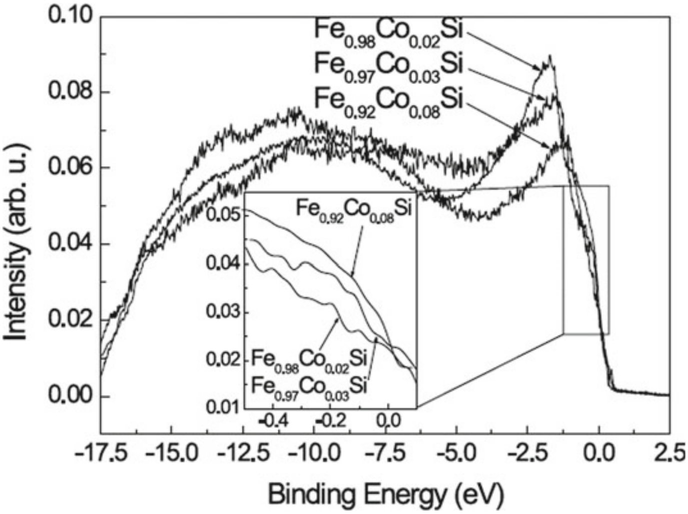

Fig. 10 UPS spectra of $Fe_{1-x}Co_xSi$ single crystal composite. Image adapted from Menzel et al. [97]; Copyright, Elsevier Publishers, 2004

4.7 X-ray Absorption Near Edge Structure Spectroscopy

X-ray Absorption Near Edge Structure (XANES) is an advanced electronic characterization, which uses inner shell excitation to probe the final electronic states that can be either unoccupied or partially filled. The XANES technique is element-specific and examines local bonding-sensitive structures in nanomaterials. The XANES technique is based on the absorption of photon ionization by an electron, which leads to the formation of an empty state from a core level [98]. When the photon energy is equal to or greater than the binding energy of the core-level, an electron in that core is activated. When the photon energy is probed, the excitation results in absorption edges. Therefore, the energy of an absorption edge matches the energy at the core level, which is particular to each element. The absorption edge in the XANES spectrum and associated energy counts in the vertical axis are produced by the enhanced absorption energies corresponding to the absorbed core electrons. The quantum number theory is also used to describe how the absorption edges are categorized. K edge [1s], L edge (2s, 2p), M edge (3s, 3p, and 3d), and N edge (4s, 4p, 4d and 4f) are few examples. Pre-edge, main edge, and post edge are the three sections that make up a typical XANES spectrum. The local symmetry of the relevant atom is said to be responsible for the pre-edge. The post edge is linked to interactions between the parent atoms and surrounding atoms from doping and functionalization, whereas the main edge is caused by the effect of the oxidation of the localized bonds inside the atoms [99, 100].

XANES spectrum data can be analyzed to probe the elemental content within a composite. In the analysis, the XANES spectrum is fitted with a Gaussian function to extrapolate an area under a curve. The area can be integrated to quantify the elemental content. The analysis can be applied to study the impact of nucleation resulting from doping/functionalization in heterostructures. The use of XANES in probing the electronic structure of magnetic nanomaterials is very efficient and has led to different reported studies. A previous study by Gyergyek et al. [101] examined the electronic structure using of cobalt ferrite nanoparticles using XANES. Their results indicated contributions from Fe^{3+} valences, which have a corresponding influence on the obtained magnetic properties. of cobalt ferrite heterostructure. Additional significant previous reports on the use of XANES for the characterization of the electronic properties of magnetic materials are indicated in Table 2.

4.8 Magnetic Hysteresis Loop Measurements

Magnetic hysteresis measurements are crucial to understanding the magnetic features of nanomaterials. The features can range from magnetic transitions, remanence, coercivity and saturation magnetization. These features can be used to classify the magnetic types and their possible applicability. The two main magnetic characterization devices comprise a superconducting quantum interference device (SQUID) and vibrating sample magnetometry (VSM). The principle of the SQUID technique is based on superconducting Josephson junction and flux antenna. Although the SQUID technique is very responsive to weak magnetic fluxes, it suffers some set-back. The SQUID technique lacks sensitivity to magnetic fields, owing to the minute area of sample interaction [102]. The issue associated with the low magnetic field sensitivity results in a limitation to large-scale applications. Vibrating sample magnetometry, on the other hand, is based on the principle of Faraday magnetic induction. The change in the magnetic field, as proposed by the Faraday law, leads to the generation of an electric field. The generated electric fields can be used to probe the changing magnetic field in a magnetic nanomaterial. The working principle of the VSM technique involves vibrating a magnetic-based material that possesses a uniform field, resulting in the generation of electric current from the sensing coils. In a situation when a sample is well aligned at certain angles and undergoes a mechanical sinusoidal motion within the sensing coils, a magnetic signal is generated. The magnetic signal is represented in the form of a hysteresis loop, which can be used to classify the nature of magnetization and strength of the nanomaterial.

The nature of the magnetization of a nanomaterial can be classified based on the parameters such as susceptibility, magnetic saturation, remanence and coercivity. Susceptibility measures the degree of the magnetic response of material by exploring the ratio of the magnetization M to the material to the applied magnetic field. Saturation magnetization refers to a state of magnetization where the applied magnetic field does not affect the magnetic response of the nanomaterial. Other parameters such as remanence and remanence are quantities used in qualifying the class of the magnetic nanomaterial. For instance, depending on the magnitude of the remanence and coercivity, the material can be classified as either a soft or hard magnet. Furthermore, the magnetic phase transitions of the magnetic nanomaterial can be established by exploring the magnetization vs temperature relationship. The obtained trend from the M-T curve can be used to predict the mechanism behind the magnetic type. Generally, the VSM and SQUID setup has proven effective in establishing the magnetic properties of different classes of magnetic nanomaterials and one out of the numerous reports on SQUID/VSM-based measurements was is presented by Ikram et al. [103]. Ikram et al. used SQUID measurement to show the impact of Tb^{3+} and Dy^{3+} concentration on the magnetic properties of $CoFe_2O_4$ heterostructures (see Fig. 11). Their report was able to extrapolate magnetic parameters such as magnetocrystalline anisotropy constant, Coercivity Hc and Bohr magneton μB. These values provide crucial insight into the magnetic behaviour and potential for different applications. Other selected previous reports which outline the magnetic properties of nanomaterials using SQUID/VSM are summarized in Table 2.

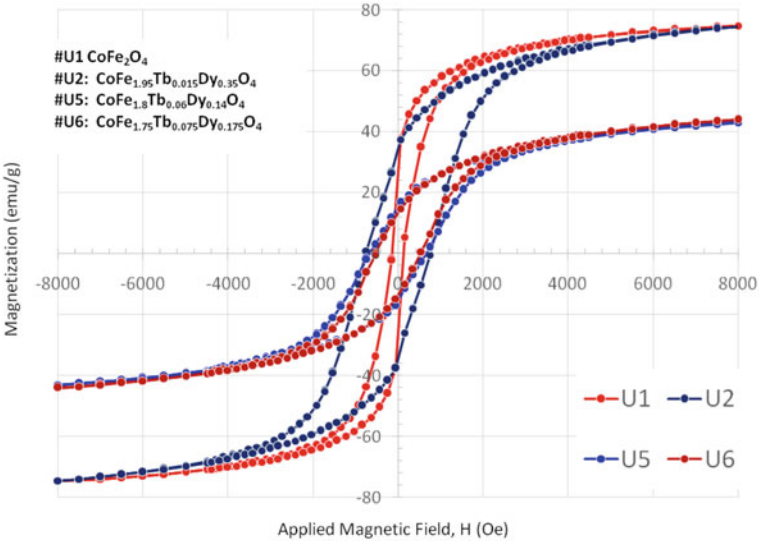

Fig. 11 Magnetic hysteresis plot of $CoFe_2O_4$ heterostructure using SQUID magnetometer. Image adapted from Ikram et al. [103]; Copyright, Elsevier Publishers, 2020

5 Conclusion

Magnetic nanomaterials are important for different applications such as memory devices, ferroelectrics, biomedicine and therapeutics. These applications are based on the manipulation of particle size, morphology and structure. Hence, the synthesis and characterization techniques used in studying magnetic nanomaterials are crucial. The importance of magnetic nanoparticles is examined in the current chapter, which also discusses various synthesis processes and strategies for characterizing them. The synthesis method focused on sol–gel, hydrothermal and green synthesis approaches. The characterization properties focused on the microstructure, morphology, electronic and magnetic properties of magnetic nanomaterials. The summary of a previous report on the class of magnetic nanomaterials with their synthesis method and characterization is presented for easy reference. In general, this chapter will give a summary of available magnetic materials and their properties, which can be informative for the material science research community.

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Utility of Magnetic Nanomaterials for Theranostic Nanomedicine

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Abstract A leading cause of global death is cancer; hence its early detection and treatment are crucial. With the evolution and development of nanomaterials (NMs), there has been an amplified study on the advancement of modern detection and treatment methods using magnetic nanoparticles (MNPs') with theranostic (TC) potential as nano-medicine for cancer treatment. Recent research in nano-medicine has begun

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to explore the diagnostics and treatment combination (TC) as a technique to offer further adaptable, individual, and specific care for cancer treatment to better patient results. MNPs' have shown huge potential in this regard, as they have become key candidates to be employed in a TC platform to achieve this concept of total cancer treatment in humans owing to their extra benefit of being remotely identified and controlled by utilizing a peripheral magnetic field (MF).

Keywords Theranostic · Therapy · Cancer · Magnetic nanomaterials · Diagnostic

1 Introduction

Comprehensive health care budgets have been growing abruptly over the past decade, but there has been a remarkable decrease in disease-related fatalities to permit such a severe cost increase. There has been a conceptual shift in the management of disease and clinicians are steadily moving from the conventional one drug fits all technique toward the concept of individualized medicine-the correct drugs for the right individual dispensed at the proper time [1]. A prominent cause of loss of life and a wide-reaching health problem is cancer. It is projected that by 2018, new cases of cancer and related death by cancer will be between 18.1 million and 9.6 million. It is a disorder that is typified by the uninhibited proliferation of cells that expand from an early central point to other sections of the body and thereby resulting in human death. Hence, it's early detection and treatment to decrease its spread and mortality are paramount [2].

Cancer shows different capabilities and hallmarks, which include avoiding growth suppressors, cell death resistance, proliferative signalling sustenance, supporting replicative immortality, stimulating angiogenesis, and triggering metastasis and incursion [3]. While cancer is a leading reason of death, treatment choices are relatively limited and, in most cases, precise diagnosis and prognosis are complicated. Hence, great attempts in biomedical study have been dedicated to refining the sensitivity and precision of the diagnosis with the objective of early on identification and improved effectiveness of the techniques used for therapy [4].

Traditional NPs systems have been utilized in the past to attain disease administration distinctively. To satisfy all the required purposes, which bring matters of compliance and protection of patients into focus by various administrations, the TC NPs system has been developed to execute all facets of disease management in a particular setting [5].

The current medical treatment employed is chemotherapy, surgery, treatment via radiation, targeted treatment, hormone treatment, as well as green treatments like immune, cell and palliative treatment. Presently, the drawbacks of cancer treatment

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via clinical, immune-treatment, cell treatment and palliative treatment include their noxiousness, side effects as well as the present issues of specific or numerous drug-resistance. Hence, the development of targeted therapy, which was capable of accomplishing precision, efficacy, and success at the cellular and molecular level to decrease impairment and noxiousness to regular cells is imperative and has progressively become the conventional treatment for cancer [3].

In the medical management of cancer patients, a critical issue has been the cancer resistance development to chemo- and radiotherapy. While advancement has been made in the identification and therapy of cancer, the survival of tumour patients remains at a low level-slung, mostly for patients detected at the subsequent phase. Hence, there is an imperative requirement for the advancement of sensitive diagnostic and efficient therapeutic (TRC) procedures for the development of a cancer diagnosis in patients [6, 7].

The development and improvement in the detection and treatment of diseases to a huge extent have been the focus of medical research [8]. Hence, a compelling purpose exists for the analytical and TRC agents creation, which was aimed at specific molecular targets, which can affix themselves to these targets and amass in the designated parts of the organism as well as techniques for their movement across the body. Also, they should have high sensitivity to outside stimuli to increase the management of their movement and their rate of release from their carriers. Application of the aforementioned needs an elaborate and valuable complex of various biochemical and biophysical knowledge platforms. At the turn of the millennium, a new paradigm and term "TCs" was developed as a complex solution to the above-mentioned problem. The phrase "theranostics-TCs" derived from the combination of the words "therapy" and "diagnostic" was first proposed by John P. Funkhouser from PharmaNetics, Inc. in 1998 [9].

TC NPs have gained increased consideration for the management of disorders in current times due to their instantaneous delivery of both imaging and TRC agents. The management of disorders involves the high specialized identification and diseased cell treatments as well as drug delivery process monitoring and TRC effectiveness [5]. The disease specificity and selectivity annihilation can be enhanced by the utilization of peripheral activatable TC agents to create concentrated cytotoxicity with not enough collateral harm. The capability to manage drug dosing in terms of location, time and quantity is a critical goal for the science of drug delivery, as enhanced management increases TRC impact while reducing side impacts [1].

The worldwide fad to enhance the effectiveness, techniques multi-functionality and safety and processes being created for biomedicine (BMD) through different convergent nano-technologies is more obvious. This method is targeted at eradicating various crucial constraints characteristic of conventional techniques for diagnostics and therapy. The highly widespread and consistently utilized techniques of contemporary medicine are incapable to identify cancer precisely at the initial stage. Also, tailored treatment is taken into account by the inherent particularities of a specific patient and is out of the reach of many individuals as the techniques regularly utilized lack sensitivity while unique ones are exceptionally pricey. Also, the action of the drug used is not confined, leading to the prospect of side effects, which increase with the therapy cost [9].

Lately, a new role is being played by nanotechnology (NT) in the biomedical sciences by offering various platforms of NT [4]. To prevail over fundamental restrictions in traditional methods that would allow for more useful and better infection identification and therapy, there has been intensive utilization of NT in medicine (nanomedicine-nmed). It also plays a critical role in the tailored treatment methods, which are useful for disease treatment with unpredictable representations among individuals and confronting the patient's unpredictable TRC responses. This is ascribed to the NMs' exclusive physical, biological, and chemical attributes when compared to their bulk equivalents. MNPs are of particular applicability in nmed owing to their extra benefit of being remotely detected and controlled by applying a peripheral MF [8].

Owing to their distinctive properties, MNPs have become the engine in the TC nmed field and can be employed in current imaging approaches like magnetic resonance imaging (MRI) and X-ray Computed Tomography (CT) and in developing analytical techniques like Photoacoustic Tomography and Fluorescence Molecular Tomography. With regards to treatment, they are mostly preferred for applications in drug delivery owing to their huge variation in shape, nature, structure and functionalization or surface coating [10]. The applications of MNPs involve their utilization as probes for examining disease status and problem mitigating through drug delivery. They have also been effectively utilized in the biosensor, fluorescent-magnetic bioimaging probe model and drug delivery nanocarrier synthesis. Specifically altered MNPs have also been employed for cancer detection and circulating tumour cells (CTCs) as well as the detection and attachment to the cell membrane receptors [11]. The objective of this chapter is to look at existing literature on the development and capability of MNPs in the identification and treatment of cancer in patients employing MRI, photothermal treatment (PTT), magnetic hyperthermia (MHT), and photodynamic treatment (PDT), as well as their blends. Figure 1 illustrates MNPs' applications for the identification and treatment of cancer.

2 Routes for Iron Oxide Magnetic NPs (IOMNPs) Synthesis

A state-of-the-art tendency in material science is to customize and put together conventional products with manipulated properties for specific applications [12]. For application in BMD, NT has improved the structures and design, obviously the important MNPs requirements and properties. Their popularity has increased and appeared as critical biomedical functional NMs owing to their extraordinary features like biocompatibility, high saturation magnetization, lesser noxiousness, chemical stability, and the capacity to work at the cellular and molecular echelons. They are utilized for the delivery of genes, delivery of drugs, diagnosis, chemo-treatment, photo-treatment, imaging mechanisms, and biosorption due to their inimitable features and in combinable techniques for TCs. Extensive variability

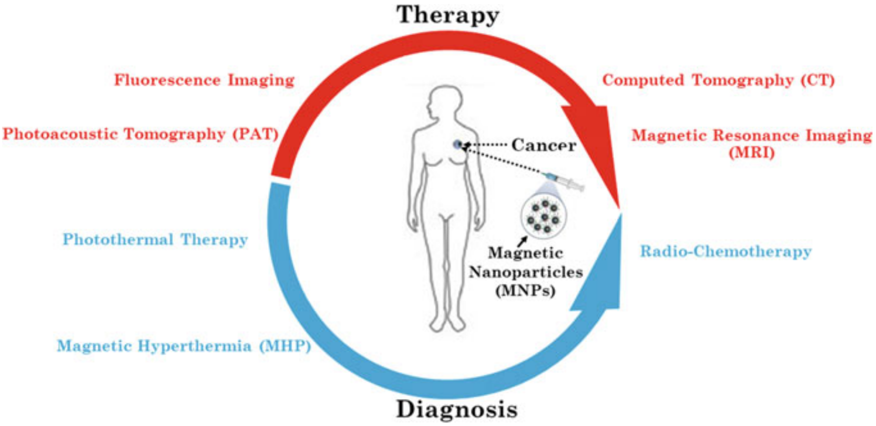

Fig. 1 The application of MNPs for cancer diagnosis and treatment

of NMs has been utilized for improved contrast agents (CAs) encapsulation, TRC payloads biocompatibility and transportation and providing functional groups to couple biomolecules to improve MNPs efficiency employed for TC applications [13].

Inorganic NPs have added distinct and diverse material properties subject to their size and structure when associated with organic NPs [4]. MNPs have unique importance in the basic theory but have a broad array of functions in the BMD field. These magnetic materials are mostly magnetic combined materials comprising of ferromagnetic elements like Fe, cobalt, nickel or their oxides and alloys [3, 5]. Different types of materials that are magnetic are employed for the synthesis of MNPs and the main task is getting NPs that are stable in natural environments, are non-noxious and show the required magnetic properties. In biological media, sturdy magnets of rare earth elements are not chemically stable and are toxic to cells. While pure metallic magnets are disposed to deterioration. Hence, one of the easiest ways out is the use of iron oxide NPs (IONPs) like magnetite Fe_3O_4 or hematite (Fe_2O_3), which are non-noxious, and extremely biocompatible [11].

IOMNPs are generally created in the nano-dimensional rule and huge-sized particles that are magnetic show remanent magnetization (Mr) and coercivity (H_c) values because of their multiplex-domain composition attributed to various crystallite positionings as depicted in Fig. 2.

But with the sizes of particles decreasing to a regime of sub-micron (nanometer-nm), the multiplex-domain composition will get transformed into a single-domain structure and the value of H_c enhanced to the extreme. The decreased nm size at which the single-domain composition of these particles is defined as the single-domain dimension with a detailed analytical radius (r_c). With the further reduction in the magnetic particle size, these particles will possess superparamagnetism and this decreased size is known as the superparamagnetic (SP) size, which is generally in the size array of 4–20 nm for Fe_3O_4/Fe_2O_3 NPs at ambient temperature. SPIONs

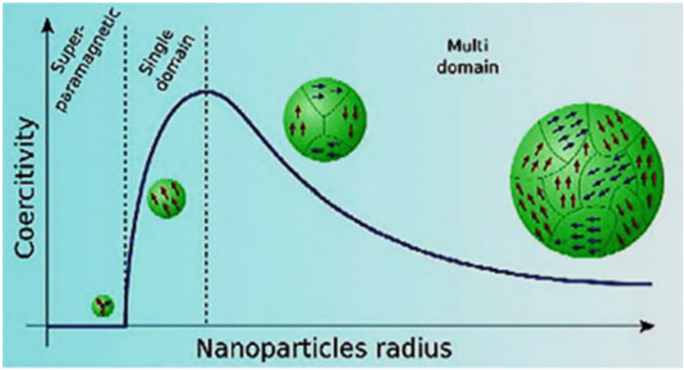

Fig. 2 Graphic illustration of the variation in the coercivity with the MNPs size. [14] Adapted from Akbarzadeh et al.; Copyright, Springer Nature, 2012. Reprinted with permission from Springer Nature from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

specifically Fe_3O_4 NPs have a transposed spinal crystal composition made of divalent Fe (Fe^{2+}) and trivalent Fe (Fe^{3+}) ions at the octa-hedral locations and a single trivalent Fe (Fe^{3+}) ions at the tetra-hedral locations. The O anions (O^{2-}) are assembled amongst the Fe ions to create a closed-filled range of cubic formations in Fe_3O_4 and maghemite ($\gamma - Fe_2O_3$) NPs. For $\gamma - Fe_2O_3$, it has a comparable spinel structure to Fe_3O_4, with the single variation being that all Fe ions are in the trivalent form (Fe^{3+}). Owing to the unmatched or unpaired 3d electrons in Fe^{3+}/Fe^{2+} cations' presence in their crystal composition, the magnetic moments in SPIONs stem from. But these cations are situated far away from each other to stop their interaction or magnetic moment formation. Yet, through the nonmagnetic O^{2-}, there is an interchange link between the cations resulting in the creation of magnetic moments [15].

The magnetization directions of MNPs are aligned along the direction of the field to realize magnetic saturation with a total magnetization reached when they are placed in an external MF. While the susceptibility determines the ease at which MNPs can be aligned. The strength of the field decrease leads to a specific level of reduction in the magnetization owing to the magnetic relaxations (MXs), thus their magnetization direction tends to be maintained and have a residue magnetization at a null field strength. When ferromagnetic NPs size is decreased to a point where the thermal energy (TE) is equal to the magnetic anisotropy energy, the NPs become magnetically unpredictable and are said to be SP. MNPs in an SP form have extremely feebler magnetic-dipole interactions and hence they are effortlessly strengthened and dissolved in an aqueous solution [16]. The key magnetic factors important to the TC usage are the M_r (the remanent magnetization after the peripheral MF is removed), H_c (defines the reverse MF strength required to take remanent magnetization to zero), Curie temperature (T_c), saturation magnetization (M_s) (the optimum proportion of material magnetization that can be attained under the external MF influence), blocking temperature (T_B), and anisotropy energy density (K) (the property of the material that suggests the inclination of the magnetization to turn along a positive particle axis). These factors are impacted by the material, size, core–shell (functionalization), composition and shape of the NPs. As the particles' volumes reduce, the NPs' magnetic anisotropy energy (KV) diminishes also. Decreasing the particle size beyond a certain significant size will result in a specific magnetic domain creating a huge spin known as "super spin", which leads to a huge magnetic moment on an individual particle (~10,000 Bohr magneton). Above the characteristics temperature (T_B), the SP behaviour is very comparable to a paramagnetic material [17].

MNPs comprising of Fe oxide (Fe_3O_4 or Fe_2O_3) and gadolinium (Gd) (complexes of chelated organic Gd) have greatly been exploited as CAs in MRI owing to their capability to separate into Fe and oxygen (O) inside the human body and can be removed securely and employed for metabolic and system transportation of O. When they are synthesized into NPs of 10 nm diameter, IONPs start to show SP behaviour, which leads to enhanced dispersive properties in MF absence and this is of prodigious importance in the application of objective drug delivery [5]. MNPs show non-lasting magnetism and this type of magnetism is currently primarily utilized to research the MNPs' function in vivo. They have detailed substantial surface areas and can hold a range of proteins, miniature molecules, Ribonucleic acid (RNA), etc. Their magnetic properties enable their enrichment and separation and their movement and position in directions. Also, they have a magnetocaloric impact in an elevated frequency MF, which ultimately destroys tumour cells [3].

Notably, the application of MNPs in BMD is impacted by the composition and size of the IO. For angiography and tumour permeability applications, extreme-modest SPIOMNPs are desired. Modifications in IO particles' size and shape are considered by the substantial changes in the proportion of relaxation constants. These factors impact their heating-producing power, plasma half-life and bio-distribution, and determine their usage. These are the motives for the classification of the artificial techniques for MNPs synthesis as a function of the particle's size (very modest, intermediate and huge particle) and shape (anisometric and spherical) [18].

The MNPs' chemical, magnetic, and physical properties vary immensely on the technique of synthesis and their surface alterations and with considerable development made in the direction of MNPs' shapes, composition, core–shell shape, and size variation [17]. Special consideration should be given to the preparation techniques that permit particle synthesis with practically unchanging dimensions and structure. This objective can be accomplished by the precipitation of a consistent solution under precise terms or by manipulating the growth of the particle through a process where a precursor in vapour or aerosol form is putrid. In the instance of MNPs application in BMD, their synthesis techniques are grouped into those that create MNPs' from solution methods or vapour or aerosol forms and composites formed that consist of MNPs that are dispersed in submicron-sized inorganic or organic substances that generally have a spherical form. Another set of techniques that will be discussed for MNPs synthesis employs size range standards to create standardized NPs set out from polydisperse particles [12]. Substantial energy has been devoted to the strategy and production of MNPs that are ferromagnetic with precise parameters [13].

The methods used for the production of MNPs' can also be categorised into chemical, biological and physical procedures [19]. Aerosol/vapour-phase, flow injection, coprecipitation, oxidation, sol–gel, sonochemical decomposition, electrochemical, microbial, gas-phase deposition, herbal plant extracts (biosynthesis), thermal putrefaction or reduction, laser-pyrolysis, and hydrothermal methods facilitates MNPs synthesis via the chemical methods. MNPs are effectively formed by the solution phase using chemical methods, owing to the precise impact on the size, structure, and composition of MNPs. While the physical methods utilized for the synthesis of MNPs include laser-induced pyrolysis, gas-phase deposition, laser ablation, high-energy ball milling, aerosols and electron beam lithography [20]. The physical production approach persists due to the mechanical grinding down technique, pyrolysis, or thermal quenching. For the mechanical grinding down technique application, mechanical force is placed forward employing a universal ball mill to convert the starting material into particles that are nanosized. While thermal quenching is an approach which joins a quick satiate method to create amorphous elements with precise size crystallization using the thermal method. The pyrolysis approach employs high-pitched pressure precursors that are carbon-based gas or liquid, which are forced via an opening, to produce oxidized MNPs when burned into ash. These techniques make up an extensively recognized method deemed to be a sustainable alternative in terms of mass fabrication. Issues relating to size distribution uniformity can evolve and compromise the performance of MNPs' employing these techniques [21]. Biological methods of MNPs synthesis consist of fungi, bacteria, or protein and microbial facilitated methods. These methods are effective owing to the simplification of NMs' mass production and improved purity, but they do not offer superior management of the shape and size of NPs. The methods are further grouped into non-aqueous and aqueous routes, with the water-soluble (aqueous) route being highly preferred to the non-water-soluble route owing to sustainability and low cost. Figure 3 shows MNPs with suitable exterior chemistry applying the different synthesis methods [20].

MNPs creation through the physical techniques involves the magnetic responsive materials decomposition to target the preferred locations. Owing to their high energy requirements, experienced workforce and adjusted complicated factors for

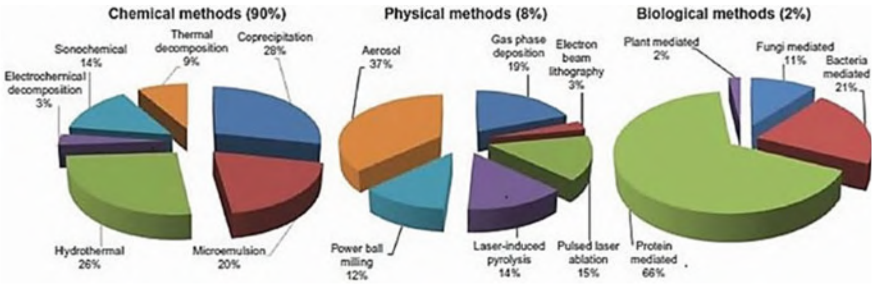

Fig. 3 MNPs with suitable exterior chemistry, applying the different synthesis methods. [20] Adapted from Aigbe, and Osibote; Copyright, Springer Nature, 2022. Reprinted with permission from Springer Nature

their process, these techniques are problematic. While biological techniques are unique and highly focused, such that they comprise of magnetosomes in highly specified lipoprotein compartments that exist within the existing body [13, 22]. This allows the host to create MF inside it that reacts to the earth's MF. The extremely resourceful technique that facilitates exceptional handling of NPs morphology, shape and size is the chemical technique. These techniques are modest and extremely productive and can be carried out devoid of any complex instruments. They are also eco-friendly and can effortlessly be scaled up for huge NPs production when equated to the other approaches. Simple dispersity in NPs with tunable dimensions is crucial for biological and bio-medical uses. The major task in the MNPs preparation using these techniques for TC uses is to regulate the NPs distribution, size, magnetic properties, surface chemistry and shapes. In vivo uses, any chemical or biological techniques are employed to synthesise magnetically sensitive NPs. But physical methods have also been utilized for NPs production employed for in vitro purposes like catalytic events and metallurgical procedures and numerous other manufacturing processes [13].

One of the all-purpose MNPs authorized by the Food and Drug Administration (FDA) for biomedical purposes like disease diagnostics and treatment is SPIONs [15, 23]. But a detailed research is needed to employ these SPIONs efficiently for TC purposes under scientific situations. Hence, scientists are perfecting the techniques for their synthesis to get superior characteristic SPIONs with excellent colloidal stability, narrow size distribution and superior magnetization. The hydrolytic and non-hydrolytic synthesis chemical paths are extensively employed for the production of superior characteristics SPIONs. hydrolytic synthesis methods are employed as traditional paths to precisely produce hydrophilic SPIONs centred on the chemical reactions with Fe precursors in water-soluble environments. Furthermore, produced SPIONs through hydrolytic techniques are further applicable for their direct biomedical uses. The key artificial paths used for the synthesis of SPIONs are hydrothermal, co-precipitation, sonochemical, thermal decomposition and microemulsion techniques [15, 17].

MNPs are employed as nano-carriers for drugs, CAs for imaging in MRI, magnetic targeting and local HT. But due to their superior surface-to-volume proportions and Van-der-Waals forces, opsonization is activated and poses a key barrier to their application in BMD [24]. For biomedical applications, NPs stability is a key critical feature, and the modification of their surface enables their stability and biocompatibility. They are of great importance as CAs owing to their SP activity, extremely minimal cost and biocompatibility which facilitate their easy use by researchers. For inorganic NPs, aggregation and oxidation are observed. Further modifications of their surface with various inorganic molecules, polymeric and nonpolymeric and ligands stabilizers provide a prospect for their application for various purposes and prevent actions such as aggregations, and sedimentation [25, 26].

IONPs that are functionalized are prospective contenders for bio-medical applications owing to their special chemical and physical properties. For their TC use, MNPs should have suitable monodispersity and basic size, high Ms, and appropriate hydrodynamic diameter. They should also have excellent consistency in an organic liquid medium, biodegradable and biocompatibility with reduced noxiousness and the capacity of clearance from the human body [6, 13]. The highly organic water-soluble solution are nonaligned, hence, MNPs coated with surfactants and polymers inhibit aggregation with reduced dipole–dipole interaction among particles, gravitational settling, enhanced biocompatibility and enhance surface functionality [13, 25, 27].

To enhance the stability of a colloidal, techniques employed include the use of polymers and surfactants (organic species) and silica or carbon (inorganic species) to coat NPs [19]. IONPs alterations with organic materials are carried out through in-situ, adsorption, and post-synthesis coating techniques. Organic and inorganic materials play a role as MNPs stabilizers by attaching covalently to the NPs to facilitate these particles to acquire high-level magnetic susceptibility. IONPs are altered with outstanding groups for enhanced functionalization through the add-on of various biologically functional molecules, thereby ensuing in organic or inorganic complexes that have a core/shell nano-structure for various functions. Harmful cell therapy via the immune system is extended with the addition of functionality and these functional complexes possess properties for TC applications which can be utilized in the medicinal and diagnostic processes. Also, the chemistry of core/shell nano-structure surfaces determines their function and operational environments. Their overall noxious ness and response to pH are dependent on the surface modification which bring exact change in IONPs behaviour and by tuning the core size, coating thickness and target ligands, the nanoprobes designed are employed for specific cells, tissues and several disease biomarkers targeting [13].

Besides surfactants/surface coating molecules shielding SPIONs from aggregation, they also play a critical part in conjunction with the reactants in ascertaining the magnetic and physicochemical properties during the synthesis process. Besides, these molecules employed for surface coating allow for efficient functionalization or bio-coupling through the sway of appropriate functional surface groups to enhance their biocompatibility (decreasing noxiousness) and improving hydrophilicity (dispersibility of water) for the effective utilization of SPIONs for instant applications in biomedicals. The SPIONs stabilization is primarily reliant on the balance between the repulsive and attractive interactions, and the TE contribution. To deter aggregation, the typical NPs diameters can be assessed by employing Eq. 1 which associates the TE with the dipole–dipole pair energy. It should be noted that the magnetic interaction will decrease when $D \leq 10$ nm (K_B, T, B and u_o represent Boltzmann's constant, overall temperature, magnetization intensity and free space permeability) [15].

$$D \leq \left(\frac{72K_BT}{\pi u_o M^2}\right)^{1/3} \tag{1}$$

Biocompatibility is attained, with the coating stopping off any noxious ion seepage from the magnetic-core into the biological environment as well as the magnetic-core safeguarding against corrosion and oxidation. Also, the specific surface coating can stop protein adsorption, thereby improving the circulation time in the blood and boosting the possibility of the NPs getting to their target tissues [17]. In the succeeding sub-sections, the state-of-the-art synthesis techniques utilized for the preparation of MNPs for medical application will be described.

2.1 Thermal Decomposition Technique

A key non-hydrolytic production method is employed for the hydrophobic SPIONs with regulated magnetic properties and physicochemical properties like shape, crystal structure, size, and composition [15, 22]. In thermal decomposition method consist of the organometallic Fe precursors decomposition in natural solvents at elevated temperatures. Though this technique can synthesize mono-dispersed particles of elevated quality owing to the distinct nucleation and growing process, it is a complicated process that creates hydrophilic NPs not usable openly for biomedical applications without a painstaking post-synthesis process and might likely result in magnetic properties loss and agglomeration [17].

This technique is founded on Fe precursors decomposition with or without surfactants' presence in an elevated boiling-point natural solvent by heating them at an extremely elevated temperature range of 200–350 °C. To avoid superfluous IO phases, the decomposition of the precursor happens owing to the chemical bonds splintering through an endothermic reaction. SPIONs magnetic and physicochemical properties can be exact by the optimization of precursors/surfactants quantity, time of reaction and temperature of the reaction [15].

It is an up-scalable, laggard production technique that is utilized for non-magnetic organometallic precursors in the presence of an organic solvent. The organometallic precursors are derived from clean metal that is oxidized at 100–350 °C and the oxidative medium and thereby forms Fe oxides. Metal acetylacetonates or carbonyls are some of the present metal precursors utilized in this technique and fatty or oleic acids are the preferred surfactants also used for this method [21]. These techniques have various advantages over traditional methods due to the specific size and shape, superior crystallinity and thin particle size distribution control. But non-polar solvents and various non-biocompatible surfactant utilization have led to scepticism in the medical community for their appropriateness in biomedical applications [18]. Since SPIONs created using this technique are hydrophobic and cannot be used directly for tumours treatment, however, surface change methods such as ligand exchange or bilayer surfactant stabilization addition are needed to change the surface of SPIONs' hydrophobic nature into hydrophilic nature. Currently, the one-pot thermal decomposition technique employing polyol-based surfactants has been utilized broadly to openly create hydrophilic SPIONs for cancer TC use [15].

2.2 Microemulsion Technique

A microemulsion is a visually translucent and thermodynamically stable solution, that is grouped into three main classes which are oil-in-water, bio-continuous and water-in-oil microemulsions. The most utilized microemulsion method is the water-in-oil for SPIONs synthesis, where the reverse micelles comprised of water-soluble droplets of reactants, enclosed by a surface-active agent monolayer created in a non-stop oil phase, which may possibly react with each other to create SPIONs. Also, SPIONs synthesis can be accomplished by either mixing two or more microemulsions that comprise of various Fe precursors and combining a precipitating agent dropwise into the microemulsion containing the Fe precursor. Within the droplets, the reactions may occur, as they primarily behave as a nanoscale reactor and the final NPs can be gathered by eliminating the unnecessary solvents or surfactants. The SPIONs' physiochemical and magnetic properties are considerably reliant on the size of the droplet, precursors concentration and surfactant or solvent categories [15]. The oil-in-water technique entails the utilization of a water-soluble form (which contains the salts of the metal, pH controllers, and covering agents), an oily phase such as hexane and surfactants acting as stabilizing agents in the interface of oil/water such as sodium dodecyl sulfate (SDS), bis(2-Ethylhexyl) sulfosuccinate (AOT) or poly(N-vinyl pyrrolidone) (PVP). The reverse microemulsion can also be accomplished and is centred on the nanosized stabilized water-soluble form dispersed in an oily phase. This process creates energetic structures that might combine and allow reaction upon blending, hence delivering a regulated nucleation growth setting. It contains a dilatory and low scalable process, which is performed at a temperature array of 20–80 °C [21].

2.3 Hydrothermal Technique

The hydrothermal technique is a traditional technique utilized to produce SPIONs [28, 15]. This synthesis technique consists of a straightforward and effortlessly up-scalable production technique that is based on the metal salts hydrolysis and dehydration in a water-soluble medium under elevated temperature and elevated pressure environments that are accomplished in an autoclave apparatus using a temperature of approximately 200 °C and over 2000 psi pressure. This metal oxide particle synthesis is facilitated by the reaction conditions and the ensuing MNPs precipitation. The well-regulated variables in this method include temperature, concentration, and time of autoclaving, with the latter impacting the particle size and distribution uniformity [21]. NPs are produced using this technique by accomplishing the water-soluble chemical reactions among Fe precursors in the dearth or existence of surfactants in an airtight vessel in an autoclave, which provides extraordinary temperature/vapour pressure of up to 250 °C/4 MPa for chemical reactions. At the end of the reaction, the water-soluble mixture is refrigerated down to room temperature and the acquired SPIONs' are derived from unreacted precursors, remaining surfactants, and additional impurities exclusion. By adjusting the temperature of the reaction, time of reaction, surfactant mass and precursors, the magnetic and physicochemical properties of the SPIONs can be altered using this technique [15].

2.4 Precipitation Technique

The co-precipitation technique is the utmost generally utilized method, which is cost-efficient and a superficial production technique [13, 29]. For more than a decade, water-consistent Fe_3O_4 and Fe_2O_3 particles have been achieved through iron salt precipitation in water-soluble media. To guarantee their colloidal stability under physiological settings and improve their functionality, IONPs synthesized using this technique need to be covered with dendrimers, organic acids, sugars, polymers fluorescent compounds etc. This is taken on either during or after synthesis [18].

This is a widely employed hydrolytic technique for SPIONs production, where IONPs are created through precipitation between the chemical reactions of ferrous/ferric salts of nitrates/chlorides/perchlorates/sulphates and a base (NH_4OH or NaOH) under the water-soluble condition at an insignificant preeminent temperature of 40–80 °C. The key mechanism of reaction participating in SPIONs formations is given by Eq. 2 for Fe_3O_4. To avoid unwanted IO phase formation in the synthesized SPIONs, the reaction is generally performed in a passive atmosphere.

$$Fe^{2+} + Fe^{3+} + 8OH^- \leftrightarrows Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 \downarrow + 4H_2O \qquad (2)$$

The following topotactic conversion paths (physical transformation to crystalline solid) are the mechanism of reaction for SPIONs formation (Fe_3O_4), which are (1) nucleation → akaganeite phase → goethite → hematite/$\gamma - Fe_2O_3 \rightarrow Fe_3O_4$ and (2) nucleation → ferrous hydroxide → lepidocrocite → $\gamma - Fe_2O_3 \rightarrow Fe_3O_4$. The topotactic conversion path is greatly reliant on the variation of the pH of the water-soluble reaction mixture and while SPIONs physicochemical properties like morphology, stability of colloidal, size and shape can be changed by variation in reaction temperature, time, reactants concentration, base type, reactant molarity and stabilizing agents [15].

A graphical illustration of the various process intended to describe uniform particle creation is shown in Fig. 5. In uniform precipitation, a quick separate nucleation burst happens when the fundamental species concentration gets to a crucial supersaturation. After that, the nuclei acquired are permitted to increase homogeneously by solute diffusion from the solution to their surface until the ultimate size is achieved. To accomplish monodispersity, these two phases must be divided, and nucleation should be prevented during growth time. The LaMer and Dinegar classical model was the first to clarify sulfur colloids formation and a restricted number of cases as seen in curve 1 of Fig. 4. But homogeneous particles have also been achieved after various nucleation procedures. Through the self-improving development process,

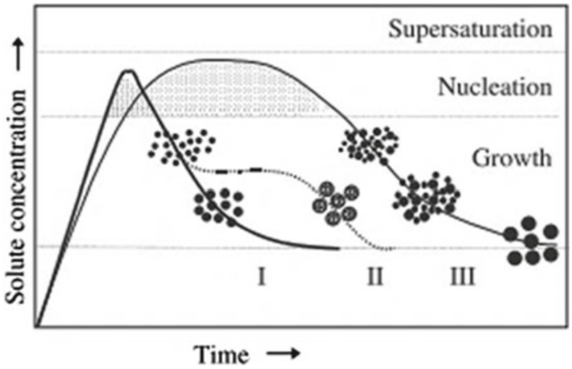

Fig. 4 Development of homogeneous particles in a solution described by (curve I) single nucleation and homogeneous development by diffusion (the standard model of LaMer and Dinegar), (curve II) smaller sub-units nucleation, growth and aggregation and (curve III) numerous nucleation and ripening growth by Ostwald. [12] Adapted from Tartaj et al.; Copyright, Institute of Physics Publishing, 2003. Reprinted with permission from Institute of Physics Publishing

the homogeneity of the finishing product is attained (Ostwald ripening, curve III of Fig. 4). Also, homogeneous particles are attained due to the agglomeration effect of considerably less significant sub-units instead of constant growth by diffusion (curve II of Fig. 4). A non-natural separation between the development processes and nucleation is attained by seeding, in which external particles are launched into the monomer solution below the key super-saturation [12].

2.5 Sonochemical Technique

This technique is based on the chemical reactions or metal precursors hydrolysis and condensation at low-slung temperatures, causing inorganic network creation. Monomers change into colloidal solutions to specify the sol and the evaporation of the solvent and particle introduction into the inorganic network results in the gel created [30]. This method depends on MNPs precursors hydroxylation and condensation in a solution (sol) that results in gelation at ambient temperature, and subsequent exposure to heat treatment stimulates crystalline structure creation, desired MNPs with precise size and shape [21]. This technique is built on stimulating the reaction among the blend of Fe precursors (ferric or ferrous salts) through ultra-sound treatment with frequency varying from 20–60 kHz to produce SPIONs. This ultra-sound treatment consists of varying expansive and compressive acoustic waves, which produce cavitation micro-bubbles in the Fe precursor solution, thereby induces nanocrystal nucleation by amassing the supersonic energy. Ultimately, the micro-bubbles may break down and be subject to the discharge of the stowed intense energy with a

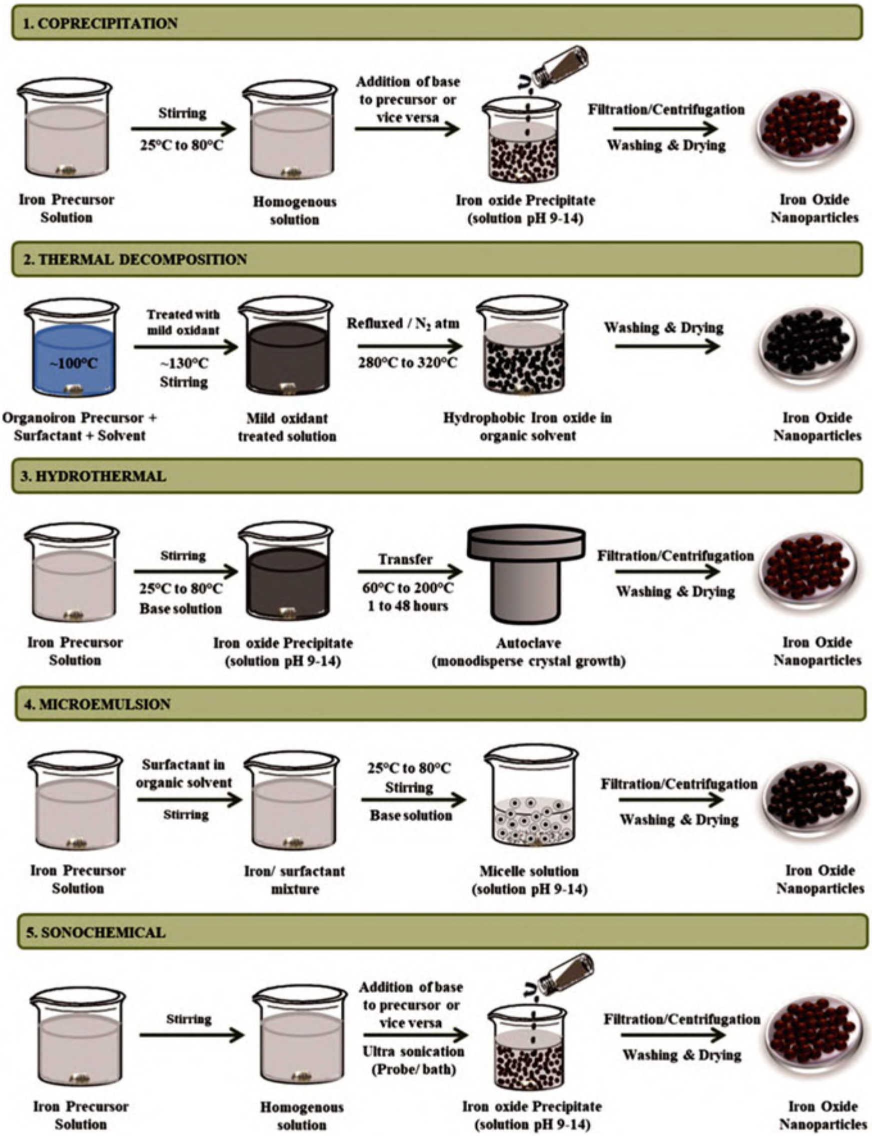

Fig. 5 Graphical illustration of regularly used chemical approaches for MNPs production. [31] Adapted from Darson and Mohan; Copyright, IntechOpen, 2022. Reprinted with permission from IntechOpen from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

thermal and cooling rate of greater than 1010 K/s that tends to improve the temperatures within the cavitation bubbles in an exceptionally rapid time (approximately 1 ns). Through the decomposition of water, H^+ and OH^- radicals are created, which further react with Fe precursor combinations to produce SPIONs. This technique is advantageous that it decreases undesirable nano-crystals growth. But this method is challenging to implement SPIONs production with controlled magnetic and physicochemical properties [15]. Through this technique, MNPs of single-phase, fine, dense, and homogeneous can be achieved. While this process is eco-friendly, it is not an exclusive technique but it shows restricted productivity and the synthesis procedure is lengthier than the co-precipitation technique [30]. Figure 5 shows the graphical illustration of regularly used chemical procedures for MNPs' production.

3 TRC Utilization of MNPs

In certainty, MNPs show, not just individual distinctive materials properties but also a combined strategy capacity for targeting cells, treatment, and imaging, which make them perfect platform materials for TCs [4, 5]. The word "TCs" represents a broad set of physical theories, nanotechnological techniques and biomedical and engineering processes which provide different prospects for diagnostics and treatment and utilize as a rule similar hybrid NPs. The following possibilities are offered, which are

1. Timely diagnostics and pharma-cogenomics
2. Three and four-dimensional (3-D or 4-D) tomography of the object in doubt, employing a molecular-level resolution (superior-resolution real-time imaging).
3. Evaluation of the disease's progression phases, treatment plan development and restorative technique choice, which is targeted at the molecular stage and customized.
4. Directed transport of diagnostic and TRC agents, its regulated delivery from nanocarriers and regulated activity, while actions are taken to protect and safeguard the degrading of the active substance during its transportation via the body and the organism from substance noxious influence.
5. Treatment examination and modification and the examination of the status of the patient after completing effective therapy.
6. Assessing the substances' biocompatibility and the processes for remote control, their noxiousness, possible dangers, and vulnerabilities

The various major TC methods developed thus far, differ in the chemical and physical effect types utilized (X-ray, radioactive, radio-frequency (RF), electromagnetic, biochemical ultrasonic and their blend) [9].

Personalised targeted TC nmed has been developed as a key method for improving the sensitivity and specificity during identification in addition to the probability of existence by utilizing NPs. A potential NPs that are the most beneficial tool for the detection, identification and therapy of tumour is the TC NPs. To prevent the unrestrained tumour cells spread, nanosystems have been designed and in practice, systems made from MNPs including anticancer medicine have shown an advanced healing index when compared to conventional chemotherapy, thereby resulting in a substantial decrease in the noxiousness of the nanosystem [32].

They tend to amass at the target site in the presence of MF, which is of enormous importance in TC applications. The magnetic moment of IONPs should be elevated and allow for their exact bonding to biomolecules of interest. They should also have the capacity to resist different biological and physical conditions [13]. Nevertheless, despite the extensive progress and technological advancement, there are particular inherent shortcomings which set limits to their medical application, which is that they lack exclusiveness, localization, and temporal and spatial resolutions. They also offer just imperfect control over drug release and activity. The risk of side impacts is relatively high, and the techniques are difficult to execute, and high-priced paraphernalia and assets are required [9].

A critical part is played by personalized treatment methods employing nmed, which is useful for disease therapy with changing representations among persons and blocks patients' unpredictability in medicinal responses. This is ascribed to the distinctive physical, biological, and chemical properties of NMs in comparison to their molecular and bulk equivalents. They also have added advantages in nmed such that they can be remotely sensed and controlled using an external MF (EMF) [33]. Owing to these benefits, they have been exploited successfully for a wide array of biomedical purposes. MNPs' distinctive properties like their sensitivity and precise registration for diagnostics are allowed owing to living tissues practically lacking ferromagnetic materials and zero signal strength weakening of the MF from biological tissue (contrasting optical and electrical methods) [8, 34].

In MNPs imaging approaches, these properties are utilized to precisely determine the location and concentration of particles like magnetic susceptibility imaging (MSI), magnetic particle imaging (MPI), and magneto relaxometry imaging (MRI). Also due to MNPs' miniature size, they can effortlessly intermingle with viruses, cells, genes, and effectively enter all sections of the human body. They are also extremely tuneable and by altering their size and process composition or synthesis, their behaviour and preferred physical properties can be achieved (slow/fast exclusion from the human body and their particular response to MF applied). Finetuning these particles by coating them with certain molecules facilitates their binding to certain entities and thereby allows molecular imaging [8].

In MNPs' biomedical use, they are categorized according to their usage in the core (in-vivo) or outside (in-vitro) of the human body. In-vivo functions are extra divided into TRC (HT) and delivery of drugs and diagnostic (nuclear magnetic resonance imaging (NMR)) applications. While the in-vitro procedure is employed just in diagnostic (separation or selection and magnetorelaxometry) [9]. For in-vivo use, NPs that are magnetically sensitive are fabricated by employing any of the biological or chemical procedures. While the physical technique is primarily employed for the production of MNPs used for in-vitro purposes. MNPs carrying inorganic or natural surface coverings have accomplished growing importance in the material science sector owing to the ensuing instruments allowing a well-regulated sensory system for advanced bio-medical usage from medicinal and diagnostic to bio-separation [13].

In planning an effective nano-platform-based TRCs, these four critical attributes need to be taken into account, which is choosing a potential TRC, varying from tiny molecule drugs to bigger peptide or nucleic acid, a steady carrier, adopting an aiming and drug delivery approach and prudently singling out an imaging agent [35]. Owing to their magnetic properties, MNPs have been applied generally as CAs in the screening of tumours employing MRI, computed tomography (CT), near-infra-red imaging (NIR) and magneto-acoustic tomography (MAT). They are also utilized in the therapy of tumours via PDT, PTT and MHT. All these different approaches are employed in oncology, but the most excellent medical impact is generally guaranteed through the blend of strategies as the integrated model allows MNPs to achieve several tasks concurrently [36].

3.1 MHT

MHT is a positive non-intrusive method for the treatment of cancer [37, 38]. The word HT is derived from two Greek phrases "hyper" and "therme" connotating "rise" combined with "heat" in that order, owing to the condition attributing it to improving body temperature. HT has been widely considered by employing biocompatible MNPs as heat facilitators for the treatment of tumours owing to the elevated effectiveness and a particular level of side impacts. It is a pioneering and novel heat treatment where MNPs are the heating-generating agents [39, 13].

HT is one of the tumour therapies among radiation treatment, chemotherapy, surgery, gene, and immune treatment. It is thought of as a synthetic approach for improving the temperature of the body cell by supplying heat taken from peripheral sources to prevent or destroy the further growth of malignant tissues [39]. The generated heat from MNPs in a non-disturbing AMF to the cancer cells causes cell fatality through irreversible physiological variations is identified as HT as depicted in Fig. 6 [13, 40].

HT refers to a body temperature increase by 1 °C. It also refers to the temperature array rise to 39–45 °C. The four kinds of HT include fever, movement-associated HT, deficient temperature drainage HT and medication-induced HT. For wholesome human somatic cells excluding neurones, they can endure at a temperature of 44 °C for a minimum of one hour. Hence, wholesome tissues are not harmed by HT except if the temperature exceeds the stated value above [41, 42]. For a temperature array of 45–50 °C, HT causes thermal extirpation. Though it can be unsafe for an organism, it can be of medical purpose, particularly when focused against certain tissues or cells. TRC HT is grouped by matching the size of the area where the temperature is increased, and it is grouped into whole-body and local regional HT. In constrained body areas, temperature increase permits for the determined TRC impacts on the suitable sections of the body while reducing adverse impacts of heating in other body areas. One of the viable therapeutic techniques for increasing temperature in

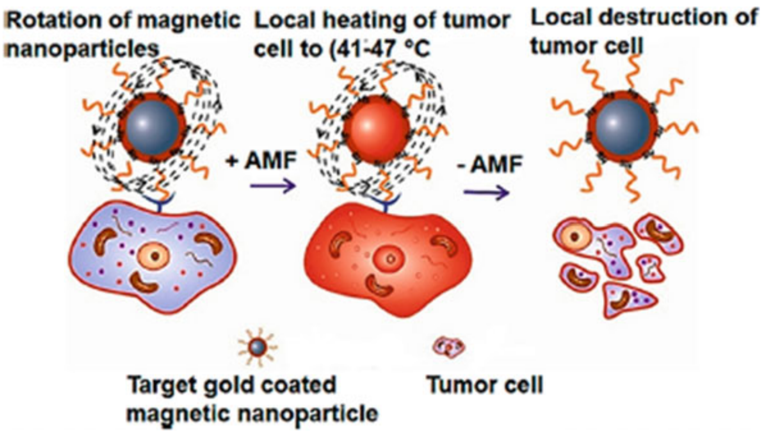

Fig. 6 Principle of HT. Through the application of AMF, MNPs are aimed at tumour cells. Subsequently, the heat produced by the MNPs produces constricted heating of the tumour cells with a temperature range of 41–47 °C. CITATIONKhi21\l7177; Adapted from Khizar et al. Copyright, ACS Publications, 2021. Reprinted with permission from ACS Publications

a particular body section is MHT [41]. The concept of employing SPIONs for HT was first proposed in the 1950s by Gilchrist et al., and its original biological system application was performed in 1979, with various MNPs types having been studied for this objective since then [17, 37, 43].

With the upswing in NT, MNPs introduction has further advanced this method into a well-studied field. The extremely important benefit of MNPs' mediated MHT remedial mode is in the intense tissue permeation and mag-selectivity cancer cells obliterating devoid of impairing the wholesome tissues. This technique assists in understanding intracellular HT, as it precisely provides medicinal heating to the tumour cells, and this intra-cellular HT can be more developed by the cell-targeting ligands conjugation with MNPs'. The local and uniform heat leads to better selectivity and therapy efficiency. Owing to the benefits of these TRC methods, MNPs-MH-based benign tumour therapy has lately been transformed from the research laboratory to medical tests and they have been utilized for glioblastoma and prostate cancer (PC) therapy [44].

MHT involves the conversion of electromagnetic energy from external AMF into heat employing MNPs and the MNPs act as the nano heat centres creating heat by relaxation loss, thus heating the tissue. The key objective of efficient treatment of cancer is the destruction of cancerous cells with minimum harm to cells that are normal. This technique can be utilized for selective heating of a miniature region, as it presents the capability of being an extremely discerning and non-intrusive method for TRC cancer therapy [17].

About MNPs in TRC applications, MHT is deemed the utmost capable treatment for cancer therapy. In MHT, a superficially utilized alternating MF (AMF) is applied to the MNPs' thereby heating up the MNPs and enhancing the temperature of their environments. With the implant of particles in a tissue tumour, the local heating of the tumours is permitted without damaging wholesome cells. Precise delivery of the medicinal agents such as drugs, genes, radionuclides etc. attached to the particles at the desired location is possible with the internal or external application of applied stimuli like osmolarity, temperature, pH, and MF intensity (MFI). This delivery of the local drug permits the reduction of the overall dispensed dosage resulting in to a lesser extent general side effects [8].

MHT treatment is a confined thermal treatment utilized for cancer/cancerous tumour therapy in which SPIONs perform as heating-producing agents. SPIONs are usually delivered and confined near a tumour location through active/passive/magnetic targeting and consequent exposure to an AMF for approximately 1–2 h specific time. The heat produced by the process increases the tumour temperature to approximately 42–45 °C and is employed in cancer cell therapy. The heat-induced terminates various cellular functions as well as the propagation of cells and gene representations in tumour cells which inclines to cause the death of cells through programmed cell death. The heat generated during this treatment produces a very negligible impairment to the adjacent typical cells/organs as associated with other traditional therapy techniques [15]. Due to this, the temperature in the interior of the benign tumour is enhanced owing to the single-domain particle's energy dissipation triggered by the Neel fluctuations of the NPs magnetic moment and peripheral Brownian fluctuations. The value of heat dissipation changes with the amplitude and frequency of the AMF and the magnetic properties of NPs. Tumour cells are destroyed with enhanced temperature due to folding, denaturation, apoptosis, protein aggregations, necrosis and coagulation and unintended response which is facilitated by the immune system activation supported by over-expression of heat shock protein. Also, the heat created through this technique can be regulated by adjusting the SPIONs' magnetic/physicochemical properties such as the shape, size, Ms, dispersion medium, applied AMF and surfactants [15, 37].

HT can be induced in SPIONs via the exchange by suppression of anisotropy wall by the MF, Brownian spin, thermal activation and the combination of the preceding factors [45]. The two mechanisms accountable for the creation of heat from MNPs are hysteresis losses and the Brownian Neel relaxation (BNR). The BNR generally happens in SPIONs and it entails the quick spin of the magnetic moment within the domain in the instance of NR and in the instance of BR, it involves the physical spin of NPs within the fluid in the peripheral AMF presence. The subsequent equations give the Brownian (τ_B) and Neel (τ_N) relaxation times which sturdy changes with the NPs hydrodynamic size of nanoparticle and extremely changes with the fluid viscosity and the effective relaxation time (τ) (Eqs. 3–5).

$$\tau_B \frac{3\eta V_H}{kT} \tag{3}$$

$$\tau_N = \tau_O exp \frac{K V_M}{kT} \tag{4}$$

$$\tau = \frac{\tau_B \tau_N}{\tau_B + \tau_N} \tag{5}$$

τ_0, K, V_M, k, T, η, and V_H represent the distinctive flipping frequency, the magnetic anisotropy constant, the volume of NPs, the Boltzmann constant, the temperature, the fluid viscosity, and the NPs hydrodynamic volume, respectively. The dissipation of heat from MNPs is due to the delay in the magnetic moment relaxation under the peripheric AMF application with a time delay, which needs a magnetic reversal lower than the NPs' relaxation times. The dissipation of heat (P) changes with the frequency (f), the AMF amplitude and the NPs' magnetic properties (Eq. 6).

$$P = \mu_O \chi f H^2 \tag{6}$$

μ_0, χ, and H signify the permeability of free space, the magnetic susceptibility, and the AMF strength, respectively [37].

In guiding NPs to tumours, further, improvement has been made by employing targeting agents like antibodies for this purpose. This technique is appropriate for efficient cancer treatment if particles concentrations in the benign tumour are extremely adequate and substantially greater in the surrounding regular tissue and a high enough specific absorption rate is possessed by the particle which is given by the specific heat absorption rate (SAR) in Watts per gram (Eq. 7).

$$\text{SAR} = \frac{c\Delta T}{\Delta t} \tag{7}$$

c and ΔT represent the precise heat capacity and increase in temperature in the interval of time (Δt) to transport substantial intra-tumoral amounts of heat with AMF that is highly allowed by the ordinary cells. The values of SAR change with the NPs' shape, size, and magnetic properties as well as the amplitude and frequency of AMF, the attributes of the materials employed for coating and the functionalization of the material surface [37, 43, 46].

The various NPs heating tools explored for TRC purposes are optical heating employing laser, small bubbles heating employing ultrasound and IO heating owing to AMF which involves the use of physical processes known as hysteresis heating. Optical techniques efficiently heat particles but are relentlessly constrained by laser light reduction by the cells. While ultrasound heating is encouraging, due to energy being focussed on a certain spot, it nevertheless deteriorates from the change of sound speed in most cells and in various applications, from the narrow applicator aperture. To achieve therapy of cells positioned practically wherever in the human body at crucial depths is achievable by applying magnetic particle heating. Particles utilized for heating may also be appropriate for medical imaging purposes also [43].

There is selective or entire body heating in specific regions in various ways. For high temperatures utilization, there are three vital medical methods used, which are whole body HT (WBHT-employed for the treatment of metastases over the entire body), regional HT (RHT- body parts like the limb, organ, or body hole are heated) and local HT (LHT-superficial local and interstitial local HT) [37, 39]. Tumours are heated with microwave energies of wavelengths varying from 433 to 2450 MHz, radio frequency varying from 100 kHz to 150 MHz, ultrasound, perfusion of hot water (blankets, tubes), NPs ferromagnetic seeds, resistive wire implants and infrared radiators. WBHT is often employed in childhood refractory malicious solid cancers to enhance cancer sensitivity to chemotherapy and its impacts. While LHT is employed for heating a small-scale area comparable to cancer of $\leq$3–5–6 cm in the lengthiest thickness. In the RHT, it is normally blended with radiation treatment or chemo-treatment, and it is most time dedicated to developed cancer located in the abdomen treatment such as prostate, cervical, bladder, colorectal and ovarian carcinomas, main and lower pelvis or thighs (soft cell sarcomas) [39].

In the study by Bhardwaj et al. [47], self-adaptable temperature-manipulated NPs were synthesized (Mn-Zn Ferrite NPs) and their impact on the killing of cervical and breast tumours was considered. Testing the synthesized MNPs on the tumours, it was reported that various sessions of HT on the tumour cells utilizing a 24–72 h window using trypan blue assay of at least 3 shifts of 1 h were needed for the overall elimination of the tumour cells, with cell viability decreasing to 25%, 15.8% and 0% owing to HT sessions employing MF, MF alone and MF along with three HT sessions after 72 h are indicated by Fig. 7.

Magnetoliposomes (ML), which comprised of SPIONs stabilized by phospholipid-bilayer exposed to AMF of 40–47 kAm amplitude and 270 kHz frequency to produce heat, were explored for HT impact on human Pancreatic ductal adenocarcinoma (PDAC) cells (Mia PaCa-2 and PANC-1). The impact of MHT on the viability of the cell of the organoid cultures and the cell lines was explored at two diverse time points. No cytotoxic impacts at 300 and 225 μg(Fe)/mL ML concentrations were shown by the cells of Mia PaCa-2 and PANC-1 and PDAC organoid cultures. MHT therapy had the uppermost effect on the viability of cells using ML, which resulted in outstanding cell viabilities of 2 and 24 h post-therapy [48]. While in the study by Parekh et al. [49], the co-precipitation procedure was employed to produce auto-tunable temperature-sensitive IONPs of the size of 11.3 ± 0.2 nm and utilized for MHT to determine the cytotoxicity of cervical tumour cell line HeLa under MF induction heating of 350 kHz frequency and field of 14.2 kA/m and without MF induction heating. Cell death of approximately 75% was noticed for the cytotoxicity assay after the utilization of MF induction heating for 24 h of the cell interface with the magnetic fluid, with just about total death of tumour cells observed with interaction time increased to 36 h and HT heating session of 1 h (Fig. 8).

Particle-size precise SPIONs of $\gamma-$ Fe_2O_3 and Fe_3O_4 were prepared through the hydrothermal technique and were improved with whey protein isolate (WPI) to create spherical/diamond-shaped structures of bio-altered SPIONs with a diameter range of 20–100 nm. To carry out HT experiments, SPIONs loaded with adriamycin (ADM) were utilized in vitro and in vivo test of HepG2 cell inhibition in the skin of mice placed at the centre of an AC electromagnetic coil with MF of parameters of frequency (f) of 100 kHz, field (H) of 169 Oe (13.62 kA/m) and H.f of 1.36×10^9 A/ms. It was noticed that the size of the $HepG_2$ cancer cells was decreased with the consistent surface consumed and gelled thereby causing the cancer cells to lose

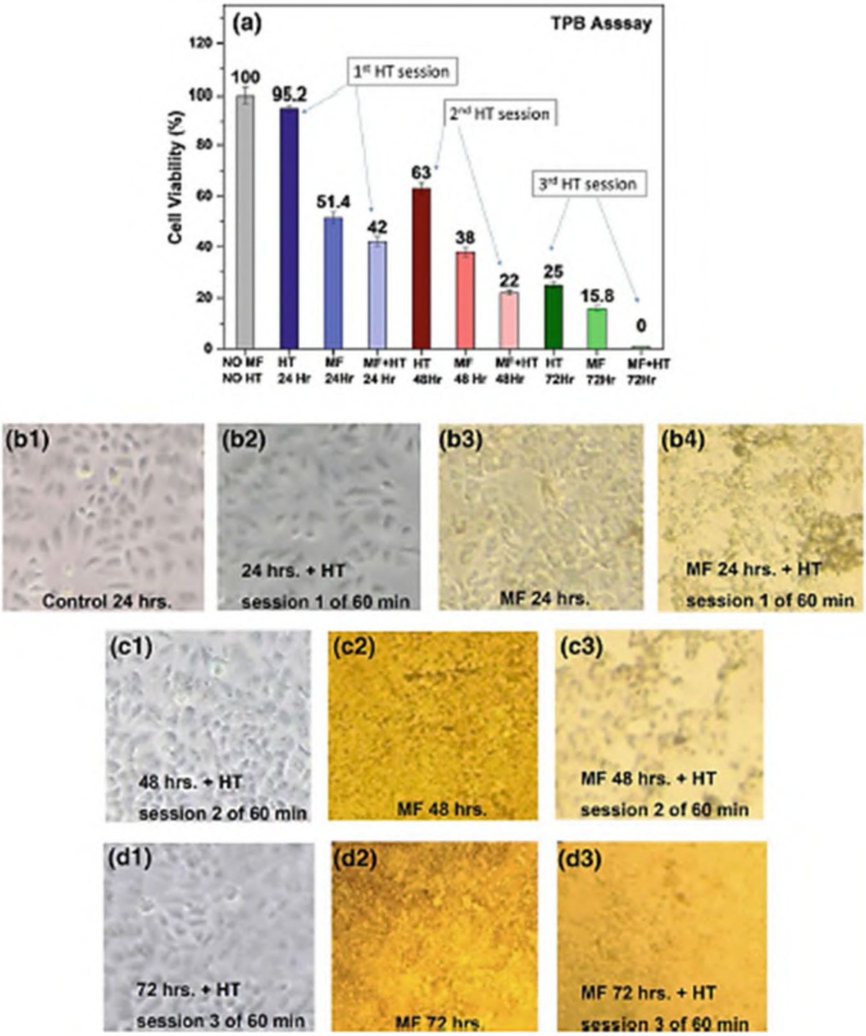

Fig. 7 Various HT sessions of 0.35 mg/mL MF concentration **a** HeLa cells viability employing Trypan blue assay after 24–72 h therapy **b1**–**b4** HeLa cells morphology after 24 h, **c1**–**c3** after 48 h and **d1**–**d3** after 72 h. [47] Adapted from Bhardwaj et al.; Copyright, Springer Nature, 2020. Reprinted with permission from Springer Nature from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

their biological movement when the cells were treated in vitro and in vivo using WPI-altered SPIONs for HT therapy [50]. While the chemical co-precipitation and thermal decomposition techniques were used to produce SPIONs-based ferrofluids, which were functionalized with carboxyl (terephthalic acid-TA) and used to study the heating efficiencies of TA@SPIONs on in vitro MHT therapy of MCF-7 breast

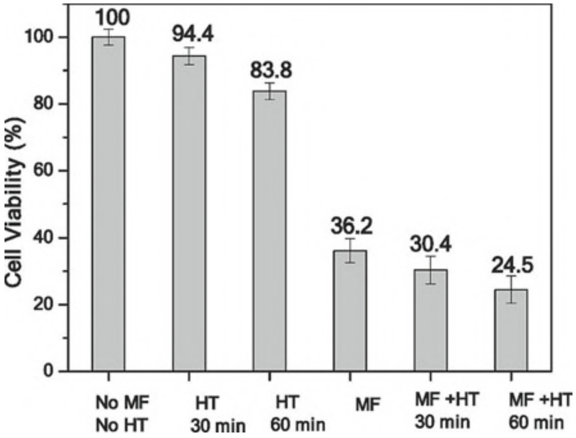

Fig. 8 Viability of cell employing magnetic fluid in the presence and absence of MF induction heating after 24 h at 350 kHz frequency and 14.2 kA/m applied field. [49] Adapted from Parekh et al.; Copyright, Elsevier, 2020. Reprinted with permission from Elsevier from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

tumour cells. An outstanding time–temperature increase was noticed employing the water-soluble ferrofluids under the applied AMF and this resulted in elevated SAR varying from 23.4 to 160.7 W/g_{Fe} owing to improved magnetic response through π-conjugations of TA molecules short-chained on the SPIONs. It was reported that TA@SPIONs-based fluids of 1 mg/ml concentration in MCF-7 tumour cells, whose temperature was kept at 45 °C under the exposure of AMF for 1 h, demonstrated stimulated substantial mortality of cells [51].

3.2 MRI

MRI is a non-intrusive TRC diagnostic tool that examines the variation in the hydrogen protons in water molecules magnetization enclosed in tissue when positioned in an MF and subjected to a radio frequency electromagnetic wave pulse [17].

MRI are diagnosis method in radiology that utilize magnetism, computer expertise and radio waves theories to create structural human body images. An efficient way to identify the cancerous tumours positioned hidden within the body is the utilization of NPs-based CAs for MRI [15]. MRI is intensely utilized for the screening of cancer throughout and after chemotherapy. In spite of the common imaging methods which need ionization radiation, MRI employs ion magnetic properties for image prediction. With no application of magnetic moment, there is a randomized location of the protons and there is a corresponding or antiparallel alignment of protons when the MF is applied. To improve the image quality of MRI, CAs like those based on MNPs are utilized. The advancement of sensitive MNPs and colloidal magnetic particles for biomolecules control and simple magnetic separation is of excellent significance for initial disease discovery and therefore in treatment administration and the initial phase of tumour therapy. Discerning tumour cell detection can be accomplished by antibodies, hence various immune sensors have been created for this application. While the use of MNPs functionalized with antibodies specialized for a variety of cancer cells, the exposure via the certain immune sensor can be linked with imaging via MRI and the therapy of cancer via HT. This approach presents a considerably enhanced rate of persistence among oncologic patients' treatment responses [36].

MNPs are generally employed for diagnosis and efficient delivery of drugs owing to the ease of their imaging by MRI. Nevertheless, MRI is an efficient technique for imaging tissues hidden inside the human body with high resolution, there is a necessity for peripheral agents that can improve the contrast to show objects distinctly. To improve the contrast by enhancing the photon relaxation time, various metallic NPs such as Gd, manganese (Mn) and SPIONs are utilized. Gd-based CAs for MRI are now Food and Drug Administration (FDA) authorized. But IONPs are generally used owing to their excellent magnetic properties, huge surface area to volume proportion and their capability to deliver drugs which makes them appropriate for nano-TCs [52].

IONPs were first employed as a T_2-MRI contrast agent (CA) and several novel magnetic modifications have been created to enhance the sensitivity of the signal for improved MRI diagnosis. Also, these NPs platforms can adapt other corresponding imaging sensory systems, medicinal drugs and aiming ligands and attain extremely precise imaging and efficient restorative purpose. Furthermore, their platforms can act as magnetic switches for the control of the molecular level of cell functions and signalling [4].

In the recognition and planning of cancer therapy, an important instrument utilized is MRI. But a specific imaging method is not suitable enough to assess various attributes of cancers owing to the sensitivity, resolution and specificity of detection drawbacks. In cancer therapy, the exact distinction between tissues that are cancerous from tissues that are healthy should be carried out during diagnosis to sidestep serious harm to regular/nearby tissues and have efficient therapy. This is achievable by employing multi-modal diagnostic methods like MRI as an accessory to fluorescence imaging, to improve the spatial resolution and detection sensitivity in the imaging of cells. This is achieved by creating a multi-functional NPs system through the coupling SPIONs (MRI) along with other fluorescence agents such as quantum dots (QDs) and fluorescence dyes such as carbon QDs, and fluorophores [15].

The generally utilized MRI CAs in medical treatments are centred on Gd complexes (Gd(III)) including OptiMARK (Gadoversetamide, Gd-DTPA-BMEA), Omniscan (Gadodiamide, Gd-DTPA-BMA), Magnevist (Gadopentetic acid, Gd-DTPA), and Multihance (Gadobenate disodium, Gd-BOPTA) are employed as constructive CAs. However, great fears about Gd-based complexes and nephrotoxicity possible well-being threats have been raised by different research studies. Hence, getting a substitute for Gd-based CAs for MRI imaging is critical. Lately, SPIONs were introduced as a negative MRI CA (FDA approved) owing to these NPs inclining to unwind in a crosswise direction and being green/biocompatible and dependable in comparison to the complexes of Gd [15].

Typical imaging employing MRI is founded on proton density (PD), longitudinal (T_1) and transverse relaxation (T_2) classifications [53]. T_1 is known as the rotation lattice relaxation time, which correlates to exactly how swiftly the magnetization that is corresponding to the fixed MF improves after a perturbation is used on the system. While T_2 correlates to how swift the magnetization in the plane at right angles to the unchanging MF loses coherence. The processes of transverse and longitudinal relaxation are separately and concurrently executed. Though T_2 is generally far from the point (shorter) of T_1, this variation allows for the distinguishing of tissues [54].

The magnetization mapping gives an organ image, with protons in various tissues with variable water concentrations reacting inversely. To improve the images, CAs are utilized, and they impact the proton's performance in their locality leading to clearer images. In MRI, CAs employed are T_1 and T_2 CAs which are based on their impact on the proton MX activities. The most popular T_1 CAs utilized are paramagnetic compounds consisting of metal ions (MI) Gd^{3+} or Mn^{2+} and chelating ligands like diethylene triamine penta-acetic acid (DTPA). The chelate stops MI from binding to chelates in the body making the paramagnetic ion less noxious. T_1 CAs largely decrease the longitudinal relaxation time, which is because of the exchange of energy between the spin and surrounding lattice (spin–lattice relaxation) and will cause a sharper indication. While T_2 CAs, comprising of SPIONs like Fe_3O_4 have a sturdy impact on the transverse relaxation time. In EMF, NPs are magnetized, and induced MF locally is created. These induced fields agitate the MX processes of protons in water molecules reducing the T_2 relaxation time, resulting in MR images blackening [17].

The application of MNPs in diagnostic is achieved in MRI and this method is based on the variation in the nuclear MXs of the protons of water in biological media and around sturdy tissues. The nuclear MX rate of its surrounding protons is changed by the CA and the signal contrast is modified. Its contrast improvement effect is determined by the relaxation rate ($R = \frac{1}{T}(s^{-1})$) and the relaxivity ($\mathrm{r} = \mathrm{R/concentration}\ (\mathrm{mM}^{-1} * \mathrm{s}^{-1})$). A better contrast impact is associated with a higher relaxivity [16]. Also, MRI through SPIONs in a real-time setting can be accomplished for instantaneous routing, localization, and drugs are released at the sites of a tumour to track their bioavailability. While combined targeting consists of magnetic and active targeting methods and a conventional combined drug delivery method may comprise of SPIONs, chemotherapeutic/anticancer drugs, moieties targeting and/or carrier [15]. With regards to MRI, the key focus in recent studies has been the creation of MNPs specifically SPIONs for the improvement of contrast in unhealthy tissue [55].

Biocompatible IONPs payloads coupled with a prostate-specific membrane antigen (PSMA)-aiming antibody, J591, through 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[amino(polyethylene glycol) (PEG-DSPE) linkage to improve MRI in orthotopic prostate tumour (PT) bearing NOD/SCID mice for 2 and 24 h after intravenous inoculation of J591-MNPs was explored in this study. The tumour cell viability was not impacted by the MNPs in vitro and antibody specificity and improved cellular Fe uptake were not compromised by their coupling to J951. The contrast of the cancer cells was amplified in vivo by employing PSMA-targeting

MNPs, hence having the potential to improve MR recognition and localization of PTs [56]. Ferrimagnetic H-ferritin (M-HFn) NPs created were employed for in vitro MRI and immunohistochemical staining of MDA-MB-231 breast tumour cell application, performed at 7 T and gestated for 24 h. It was noted that the relaxivity, magnetic properties and peroxidase-like activity of the created NPs were size reliant and substantially improved the MRI and cancer cell staining implementation owing to the huge core magnetite core in the NPs as depicted in Fig. 9 [57].

MNPs synthesized via the precipitation method and coated with poly-L-lysine (PLLMNPs) to enhance their biocompatibility and stability were utilized for the joint MHT and MRI appropriateness by calorimetric and parametric mapping extent for cancer cells. It was reported based on the approximate heating rates, that the SAR values of the PLLMNPs were approximately 14–15 W/g at 190 kHz frequency and AMF of 8kA/m. While the significant impact of the PLLMNPs on the transversal relaxation time (T_2) with the relaxivity (r_2) which was approximately 487.94 m/Ms was reported for the MRI parametric mapping measurements. These results showed the prospective efficiency of the NPs as a negative CA for MRI use in BMD [58]. In the study by Wu et al. [59], Fe_3O_4 was prepared and activated with carbodiimide and cross-connected with α-ketoglutarate chitosan (KCTS). The surface of the prepared MNPs was combined with antibodies of lymphatic vessel endothelial hyaluronan

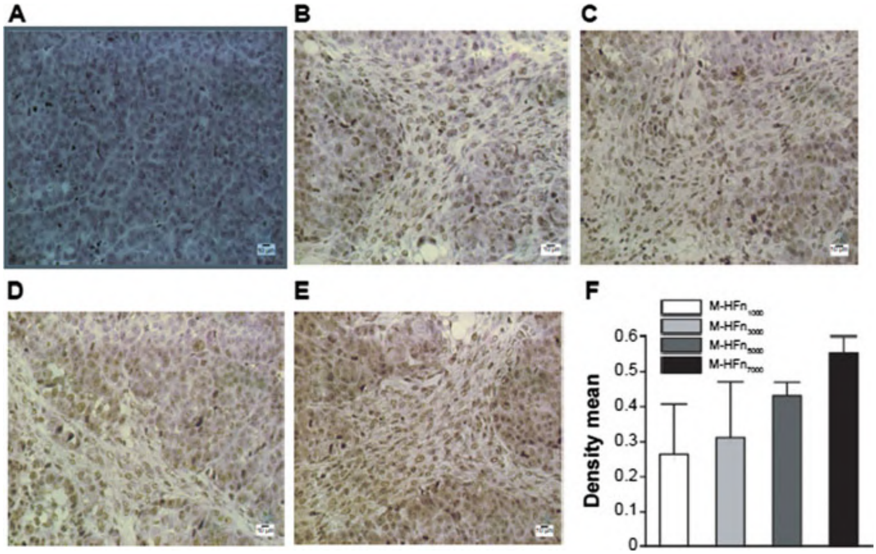

Fig. 9 Schematics of immunohistochemical staining breast tumour cells by the gestation with NPs **a** without the gestation of the NPs, gestation **b** with M-HFn1000, **c** M-HFn$_{3000}$, **d** M-HFn$_{5000}$, and **e** M-HFn$_{7000}$ Fe atoms loading and **f** various density mean showing the section of tissue therapy using the NPs of huge core sizes which improved immunohistochemical staining efficiency. [57] Adapted from Cai et al.; Copyright, Dovepress, 2015. Reprinted with permission from Dovepress from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

receptor 1 (LYVE-1) and Podoplanin and employed as a dual targeting magnetic nanoprobes to determine the lymphatic endothelial cells (LECs) in cancer metastasis. As observed in Fig. 10a, the in vivo image of the cancer cells showed no fluorescence before the synthesized KCTS-LECs@Fe_3O_4 dual antibody was injected into NOD/SCID mice and while there was improved fluorescence reaching the peak of 12 h from the cancer cells with the inoculation of the KCTS-LECs@Fe_3O_4 dual antibody. Also, there was a steady decline in cancer cell imaging, reaching its lowest phase after 12 h and resulting in continuous improvement with time (Fig. 10b).

While in the study by Zhu et al. [60], SPIONs coupled with PSMA targeting polypeptide were created as a CA, employed in vivo and assessed in LnCaP PT-bearing mice using the MRI method. Precise uptake of the created polypeptide-SPIONs (PPE@SPIONs) by PSMA-expressing cells was reported in vitro. The signal of MRI imaging was reported to be exclusively improved in PSMA-expressing cancer cells with the established PPE@SPIONs and additionally, diverse accretion of SPIONs in the cancer tissues was also noticed from the Prussian blue staining.

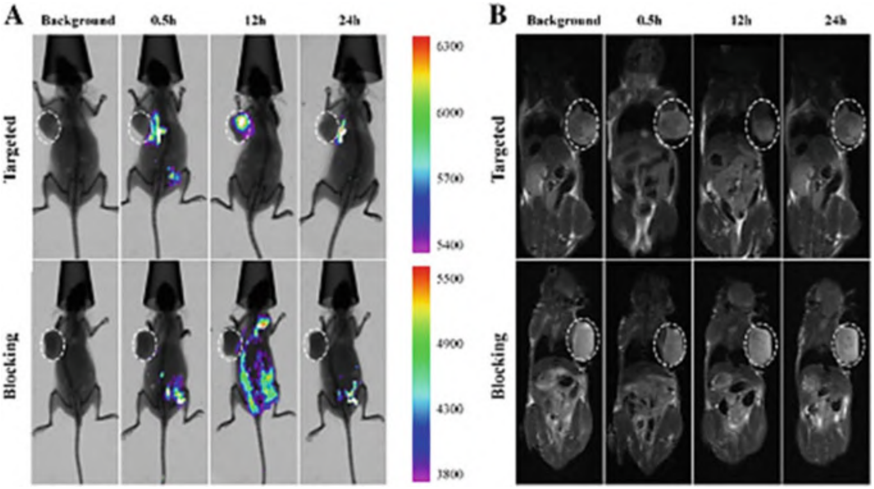

Fig. 10 Representations of the imaging through fluorescence and MRI colorectal tumour intravenous xenografting cancer models of NOD/SCID mice **a** no intravenous injection of the KCTS-LECs@Fe_3O_4 to the cancer cells in sedated NOD/SCID mice and fluorescence imaging at pre-injection and post-injection at 0.5–24 h and intravenous injection of the KCTS-LECs@Fe_3O_4 to the cancer cells sedated NOD/SCID mice and imaged using 3 T MRI image scanner at pre-injection and post-injection at 0.5–24 h. [59] Adapted from Wu et al.; Copyright, Springer Nature, 2015. Reprinted with permission from Springer Nature from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

4 Optical Intrusion Techniques Employing MNPs for Cancer Treatment

The two therapy techniques associated with optical intrusion are PDT and PTT The two emerging tumour therapy techniques with huge potential are PTT and PDT, with resources being utilized in these methods under rigorous study. Almost all NMs employed in these techniques are due to their distinctive fluorescence properties [61]. These emerging techniques in cancer treatment using MNPs are further discussed in the following sections.

4.1 PTT

Thermal treatment (HT) has progressively advanced in the treatment of tumours owing to the leading impact of tissue extirpation for a prolonged period. Bear in mind that aiming HT at certain cancer sites can efficiently impede unwarranted harm to regular tissues, hence PTT has become an exceptional therapy preference. In this technique, vibrational energy via PT properties of MNPs is released and converted into TE, thereby leading to the killing of cancerous cells [62]. In cancer treatment, a decent substitute to utilize as photothermal (PTT) agents is MNPs. Such NPs are employed in a mixture with other materials or employed as PTT agents and the mixture of MNPs with other photothermal agents inserts extra capacities into the TRC system. Along with the MNPs with two-fold magnetism and near-infrared (NIR) absorption functions, IONPs stand out as appropriate NPs for PTT. PTT have an excellent prospective for biomedical usage as it can be guided magnetically to the location of concern and their dissemination in cancer cells and other organs imaged. AMF blending with IR absorption into a specific composite makes it feasible for NPs to be steered to the cancer cells. They also can be employed to visualize cancer location via MRI or thermal imaging for true-time therapy monitoring thereby increasing the effectiveness of the heating [13].

PTT denotes the utilization of desirable agents such as infrared wavelength and materials. Direct local and systemic delivery are the conventional techniques for distributing MNPs to tumour tissues. In MNPs, direct local delivery is probable when the tumour position and degree are recognized and effortlessly available for delivery, which is generally via an injection. While in systemic MNPs delivery, designed MNPs are injected into the blood flow and extensive circulation leads to the accumulation of extremely vascularized tumour tissues [39]. In this technique, materials having outstanding PT conversion effectiveness are utilized to enhance the targeted tumourous region temperature, thereby leading to the death of the tumour cells [61].

Employing this technique involves unhealthy tissue irradiation with electromagnetic radiation using the VIS–NIR light to cause thermal impairment to tumour tissues [1, 63]. In this technique, laser energy is sorbed by the photo-absorbers and transformed into heat. They can cause genetic alterations extending from the structural changes in protein to tissue carbonization. The increase in temperature using this method ranges between 45–300 °C and the medicinal impacts can be gotten at sufficient depths by employing the NIR irradiation. Their three-dimensional specificity and negligible intrusiveness make this technique an attractive medicinal sensory system in comparison to other intrusive medical techniques. To treat tissues, continuous wave or pulsed lasers are used in PTT. In the pulse laser utilization in PTT, extreme heat is made as the width of the pulse laser employed is briefer than the tissue thermal relaxation time (usually > 100 W). While in the continuous wave laser utilization in PTT, adequate laser energy is required to be accumulated in the target region prior to loss of heat in the tissue owing to blood perfusion. To get a useful thermal medicinal response, the laser parameters should be selected correctly and the radiance of the laser needs to be selected at a wavelength where the unhealthy tissue has an above-average absorbance than the neighbouring tissues [1].

The effectiveness of PTT in tumour research is generally studied using in vivo, in vitro and in-human medical assessments. In the in vitro PTT, it involves the main stage in NMs assessment as a prospective PT agent in the organic environment, where NPs are transfected to the cancerous cells and simmered at 37 °C for a specific amount of time using laser light to illuminate the NPs coopted by the cell and leading to the death of cells resulting from the heat generated by the NPs. The impact of in vivo PT depends generally on the NPs, concentrations in the cancer cells and the NPs are inoculated into mice via intratumorally or intravenously. Factors that impact the incorporation of NPs into cancerous cells and subsequent treatment using laser light are the inoculation time, their shape, size and surface chemistry [64, 65]. When the power of the laser is minimum, the exposure time of the laser is extended. The other way around is the effect of the power of the laser when it is above average, the time of exposure to tissue is decreased. The various classes of lasers employed for PTT treatment differ from each other by the length of adsorption and wavelength. The near-infrared laser (NIR) is generally employed in PTT owing to its 1000 nm profound penetration impacts and can be employed in the continuous and pulse modes. The death of cells as a function of the laser and temperature exposure time is given by the Arrhenius rate analysis [64]. In this segment, the detailed use of various MNPs for the PTT of cancer cells from prior research will be reviewed.

An in vitro chemo-treatment and PTT of hepatocellular carcinoma (HCC) employing polydopamine (PDA) covered Fe_3O_4 NPs and the functionalization of spheres (sMAG) with a derivative of folic acid (FA). It was reported that NMs bearing the FA targeting moiety were effective in the destruction of the tumour cells (HCC) using the dual techniques, with the magnetic sphere showing more effectiveness in this sensory system and elevated PTT response [66]. Synthesized MNPs coated with carbon (C@MNPs) were employed for PTT through the irradiation of human PC3 cells (human fibroblast sarcoma (HT1080) cells with a NIR laser beam. Death of cells in C@MNPs and laser beam presence was confirmed by the changes in the morphology and the propidium iodide fluorescence enclosure analyse [67]. While fabricated $C@Fe_30_4$ NPs were assessed for PTT to destroy human lung adenocarcinoma A549 cells employing in vivo NIR treatment. It was reported that 98% of cells were eradicated in 10 min of using 808 nm NIR laser treatment (2.3 W/cm^2) on the NPs to generate rapid heat. The NPs provided a superior PTT impact through intratumoral delivery and NIR radiation of the cancer xenografts. Figure 11a depicts mice images after the administration of the fabricated NPs, which were illuminated with NIR laser light. It was reported that the size of the cancer was significantly decreased and the temperature out of the cancer tissue xenograft increased to 49.4 ± 3.9 °C within 10 min with the application of NIR laser light (Fig. 11b). While in Fig. 12c, the size of cancer cells removed from the mice was reduced significantly when compared to before the treatment using NIR [68].

The coprecipitation technique was employed in this study to fabricate MNPs, which were subsequently employed in vitro and in vivo PTT of A549 cancer cells by the application of NIR treatment at 808 nm. With the irradiation of the cells using NIR, clusters of the NPs were noticed to induce elevated heat on the cells, which showed more cytotoxic against the cancer cells than the specific NPs. A statistically substantial reduction in the growth of the tumour in mice which was treated with the NPs and irradiated with NIR laser light was noticed, with cancer size decreasing from 955.3 mm^3 in controls to 222.8 mm^3 at 19 days [69].

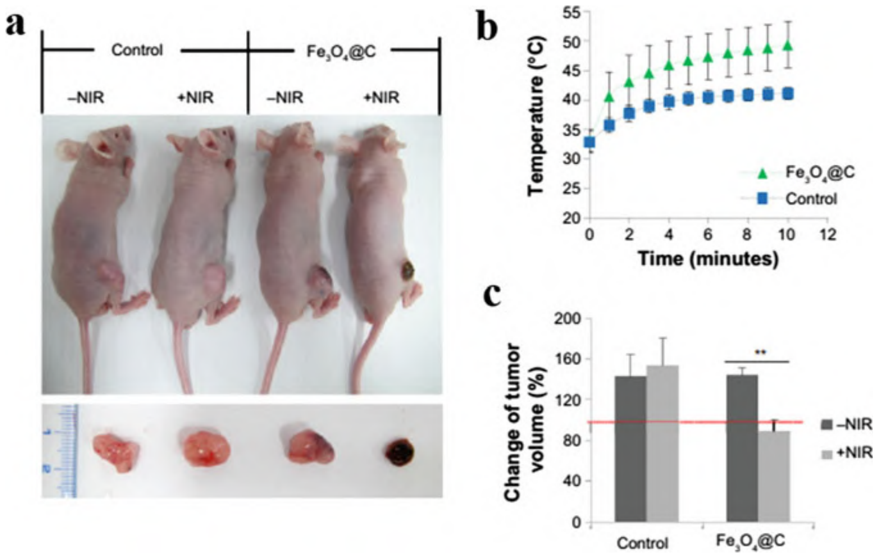

Fig. 11 Intratumoral administration of the NPs using the in vivo NIR treatment **a** cancer size variations of the mice's entire body (upper images) and removed cancer mass, **b** change in temperature on the cancer xenograft after NIR treatment and **c** cancer size variations. [68] Adapted from Lee et al.; Copyright, Dovepress, 2015. Reprinted with permission from Dovepress publishers from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

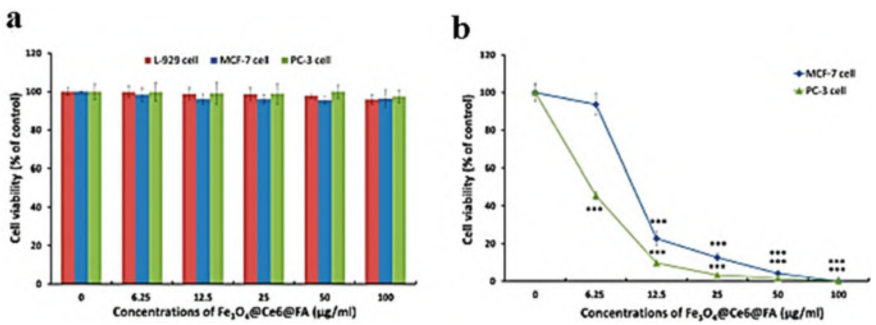

Fig. 12 **a** Cytotoxic and **b** photo-toxicity of Fe_3O_4-Ce6-FA NPs in MCF-7 and PC-3 cell lines. [74] Adapted from Choi et al.; Copyright, MDPI publishers, 2018. Reprinted with permission from MDPI publishers from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

4.2 PDT

PDT is an emerging, superficially activatable therapy sense modality for different disorders. PDT is a clinically authorized therapy for various ailments including tumours and presents various benefits over traditional chemo-treatment by offering extra selectivity via the three-dimensional light confinement utilized for the stimulation of the photo-sensitizer (PS). It involves the non-noxious drug or dye known as PS administration to a patient bearing a lesion which is frequent but not always a tumour through a general, local or contemporary process. After the appropriate maturation period with the PS, there is selective illumination of the lesion with the light of proper wavelength and the oxygen presence leads to cytotoxic species creation and subsequent destruction of tissue and death of cells [1].

PDT is a superficially stimulated and marginally intrusive sensory system for the treatment of cancer [70]. It comprises of the general utilization of photo-inducing drugs (photo-inducer), which are photoexcited in the tissue employing suitable light wavelength and power. The excitation of these photo-sensitizers (PCs) is the presence of oxygen, hence the delocalization of electrons from the ground to the excited states. This phase is trailed by light activation of a suitable wavelength, with the transport of an electron to the neighbouring tissue and thereby leading to the production of oxygen free radicals (reactive oxygen species-ROS) which triggers tumour or cancer cell destruction. To improve the PCs' impacts, the strategy of MNPs as targeted drug delivery procedures has to turn out to be of attention [36].

In the PDT, a PC is amassed in tumourous locations, and a specific wavelength of light is employed to irradiate the location of the tumour cells leading to the generation of singlet O (O_2) and further cytotoxic reactive O causing necrosis or apoptosis [61]. PDT is generally partitioned into anti-microbial PDT (AMPDT), cancer-targeted PDT (CTPDT), and vascular targeted PDT (VTPDT). Most PDT is centred on the cellular-aimed photo-chemo treatment [71].

With a whole array of photo-sensitize assessed so far, just not many have been productively moved from bench to bedside use. In tumour treatment utilization, PDT is most desirable owing to its important selectivity and specificity. This is due to the exclusive concentration of PC within the cancerous tissue, with the direct focus of light on the lesion, causing PDT ROS to be created ensuing in the cellular obliteration of tissues within the area of interest. When compared to the radio treatment, the PDT mode of action comprises of the application of electromagnetic radiation to create radical species in situ. It is a much gentler method for the therapy of cancer and the motive lies in the blend of the action mode of PC used, which are non-noxious in the absence of simulating light and the in situ stimulation by comparatively extended wavelength, visible light [1]. In this section, the detailed application of different MNPs for PDT of tumour cells from preceding studies will be assessed.

Silica layered IONPs, which were entangled in the interior of niosomes (SiO/NiO) or fluorescein (FL) entrapped magnetosomes were employed in vitro for PDT of Panc 1 cells, which were irradiated with blue lights. Upon the FL-magnetosomes photoactivation, elevated O_2 was created and there was increased magnetically cellular uptake from the Panc 1 cells by the magnetosomes. The effectiveness of the PDT in cells treated with the FL-enmeshed magnetosomes and light was improved with magnetic support [72]. To improve the TRC impact of PDT on tumour hypoxia and ROS brief half-life with a small diffusion distance, a multifunctional nano-platform was created to improve the oxygen intensity in the cancer cells and decrease the ROS distance via the Fenton reaction. The NPs (Fe_3O_4@Dex-TPP) were created via the coprecipitation technique and the PCs (protoporphyrin IX (PpIX) and glutathione-responsive mPEG-ss-COOH) were subsequently embedded into the Fe_3O_4@Dex-TPP to form Fe_3O_4@Dex-TPP/PpIX/ss-mPEG NPs. The created NPs were reported to be effective in the Fenton-supported PDT of cancerous cells. Results also show that the cytotoxic assessment of the NPs on normal endothelial cell (EC) and murine breast cancer (4T1) cells with and without laser light of 637 nm, showed that the noxiousness of the NPs treatment without the laser light was negligible, with cell viability of $> 90\%$ for EC, but it was lethal for 4T1 cells as the concentration was increased. While the cell viability for 4T1 was approximately 77% and 50% when the concentration of the NPs was greater than 200 and 25 μg/mL (concentration of PpIX was 20 and 2.5 μg/mL) when treated with laser light of 637 nm. The results showed that the created NPs cyto-compatibility was useful for regular cells but was noxious to cancer cells [73]. Fabricated multi-purposeful NPs (Fe3O4) coupled with a PC (chlorin e6-Ce6) and tumour targeting molecules (FA) were employed for the selective aiming of tumour cells (prostate adenocarcinoma (PC-3) and breast adenocarcinoma (MCF-7)) treated with 600 nm wavelength using PDT. Utilizing Fe_3O_4-Ce6-FA, the viability of the cells surpassed 95%, which was indicative of no cytotoxicity in all cells and with exceptional biocompatibility use (Fig. 12a). With the irradiation of both cancerous cells which were inoculated with different concentrations of Fe_3O_4-Ce6-FA for 2 h, the viabilities of the cell lines were drastically reduced with the increase in the concentration of NPs. This showed that the NPs were effectively viable in the treatment of cancerous cells and which were concentration-reliant (Fig. 12b) [74].

While in the study by Choi et al. [75], FA and hematoporphyrin (HP) were coupled on multi-useful MNPs to create $CoFe_2O_4$-HPs-FAs which was employed as an efficient anti-tumour reagent for PDT in PT cells (PC-3). It was reported that the same fluence at various times of exposure led to the anti-tumour actions on PC-3 cells and the creation of the reactive O. While in the studies by Li et al. [76], Wang et al. [77], Ashkbar et al. [78], and Wu et al. [79], various MNPs coupled with different photo-sensitizer were synthesized and tailored towards various cancerous cells to assess their biocompatibility and cellular uptake using the PDT coupled with other methods exposed to laser light. It was reported in these various studies that the MNPs coupled with various PCs showed a significant effect on cell reduction and were effective for their tumour cell treatment. Hence they are an exceptional device for greatly preventing cancer development using the PDT coupled with other techniques. Table 1 gives a summary of other studies carried out using the MHT, MRI, PTT and PDT techniques for effective cancer cell eradication employing MNPs.

Table 1 Summary of various studies employing TRC techniques for effective cancer diagnosis and treatment using MNPs

MNPs	Cancer cells type	TRC technique employed for cancerous cells	References
Poly(maleic anhydride-alt-1-octadecene) (PMAO) functionalized with glucose	Murine model of pancreatic cancer	MHT	[80]
MNP-based miRNA	GBM cells (U87-EGFRvIII)	MHT	[81]
MNPs	brain and prostate tumours	MHT	[82]
Iron oxide nanoflowers	Lung cancer cell lines	MHT	[83]
MNPs	Tumour necrosis	MHT	[84]
Bimagnetic Fe/Fe3O4 core/shell nanoparticles	Subcutaneous mouse melanomas (B16-F10)	MHT	[85]
SP polystyrene-sulfonic-acid-coated magnetic nanoparticles (PSS-MNPs)	SK-Hep1 hepatocellular carcinoma (HCC) cells	MHT	[86]
SPIONs	Prostate and recurrent brain tumours	MHT	[87]
Multi-layer β-cyclodextrin and F127 polymer-coated MNPs	A2780CP ovarian cancer cells, MDA-MB-231 (breast), and PC-3 (prostate) cancer cells	MRI	[88]
Magnetic glyco-NPs (MGNPs)	Cancerous cells	MRI	[89]

(continued)

Table 1 (continued)

MNPs	Cancer cells type	TRC technique employed for cancerous cells	References
PEGylated L-arginine modified IONPs (PEG-Arg@IONPs)	The human foreskin fibroblast (HFF2) cell line and Human embryonic kidney (HEK293) cell	MRI	[90]
Magnetically targeted NPs (IRFes)	Breast cancer 4T1 cells	PTT	[91]
Pc 4 encapsulated into the ligand-coupled IONPs (Fmp-IO-Pc 4)	M4E control cells and integrin β1 knock-down M4E derivatives (M4E-15)	PDT	[92]

5 Conclusion

Over the years, the study of magnetic particle applications in tumour identification and therapy has progressed, but there has only been recent momentous advancement in this research area employing NT. With biomedical applications in the TC of different diseases like cancer, MNPs have proven to be an outstanding contender in meeting the increased global TC needs for improved human healthcare. The improved ratio of the surface area to volume of most NMs built with biomolecules improved the specificity of the chemical drug complex utilized in target treatment and hence improving the efficiency of NMs-based therapy for cancer cells treatment while decreasing their noxiousness to regular cells. With payload capacity improvement, and enhancing their specificity and affinity to aim for tumour cells, MNPs could become appropriate for their utilization clinically with combined tomography and treatment with a great effect and effective result in cancer therapy. Though significant works have been made with the use of MNPs for contemporary and effective tumour treatments, there is still far more to be learned about the safety of NMs applications in TCR to improve life-expectation and prodding tumour patient existence.

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Magnetic Nanomaterials for Heavy Metals Detection

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Abstract Although heavy metals (HMs) are naturally present in the environment, human activity has allowed them to enter water, air, and soil, making them a huge global problem. In high quantities, these HMs are equally hazardous to plants and animals. After entering the body, the majority of them bioaccumulate for a longer time, causing various issues. For example, in plants, they can harm water-absorbing roots, leaves, and cell components, or even obstruct photosynthesis and mineral uptake due to drought-induced inhibition. In addition, they can harm the livers, kidneys, and lungs in animals, where they can also cause cancer. The amount, duration, and level of concentration of these HMs all play a significant role in the anomalies they cause. Because of the toxicity, persistence, and non-biodegradability of certain HMs, they are now a global issue. There are several ways that living creatures have been exposed to these HMs, but drinking water is a common source. It is crucial to find and remove these dangerous HMs. Traditional methods have a number of limitations, such as the need for specialized staff and lengthy sample preparation; as a result, magnetic nanoparticles (MNPs) are used because of their extraordinary magnetic capabilities, which showed considerable potential in the sensing of HMs.

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1 Introduction

Magnetism in materials originates from the spin and orbital movement of electrons. Every substance is composed of tiny building blocks of matter called atoms. Each atom is made up of electrons, which are charged particles and carry electric charges. These electron orbits the nucleus or centre of an atom. Their movement produces electric current and magnetic effect of each electron. The orbital motion of an electron around the nucleus of an atom is analogous to the current in a loop of wire. Hence, the magnetism of the majority of substances cancels out because of the equal amount of electrons that spin continuously in opposite directions. This is why substances like clothing materials and paper are referred to as weakly magnetic. Most of the charged ions in other materials, like iron, cobalt, and nickel, revolve in the same direction. The building block of matter in these materials becomes extraordinarily magnetic as a result, yet they are not magnets.

Nanomaterials (NM) were first defined as substances with at least one constituent particle having an exterior dimension of 100 nm (nm) or less. A nanometer equals one billionth of a meter. Nanoscale, scales nanometers or microns as its units of measurement. The number of dimensions that are larger than 100 nm (nanoscale) can be used to classify NM. As a result, all dimensions within the nanoscale range are classified as zero dimensions (0D). In zero-dimensional NM, none of the dimensions is larger than 100 nm. 0D NM are typically nanoparticles (NPs). Another type is one dimension NM, which is outside the nanoscale. One-dimensional NM (1D), include nanowires, nanorods, and nanotubes. Non-confinement of two dimensions to the nanoscale is the major characteristic of two-dimensional (2D) NM. Structurally, 2D- NM has plate-like forms and they include graphene, nanofilms, nanolayers, and nanocoatings. Outside of the nanoscale is the three-dimensional NM (3D). In 3D all materials are not confined to the nanoscale in any dimension. Large-proportion powders, nanoparticle dispersions, and a bunch of nanowires and nanotubes, including multi-nanolayers, can all be found in this class. NM can further be divided into subcategories like organic-based, inorganic-based, carbon-based, and composite-based. As demonstrated in Fig. 1 as adapted from [1], organic materials such as dendrimers, cyclodextrin, polymers, liposomes, and micelles, are used to create organic-based NM [1]. Dendrimers, on the other hand, are branched unit-based nanosized polymers.

Meanwhile, metal-based NMs and metal oxide-based NMs are included in inorganic-based NMs (Fig. 2). Silver, gold, aluminium, cadmium, copper, iron, zinc, and lead are all examples of metal-based inorganic NM [2], whereas metal oxide-based inorganic NM [3] are zinc oxide (ZnO), Quantum dots, copper oxide (CuO), nanogold, magnesium aluminium oxide ($MgAl_2O_4$), nanosilver, and titanium dioxide (TiO_2), iron oxide (Fe_2O_3), cerium oxide (CeO_2), and silica (SiO_2).

Additionally, carbon-based NMs [4] are a special category of NM consisting of carbon atoms and they include, carbon nanotubes, graphene, multiwalled carbon nanotubes, nanodiamond, carbon nanotubes (CNTs), single-walled carbon fiber, activated carbon, and carbon black (see Fig. 3 as adapted from [4]). The mixture of metal,

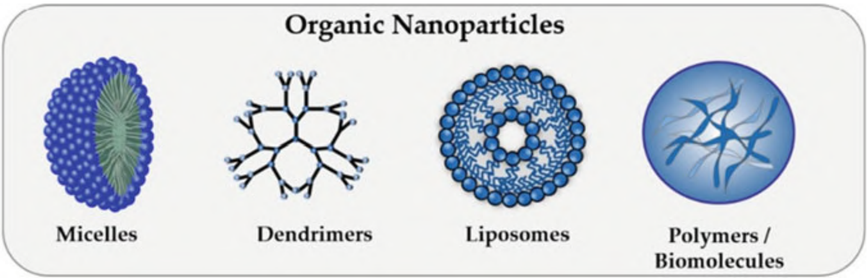

Fig. 1 Organic-based NM

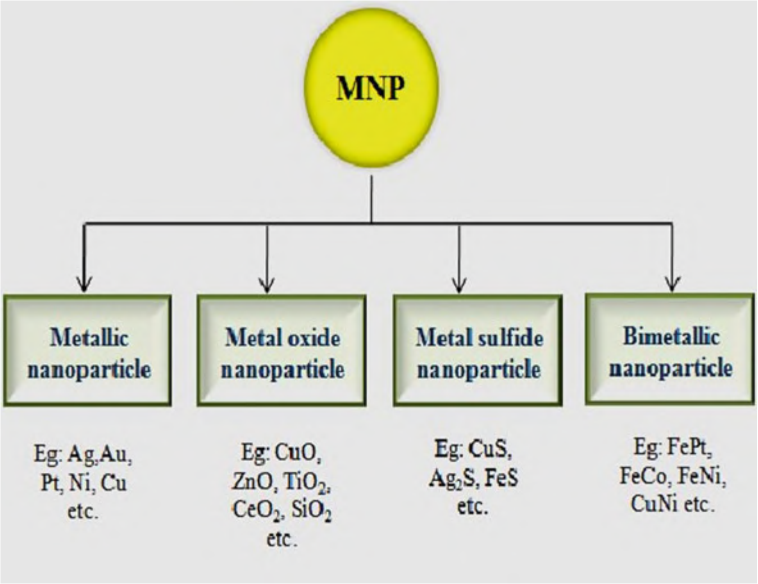

Fig. 2 Types of inorganic metal nanoparticles (MNP)

metal oxide, carbon, or organic NM is referred to as a composite nanomaterial, and these NM feature intricate structures, such as a metal–organic framework. In applications across numerous industrial sectors, purposefully synthesized MNPs with distinctive thermal, mechanical, medicinal, and commercial attributes are greatly sought after. In this chapter, we will discuss how these MNPs are utilized to detect and eliminate HMs from the environment. Their advantages over conventional heavy metal detection will also be emphasized.

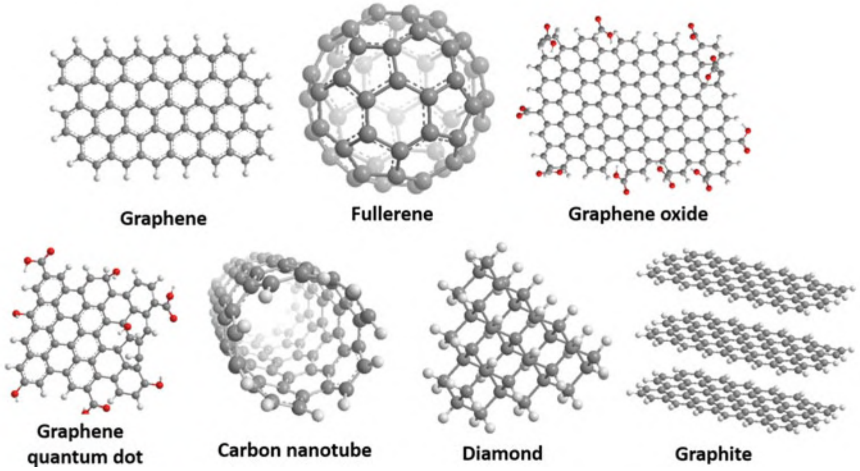

Fig. 3 Various forms of carbon NM

2 HMs

The term "HMs" has been defined differently by several writers. Their meanings vary depending on the specific weight, atomic weight, atomic number, metal density, particular chemical properties, and toxicity [5]. Very recently, *Ali and Khan,* [6] defined "heavy metal" in a more acceptable scientific way, as metals in nature, having an atomic number (Z) greater than 20 and a density which is primarily higher than 5 g cm^{-3}. Due to their functions in biological systems, HMs can be roughly divided into two major groups: essential and nonessential HMs. While nonessential HMs are not required by living things, not even at trace levels, essential HMs are very necessary for organism functionality and may even be needed for body chemistry at low concentrations [7]. However, the earth's crust naturally contains HMs. Actinides, lanthanides, transition metals, and a number of metalloids are among the more than 50 elements that fall under the category of HMs. Of those elements, 17 are considered to be extremely hazardous and easily accessible. The toxicity of several non-essential HMs, like Pb, Hg, As, Cr, Tl, and Cd, is quite high even at low concentrations [8, 9]. Other HMs that are necessary for human nutrition include Cu, Zn, Ni, Co, Se, and Bi, but they can also be hazardous in higher concentrations. HMs toxicity varies with concentration, exposure time, and method of exposure. Biological, geological, and human activities are all potential sources of HMs pollution of the environment (Fig. 4).

The wearing action on metal-bearing rocks, soil erosion of metal ions, volcanic eruptions, and forest fires are some of the geological processes that cause HMs to enter the environment [10]. HMs in the environment are a result of growing industrialisation and urbanization, which are anthropogenic sources. These metals are discharged as a result of human activities such as mining and extracting various

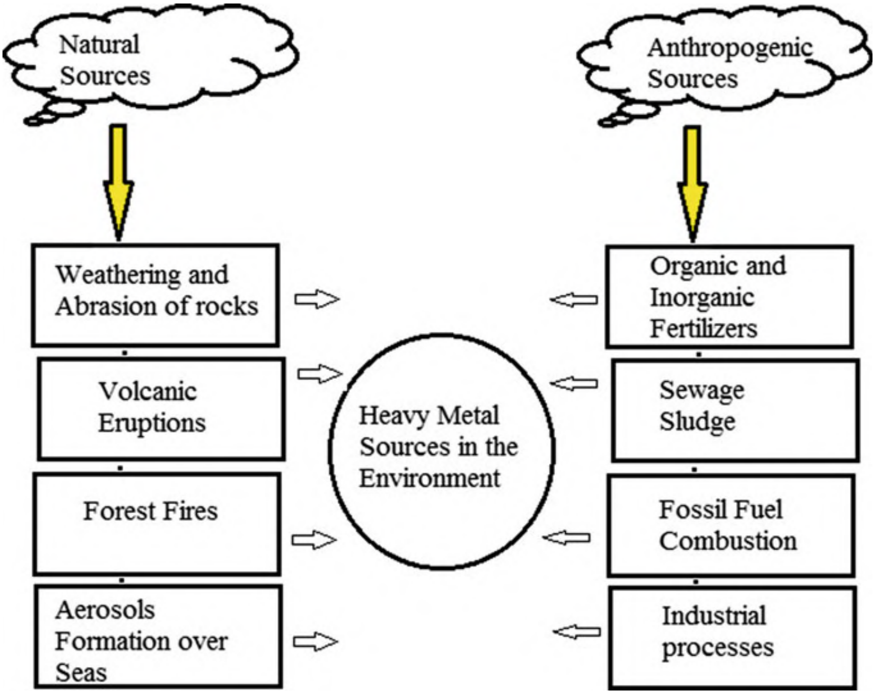

Fig. 4 Sources of HMs within the environment

elements from their respective ores, releasing domestic and industrial sewage into the environment, applying organic and inorganic fertilizers, allowing urban runoff, and burning fossil fuels [11]. Non-essential, poisonous HMs have the potential to cause cancer, are they are not biodegradable and have a propensity to build up in living things. All of these metals are mostly acquired by the general public through the air, drinking water, and food, with fish serving as the most important source of origin for mercury exposure. Additionally, smokers are not protected from cadmium at significant levels [12].

3 HMs Detection

At high concentrations, all metals or elements are poisonous [5]. Their non-biodegradability and bioaccumulation amplify risks and concerns, thus appropriate procedures must be developed for their prompt identification to prevent issues with the environment and human health. High-performance liquid chromatography (HPLC) combined with electrochemical or UV–Vis detectors, UV/Vis spectroscopy, atomic absorption spectroscopy (AAS) [13, 14], inductively coupled plasma mass spectrometry (ICP-MS) [15], flame atomic absorption spectrometry, microprobes (MP), anodic stripping voltammetry (ASV), and wet chemical methods like colorimetry and electrochemical techniques [16] are comprehensively the most used methods for the sensing of HM ions. However, there are a number of disadvantages to these analytical techniques such as sample development, cleanup, preconcentration steps, high-cost equipment, and a specialized workforce. Due to their great adsorption capacity, high surface-to-volume ratio, strong surface reactivity, size-controlling features, high catalytic effectiveness, and high level of functionalization, MNPs have recently shown tremendous potential in the sensing of HMs. MNPs utilization as nanosensors has enhanced sensitivity and selectivity [17]. The most common varieties of MNPs are often a class of NM that is made up of metals like cobalt, nickel, and iron with unique features such as paramagnetic, ferromagnetic, superparamagnetic, and high surface-to-volume ratios. These characteristics make it possible to use them in the creation and manufacturing of sensors for various purposes. In order to create specific nano sensors for the wholesome sensing of harmful metal ions, a variety of magnetic NM should be involved and employed.

3.1 Sensors for Sensing HMs

It is crucial to remember that the primary function of MNPs in the identification and removal of HMs is to achieve magnetic separation where a magnetic field is present. Due to their superior magnetic properties, iron oxide, which is found in the forms of hematite (α-Fe_2O_3) and magnetite (Fe_3O_4), is the most often utilized MNPs for the detection of HMs. Because iron oxide NPs tend to cluster readily and become nonconductive, very few researchers have employed iron oxide alone to sense HMs. Therefore, to decrease the likelihood of aggregation, the majority of research either uses surface modification paired with additional materials or functionalization. As described in Table 1, different kinds of biosensors shown were synthesized for the identification and removal of HMs from the environment. For the detection, adsorption, and separation of cadmium (Cd^{2+}) metal ions in a water sample, Zhang et al. [18] produced MNPs Fe_3O_4@$FePO_4$ with core–shell structure by coating Fe_3O_4 NPs with iron phosphate by liquid phase deposition method. A sensor constructed of Fe_3O_4/TiO_2/NG/Au/ETBD was also created by Liu and colleagues [19] precisely to detect Pb^{2+} in a highly hazardous aquatic environment. A greater linear range of sensitivity from 40×10^{-14} mol/L to 20×10^{-9} mol/L was possible with the sensor as-designed. Pb^{2+} had lower limits of detection that were 75×10^{-14}. Additionally, Fe_3O_4 NPs are simple to coat with polydopamine to create stable core–shell bifunctional polydopamine@Fe_3O_4 NPs, which are then used to conveniently modify the surface of magnetic glassy carbon (mGC) electrodes in order to sense Pb^{2+} and Cd^{2+} with high responsiveness using square wave anodic stripping voltammetry (SWASV) [20]. By covering the simple screen-printed electrode (SPE) with a solution of Fe_3O_4 and Chitosan (CHT) on an ionic liquid (IL), Wang et al. [21] effectively created a sensor. This is accompanied by the in-situ deposition of a bismuth film (Bi). The authors claim that the as-created bismuth film/Fe_3O_4/IL composite functionalised screen-printed electrode has the lowest Cd^{2+} detection limit of 0.5×10^{-1} g/L.

In addition to magnetic iron oxide NPs, nickel oxide and cobalt oxide NPs can be used to create several types of sensors whose application in the environment is the identification of HMs. Owing to the characterization of high activity and exceptional stability, cobalt oxide has garnered interest. Salimi and co-workers [22] doped cobalt oxide NPs on a modified glassy carbon electrode to create a sensor, which they utilized to detect a very small amount of the arsenic (As^{3+}) ion in an aqueous solution. With a progressive range of 10–50 μM, a modified electrode dramatically displayed a detection limit of 6×10^{-1} μM with no intrusion but other NM ions are present. Additionally, Hosseini and associates [23] created a sensitive colorimetric sensor for the detection of dopamine based on the cobalt-doped magnetite/graphene nanocomposites (Co-MGNCs) peroxidase mimetic. The created sensor exhibits excellent linear correlations for dopamine concentrations between 0.5 and 50 mM. The relative standard deviation (RSD) was below 4.0%, and the limit of detection was calculated to be 0.08 mM. Kumar and coworkers [24] developed graphene oxide and nickel tungstate (RGO@$NiWO_4$) NCs, for selective and continuous identification of HM ions in drinking water and also in complex aqueous media such as milk, fruit juices, and carbonated beverages. They obtained a lower limit of detection for Cd^{2+}, Cu^{2+} and Hg^{2+} ions to be 47×10^{-11} M, 38×10^{-11} M, 44×10^{-11} M and 28×10^{-11} M for individual detection and 10×10^{-11}, 18×10^{-11}, 23×10^{-11} and 28×10^{-11} M respectively. In 2017, Dong and Zhang [25] developed a magnetic composite sensor

Table 1 HMs from the environment resourced by nanosensors

Nanosensors	HMs selectivity	Limit of detection	References
Fe_3O_4/TiO_2/NG/Au/ETBD	Pb^{2+}	75×10^{-14} mol/L	[19]
Fe_3O_4-NPs/TA/GCE	Cd^{2+}, Pb^{2+} and Hg^{2+}	2.25×10^{1}, 8.30 and 6.02×10^{1} μg L^{-1}	[27]
Fe_3O_4@$FePO_4$	Cd^{2+}	10 μg L^{-1}	[18]
Co_3O_4 nanosheets/ITO	Pb^{2+}	5.20×10^{-1}	[28]
rGO-Fe_3O_4/SPE	As^{3+}	1.0×10^{-1}	[29]
Bi/Fe_2O_3/G/GCE	Cd^{2+}, Zn^{2+} and Pb^{2+}	8.0×10^{1}; 10×10^{1} and 7.0×10^{-2}	[30]
Balls NiO-GCE	Cd^{2+}, Pb^{2+}	16.6 and 7.90 μg L^{-1}	[31]
BF/NiO/Ag@GCE	Pb^{2+}	12.4×10^{-3} μg L^{-1}	[32]
Bi/Fe_3O_4/ILSPE	Cd^{2+}	0.05 μg/L	[21]
ILs/$NiCo_2O_4$-P	Tl^{+}, Pb^{2+} and Cu^{2+}	0.046, 0.034 and 0.029 μg/L	[25]
EG@ CoOxNPs	Cu^{2+}	94 μg L^{-1}	[26]
RGO@$NiWO_4$	Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}	47×10^{-11} M, 38×10^{-11} M, 44×10^{-11} M and 28×10^{-11} M	[24]

(ILs/$NiCo_2O_4$-P) for the continuous measurement of the metals thallium (Tl^+) lead (Pb^{2+}), and copper (Cu^{2+}) ions by coupling the porous magnetic nickel cobaltate ($NiCo_2O_4$) with ionic liquids (ILs) as modified materials. The censoring limit of the created electrode were 0.046, 0.034, and 0.029 g/L for the given metals of Tl^+, Pb^{2+}, and Cu^{2+} ions, respectively, using differential pulse anodic stripping voltammetry (DPASV). According to Ndlovu et al. [26] exfoliated graphite (EG) electrode, was modified with cobalt oxide NPs (CoOxNPs) to fabricate an electrochemical sensor which was used to sense Cu^{2+} in spiked water samples. A low limit of detection of 94 $\mu g\ L^{-1}$ was recorded.

4 Conclusion

Magnetic NM-based sensors for HMs detection were covered in this chapter. Because of its special characteristics, using nanotechnology to sensor HMs from the ecosystem is gaining a lot of attention. Since NM is incorporated with the sensor architecture, selectivity and sensitivity for detecting HMs within the environment have also improved. The advantages of using nanosensors based on functionalized NPs over traditional methods are more, among which are low cost, low limit of detection, and convenience of usage in the field of applications. Since the development and usage of magnetic nanosensors, on-site identification capability, sensitivity, mobility, and overall achievement have all been enhanced in detecting HMs in the environment. Although unimaginable revolutions and advances have been made, the detection of these HM ions using nanosensors still faces significant technological obstacles when applied to real-world samples like biological and raw water samples. To fully utilize the developing potential of nanosensors to detect HMs in the environment, cooperation between research societies, governments, and enterprises is required.

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Magnetic Nanomaterials for Dye Sensing and Removal

Joan Nyika and Megersa Olumana Dinka

Abstract Varied applications of nanomaterials have transformed various industries in the modern day. In recent years, magnetic nanoparticles (MNPs) have gained research interest from their applications in the environmental, agricultural, catalysis, medical and biosensing fields. This chapter explored the potential of MNPs in dye sensing and removal using pre-existent studies. Findings showed that MNPs are widely used in sensing various ionic and non-ionic dyes such as the azo, acid, cationic, reactive and dispersive dyes. The sensing and removal abilities were associated with the superparamagnetic, high surface area and adsorptive characteristics of MNPs. The characteristics can be improved and customized using controlled surface engineering to produce functionalized nanomaterials with high sensitivity to specific dyes. Optimizing the dye concentration, pH, temperature and adsorbent quantity can further optimize the dye sensing and removal capacities. The chapter aimed at assessing the potential of MNPs in dye sensing and removal for greener remediation of pollutants.

Keywords Biosensing · Dye · Magnetite · Nanomaterials · Superparamagnetism

1 Introduction

The nanotechnology field has had significant advancements in the modern day, which have revolutionized and improved varied fields. The list of applications of the technology is growing exponentially with the use of nanomaterials and nanoparticles

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[1, 2]. Nanomaterials are minute particles whose average sizes are 1–100 nm and making them ideal for a variety of applications. Among the nanoparticles, MNPs have recorded growing environmental, engineering, energy and biomedical applications owing to their nanoscale and exceptional characteristics [3]. Consequently, MNPs have gained the attention of scientific researchers owing to the potential used in agriculture, environment, biomedicine, biosensing and catalysis among other fields [2–6]. Figure 1 shows the applications of various MNPs as adopted from the publications of [1, 3, 5–12]. To advance the agricultural sector, magnetic nanomaterials have been used to manufacture nano-herbicides, nano-pesticides, nano-sensors, nano-additives and nano-fertilizers aimed at improving crop productivity and concurrently, enhancing the resilience of plants to pests and diseases [7].

MNPs have been applied in environmental clean-up to remove organic and inorganic pollutants from wastewater [8]. In biomedicine, MNPs have been used in drug encapsulation and release, gene therapy, radioimmunotherapy, drug delivery and formulation, chemotherapy and in hyperthermia treatment [8]. MNPs are also important components of electrochemical, optical and piezoelectric biosensors whose functioning can incorporate catalytic or non-catalytic reactions [9]. MNPs occur in different types but the superparamagnetic magnetite made of iron oxide (Fe_3O_4) is the commonest in all applications. In the field of biosensing that deals with the discovery of organisms and quantification of their physiological activity, MNPs are growing to be essential replacements for conventional labels owing to their unique aspects not present in many biological systems [1, 9, 13]. As such, there is a need to understand their properties to match them with the particular application of target.

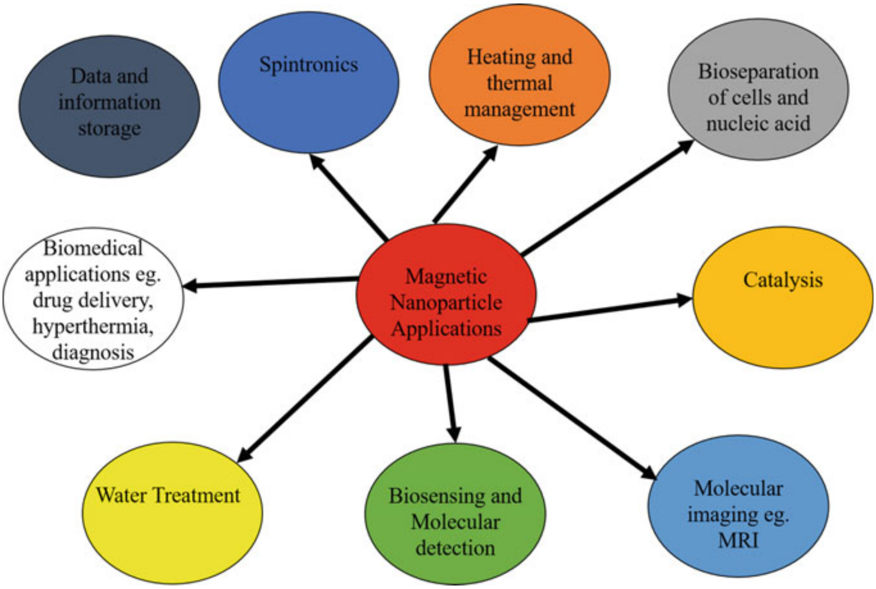

Fig. 1 Varied applications of MNPs

This is the rationale in this chapter where we examine the types and properties of MNPs and matched them with their intended use in sensing and removing dyes from the environment. The significance of such advances is to inform decisions on making shape-controlled, mono- or multi-dispersed nanomaterials whose structural design fits the intended use or is customized for the particular use. Overall, this increases the effectiveness of MNPs for sustainable environmental management. This chapter explored the types of MNPs, their characteristics and their application in biosensing and in particular, dye sensing using Fe_3O_4 nanoparticles based on preexistent literature.

2 Types of MNPs and Their Properties

2.1 Types of MNPs

There are three types of MNPs: oxides, metals and alloys. Oxides have fluctuating magnetic characteristics, which are antiferromagnetic. Oxides of cobalt (CoO, Co_3O_4) and iron (FeO) are the most significant magnetic particles [14]. Cobalt tetroxide (Co_3O_4) has magnetic properties that change under varied conditions. The material shows antiferromagnetic characteristics with bulk magnetic circulation while at 0.02 emu/g to 10kOe magnetic circulation, it has weak ferromagnetic characteristics [15]. Once exposed to magnetic fields, Co_3O_4 acts like a typical magnet but with weak ferromagnetic tendencies. CoO also has variable magnetic characteristics like loop shifts, coercivities and large movements, which are anomalous magnetic features [14].

Nanoparticles from FeO particularly maghemite (γ-Fe_2O_3) and Fe_3O_4 are also widely used due to their superparamagnetic characteristics including their ability to cause energy release, particle movement and image contrasting when an external magnetic field is availed [10].

Metals such as nickel (Ni) have both catalytic and magnetic properties and are suitable for MNPs. Ni-NPs are of great interest in research for use as biosensors, photocatalysts, heat exchangers and electrocatalysts [16]. The nanomaterial is synthesized using photocatalytic reduction, discharge route and chemical reduction techniques. Additionally, some of the synthesis methods applied for all MNPs, in general, include biological processing, sol–gel, gas-phase condensation, microemulsion synthesis, hydrothermal synthesis, thermal decomposition and ball milling [1]. The magnetic properties of Ni-NPs are dependent on their morphology, compounds containing the element and their lattices [17]. The size of the nanomaterial also influences its characteristics. According to He et al., “the Curie temperature, saturation magnetization and remanent magnetization increase whereas the coercivity decreases monotonously with the increase of particle size” for Ni-NPs. Therefore, larger particles of Ni have higher palaeomagnetism and saturation levels compared to smaller ones.

Metallic alloy NPs are a result of combining two or more metals and unlike monometallic NPs, they are more effective due to synergistic properties. They are formed by melting the constituent metals and mixing them in protective conditions such as the presence of argon gas. The approach was used to synthesize the Fe56Co7Ni7B20Nb10 alloy whose properties are diverse and complex due to its heterogeneous and multi-metal nature [18]. In another study, Lutz et al. [19] noted that alloy-based NPs possessed superparamagnetic characteristics from metallic and oxide nanomaterials.

2.2 Properties of Magnetic Nanomaterials

Using instruments such as Mossbauer Spectroscopy (MS), Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FT-IR), Scanning Electron Microscopy (SEM), Energy Dispersive X-RAY Diffraction (EDXD), X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM), various properties of MNPs have been identified [1, 20]. The aim is to determine the variations in nanomaterials as a result of changes in physicochemical aspects and use them for optimization geared to their specific applications. Such variations are in the surface morphology, size, structure, type of bonding and elemental composition of the MNPs.

MNPs have a stable metallic core and they are functionalized by an outer shell addition that has functional groups depending on the targeted use. They have a size < 100 nm and can be synthesized from any material with magnetism ability. Metallic cores of MNPs are made of mainly oxides of iron; γ-Fe_2O_3 and Fe_3O_4. Most MNPs are responsive and stable single-domain structures positioned in settings surpassing Curie temperatures (T_C), which makes them superparamagnetic nanomaterials (SPNs) [11]. Such SPNs have a high magnetic attraction, low agglutination ability at room temperature, low coercivity and low remanence [11].

The magnetism of MNPs is a result of magnetic spin moments by holes, electrons, protons, and positive and negative ions that have electrical resistance and mass. Different nanomaterials show varied categories of magnetism. The categories include ferromagnetism, paramagnetism, superparamagnetism, diamagnetism and/or antiferromagnetism and are distinguishable as shown in Fig. 2 as adapted from [21]. The formation of internal-based magnetic fields that are parallel to the applied magnetic domains for nanomaterials with unpaired electrons is paramagnetism [11]. Ferromagnetism depends on the T_C and the critical value (D_C) and occurs when ferromagnets separate into smaller magnetic domains whose diameter is smaller than the D_C [12]. The D_C of a nanomaterial is dependent on the shape of particles, the energy of a domain-wall or surface, the strength of exchange forces and crystal anisotropy and the magnetic saturation value. Superparamagnetism is a form of ferromagnetism, which occurs when one domain of ferri- and ferro-magnetic materials have a diameter of 3–50 nm, which is smaller than the D_C [4]. Superparamagnetic nanomaterials have strong thermal effects and can demagnetize already saturated assemblies, and have zero hystereses and coercivity [12]. The T_C and D_C of MNPs differ based on the specific nanomaterial as evident in Table 1 [11]. Diamagnetism is a weak repulsion to magnetic domains exhibited by all materials when their electronic subshells are full and magnetic moments cancel each other after pairing [21]. Antiferromagnetic materials have an antiparallel atomic magnetic moment of similar magnitude and hence, a total magnetization of zero [21]. Apart from the magnetic effect of MNPs, such materials exhibit the magnetocaloric effect, which refers to the heating up of magnetic particles in a magnetic field and then cooling it [22]. Due to their large surface area, MNPs exchange heat with their environs easily and hence the need to modify their structures to core-shells that have controlled heat exchange. The magnetocaloric effect is usually applied in various biomedical therapies [22].

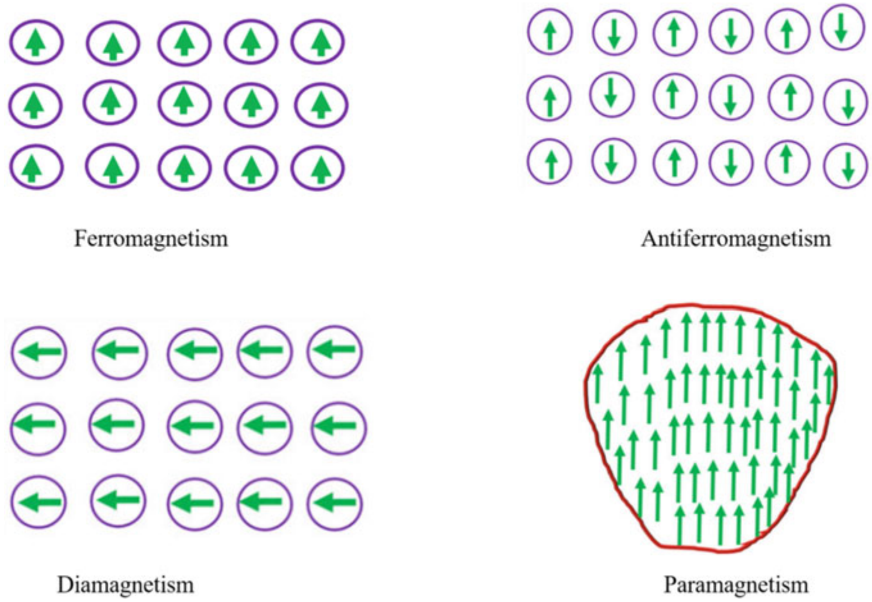

Fig. 2 Illustration of different types of magnetism exhibited by magnetic nanomaterials based on their specific spin moment direction

Table 1 Different magnetic nanomaterials and their Curie temperatures and critical values

Material	Type of magnetism	DC (nm)	Curie temperature (K)
Europium oxide (EuO)	Paramagnetic	<100	69
Chromium (IV) oxide (CrO_2)	Ferromagnetic	<100	~390
Nickel	Ferromagnetic	55	627
Strontium ferrite ($SrFe_{12}O_{19}$)	Superparamagnetic	<100	~450
γ-iron (III) oxide (γ-Fe_2O_3)	Superparamagnetic	<100	948
Iron (Fe)	Ferromagnetic	~15	1043

3 Sensing Principles of MNPs

The accurate detection of target samples, which occur in a minute or trace levels in environmental samples and have the potential to cause pollution is essential in scientific research and experimentation. Such analytical procedures require reporter molecule labelling using fluorescent dyes. Fluorescent detection is imperative in sensing technology and is preferable, "due to its simplicity, the convenience of transducing the optical signal, the availability of organic dyes with diverse spectral properties, and the rapid advances made in optical imaging" [23]. Fluorescence detection has limited detection levels due to low quantum yields, low extinction coefficients of dyes used and also low reporter molecule-to-dye labelling ratio [23]. Recent development and adoption of MNPs whose optical properties are advanced in addition to sub-micron-sizes can reverse the limitations in fluorescent biosensing.

The functioning of magnetic sensors follows the principle that magnetic moments vary in MNPs when subjected to magnetic domains and the moments change if subjected to mechanical stress from a medium that they are in especially if the nature of the material is elastic [24]. The surroundings of such magnetic fields are analyzed by quantifying performance variations of the magnetic nanomaterials. In biomedical research, magnetic sensors analyze organic tissues, culture medium, cerebrospinal fluid and blood where the magnetic materials interact with the fluids [25]. Biocompatible MNPs with iron are used in such applications to prevent damage to the organic medium made up of ions such as K^+, Na^+, Ca^{2+} and Cl^-. Interactions of the organic media with materials made of transition metals and their associated ions result in incompatibility. In MNPs that are corrosive, biocompatibility can be enhanced by coating with thin alumina, silica, titanium oxide, platinum and gold layers among other surface modifications through methods such as ionic implantation, electrolysis, sputtering and evaporation [25].

Magnetic sensor parts can also be made of silica, silicones or ceramics. MNPs can also be combined with biosensors in the latest medical advances for use in telediagnosis [26]. The nanomaterials are used as formats for biosensing and sensing because of their favorable magnetic characteristics and ability to modify their composition, size, and magnetic and electric properties at different conditions [26]. Advances in the use of MNPs for biosensing were also noted by [27] who highlighted that they are used to manufacture magneto-resistive sensors used in bio-detection. In this case, MNPs are attached to molecules targeted for analysis and magnetic sensors assess the generated stray fields resulting from the nanomaterials [28]. A case example is the formation of magnesium oxide-based sensors in the form of tunnel junctions that enable the detection of MNP-labelled DNA [29]. Biomolecules labelled with MNPs in this case are detected by such sensors after the formation of arrays. Engineered conducting polymers, magnetic composites and metals manufactured at nanoscales are also being used for sensory applications [30, 31]. MNPs are also being combined with electromagnetic absorption particles for use in sensory applications [26, 32, 33]. Biosensors that use MNPs labels for sensing include magneto-resistive sensors, magnetic particle relaxation-based sensors and magnetic relaxation switches [34].

Magneto-resistance sensors are made of materials with variable electrical resistance when subjected to a magnetic field. In such sensors, resistance is influenced by the magnetic field or magnetization [35]. The principle in the operation of the sensors is that magnetic and current force with parallel direction increases resistance unlike when their directions are opposite and result in reduced resistance. Magnetic relaxation switching (MRSw) is a detection technology used in biomedicine. MRSw combination with disaggregation and aggregation MNPs results in magnetic particle relaxation-based sensing. The switches can be used to detect bio-objects such as viruses, bacteria and DNA. The working mechanism of MRSw is however not fully described. In MRS characterization, MNPs were found to be in a diffusion-limited-fractal condition and their sensitivity and phenomena were determined using the transverse relaxation methodology [36]. MRSw has been used at nascent stages to assay the proteomics and genomics of various microbes and biological samples due to their perceived high sensitivity [37].

4 Applications of MNPs in Dye Sensing

With the rise of industrialization and population growth, dye applications too are escalating. Dyes are considered hazardous and toxic environmental pollutants that are contained in industrial effluents and municipal wastewater [38]. The entry of dyes into fresh water systems leads to contamination and pollution of the resources by raising their biochemical oxygen demand (BOD) while depriving the resource of oxygen, which is useful for the survival of aquatic plants and animals [38]. Other dyes gain their entry into food chains and have carcinogenic and mutagenic effects on various organisms. In light of these concerns, it is essential to devise methods for identifying the dyes in such effluents since such advances enable the bio-removal of the dyes to prevent their extensive pollution effects [39]. A number of researchers have produced nanomaterials for dye sensing and the eventual removal of dye molecules [40, 41]. The functionalized MNPs in this case, apply adsorption processes to sense and remove the dyes from aqueous substances [41]. The nanoparticles also introduce groups of ligands on the dyes that enhance the adsorption capacity of such contaminants [42].

MNPs have superparamagnetic aspects that make them be drawn to applied magnetic fields and once the fields are withdrawn the nanomaterials do not retain the residual magnetism [40]. Using external magnetic fields, then such MNPs can be used to isolate dyes from large water samples effectively. After sensing, desorption and adsorption of dyes in aqueous solutions, the MNPs can be reused multiple times, which makes them cheap and economical compared to conventional methods of sensing and removing dyes from polluted waters. The process of sensing and removal of dyes involves three main steps: (1) identification and adsorption of the dye, (2) separation of the adsorbent magnetically and (3) regeneration of MNPs for reuse. A representation of the steps involved in dye sensing and removal using MNPs is shown in Fig. 3 as adapted from [40].

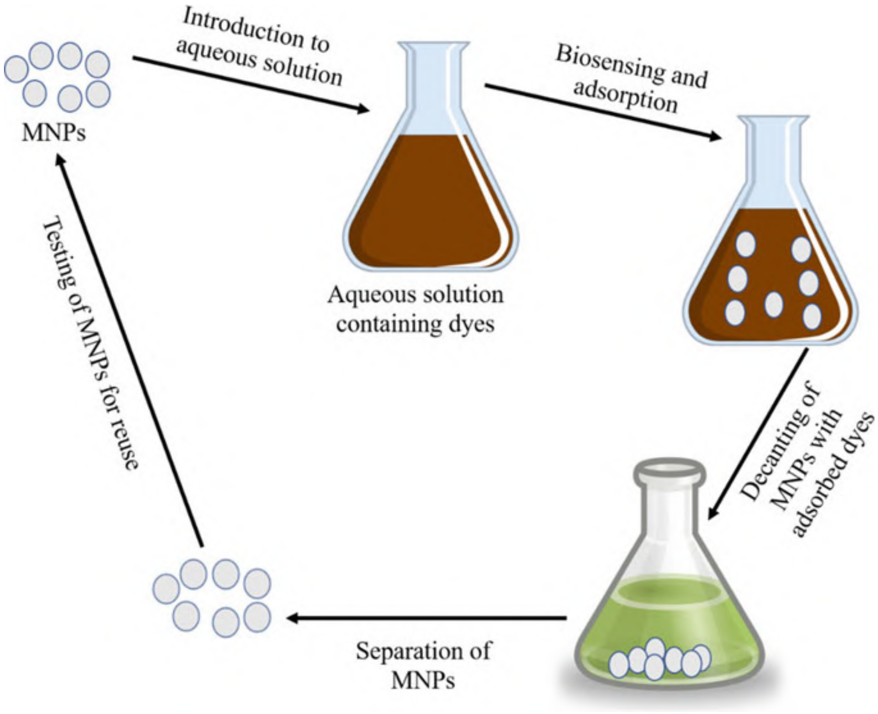

Fig. 3 Steps involved in using MNPs for dye sensing and removal from aqueous solutions

5 Studies on the Use of MNPs for Dye Sensing

The sensing and removal of various dyes using bare and/ or modified Fe_3O_4 nanomaterials have been investigated in various studies. In all the studies, the procedure for dye sensing and removal follows the steps represented in Fig. 3 as adapted from [40]. Mahmoodi et al. [43] produced a biocompatible nanomaterial comprising of sodium alginate and titanium oxide, which had high sensitivity for acid green 25 and direct red 80 dyes and eventually removed them from aqueous solutions. Absalan et al. [44] made a new magnetic nanoadsorbent, combined it with ionic liquid and used it to sense and remove 4-(2-pyridylazo) resorcinol (PAR) and reactive red 120 dyes from aqueous solutions. The removal efficiency, in this case, was 99% after which, desorption of the dye was done to allow the reuse of MNPs. Even after reuse in three runs, no notable adsorption capacity losses were recorded [44]. Xu et al. [45] applied the sol–gel process to manufacture modified Fe_3O_4@polyacylic acid MNPs for sensing and removal of rhodamine 6G dye from an aqueous solution and recorded a removal efficacy of 90% in one and half hours. Using a water–air boundary, Chowdhury et al. [46] assessed the sensing and removal of methylene blue and methyl orange using a polypyrrole-titanium oxide (TiO_2) nanomaterial.

Through octane emulsification of tetraethyl orthosilicate and oleic acid, hollow magnetic silica nanoparticles were manufactured and used to sense methylene blue and eventually remove it from an aqueous solution [47]. A 90% adsorption efficiency was realized within 2 h after which, the MNPs were acid-desorbed and reused five times more. In another study [48], Fe_3O_4 nanoparticles were synthesized and modified with a coat of sodium dodecyl sulfate (SDS) to sense and degrade methyl violet dye from an aqueous solution with an absorption efficiency of 90%. Fe_3O_4 was modified with graphene sheets and coated with carbon to identify and remove methylene blue from aqueous solutions [49]. The authors noted that such graphene-coated MNPs had high adsorptive capacity for organic dyes and could be used in place of conventional wastewater and effluent treatment systems. Safranin O dye was also identified from an aqueous solution using Fe_3O_4 MNPs modified with SDS [50]. The removal of the dye was 95% efficient after 10 min and the MNPs were desorbed and reused eight times with an average dye adsorption capacity of 80% following the eighth run. Table 2 summarizes other studies that show the wide application of MNPs for dye sensing, the dyes sensed and their removal efficacy.

The sensing and removal of dyes using MNPs are dependent on several factors. These include temperature, quantities of the adsorbent, initial concentration of the targeted dye and pH [40]. The factors are considered during the optimization of dye adsorption rates in experimental studies. Temperature variations result in equilibrium shifts between the adsorbate and adsorbent during the interactions of the dye with MNPs. Temperature rise could favor better dye sensing and adsorption in endothermic processes while the effect would have an opposite effect for exothermic processes. Absalan et al. [44] observed that the sensing and removal of resorcinol and reactive red 120 dyes using ionic liquid-modified MNPs improved from 62.6 to 90% as a result of temperature rises by 20 K. Similar results were obtained by [47, 73] who evaluated the absorption kinetics of methylene blue and acid dyes, respectively using modified MNPs.

In dye sensing and removal, the quantity of MNPs serving as adsorbents influences the rate of adsorption [44]. An initial increase in the quantity of nanomaterials raises the dye sensing and adsorption capacity because the MNPs offer many active binding sites for the dyes. As the adsorbent volume rises, there is restricted access to active sites for the dye to bind on and therefore adsorption decreases. Additionally, high levels of MNPs promote aggregation resulting from adsorbent collisions and ultimately, reduced surface area for dye sensing and adsorption [40]. Dye concentration is also directly proportional to dye sensing and removal efficiency. As the dye concentration rises, the adsorption rate increases until all the binding sites are filled on the adsorbent and after which, sensing and removal efficiency begins to reduce [47, 48]. A pH increase promotes the concentration of negative charges on the adsorbent surface increasing the sensing rate for dyes. The increase has a limit when the dye structure becomes anionic and consequently, repulsion of adsorbent by the dye occurs followed by decreased dye sensing and adsorption rates [31, 40, 65]. Absalan et al. [44] noted that pH increases from 1 to 2 resulted in 100% sensing of azo dyes by liquid MNPs. However, pH increases beyond 2.5 decreased the dye sensing and removal rate by 20%.

Table 2 MNPs used in dye sensing and removal

Magnetic nanomaterial	Identified and removed dye	Removal efficacy (%)	References
Green tea polyphenol-coated Fe_3O_4	Methylene blue	87	[51]
Polyaniline-functionalized MNPs	Malachite green	95	[39]
Fe_3O_4 nanofluids coated with cellulose	Methylene blue	63.3–95.9	[52]
Fe_3O_4 modified with polyaniline	Basic blue 3	–	[53]
MNPs modified with L-tyrosine	Methylene blue Methyl orange	94 92	[54]
Ionic Fe_3O_4 nanoparticle modified with dimethyl octadecyl [3- (trimethoxy silyl-propyl)] ammonium chloride	Reactive yellow 15	62–90	[55]
Mesoporous Fe_3O_4 nanomaterial functionalized with sulfonic acid and silica coating	Safranin O	91	[56]
Fe_3O_4 nanoparticles modified with β-cyclodextrin	Phloxine Eosin	63 48	[57]
Magnetite modified with activated carbon from bone char	Reactive 5G blue	98–99.6	[58]
Fe_3O_4 nanoparticles coated with CMK-8-modified silica	Reactive yellow 160	90	[59]
SDS-modified MNPs	Auramine O	74	[60]
Fe_3O_4 nanoparticles coated with starch	Optilan blue	72–89	[61]
Fe_3O_4 nanomaterials with sulfonated polystyrene	Congo red	85	[62]
Fe_3O_4 nanoparticles combined with activated carbon	Eosin B Methylene blue Sunset yellow	99.7 98.1 96.6	[63]
Silica coated MNPs	Everzol blue	100	[64]
SDS-modified MNPs	Basic blue 41	95	[65]
F_3O_4 nanoparticles modified with cetyltrimethylammonium bromide	Reactive blue 121 Reactive red 198 Reactive blue 5	90 90 90	[66]

(continued)

Table 2 (continued)

Magnetic nanomaterial	Identified and removed dye	Removal efficacy (%)	References
Fe_3O_4 modified with activated carbon	Methylene blue	–	[67]
Fe_3O_4 modified with copolymers of crotonic and acrylic acids	Alkali blue 6B Methylene blue Crystal violet	92 93 93.7	[68]
Fe_3O_4 modified with graphene	Cresol red Methylene blue	90 90	[69]
Magnetic chitosan nanomaterial modifier with ethylenediamine	Acid orange 10 Acid orange 7	87.8 81.8	[70]
MNPs modifies with aminoguanidine	Methylene blue Acid red 27 Acid orange 20 Acid violet 43 Acid green 25	–	[71]
Polyacrylic acid modified -MNPs	Crystal violet	–	[72]
Fe_3O_4 conjugated with carboxymethylated chitosan	Acid green 25 Acid orange 12	83.8 87.2	[73]
Fe_3O_4 coated with cetyltrimethylammonium bromide	Amaranth dye	95	[74]

6 Conclusions and Future Prospects

The potential of nanotechnology in dye sensing and removal was explored in this chapter. It was evident that nanomaterials particularly MNPs have good adsorption efficiency in their pure forms but with modification of the particles via a coating, their dye sensing and adsorption capacities can be improved. Coating using different chemicals such as cellulose, polyphenols, titanium oxide, silica, alumina and carbon increases surface area and dispersion of the nanomaterials in aqueous solutions while preventing agglomeration and ultimately, providing better dye sensing and adsorption. MNPs were further found to be easily modifiable and reusable owing to their regenerative characteristics and hence greater sensing capacity. The successful sensing and adsorption of dyes using MNPs were found to be pH, dye concentration, temperature and adsorbent dependent. To enhance the application of MNPs in dye sensing, various methods of synthesis are applied. The ability to control these methods is key to getting pure nanomaterials whose efficiency is highly rated. Some synthesis methods such as ball milling pose the risk of contaminating MNPs while control of their sizes is difficult while applying thermal decomposition. Control of temperature is also problematic while applying sol–gel synthesis.

As such, it is imperative to optimize and customize functionalized MNPs based on their specific purpose [1, 2]. Such advances prevent the challenges of toxicity and biocompatibility often associated with the long-term use of MNPs [5]. In addition, the advances can promote the development of a library of new MNPs and their associated hybrids and applications for improvement of their existent physicochemical properties. Such MNPs should have enhanced kinetic parameters, low toxicity and enhanced physicochemical characteristics. MNPs biosensing is also advancing to target analyte-particular molecules during dye sensing and using crosslinks between the aggregated nanoparticles and coatings. This development aims to modify the magnetic field directions and improve the mechanical properties of MNPs to the targeted biomolecule, in this case, the dyes [75]. The modifications can be realized through constructive and critical research on the fabrication and design of MNPs for a given purpose [12, 34]. The advanced MNPs research should incorporate experimental and computational quantum mechanical modelling techniques to enhance the wide use of nanoparticles based on findings established in bench studies [76]. This suggestion is with the precognition that each active site of MNPs has a unique function, which can result in extensive dye adsorption capacity or energies. Future studies on MNPs for dye removal should shift their focus from empirical kinetic models (most of which are reviewed in this chapter) to systematic and adsorption models that can enable full operationalization and/ or preliminary designing of pilot tests on their applicability using bench findings [76]. The systematic models will also enable the testing of MNP's efficiency in dye sensing and removal under varied environmental conditions that mimic actual conditions of dye-polluted environments.

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Magnetic Nanomaterials Applications in Solar Cells

D. M. Jeroh, L. E. Esiekpe, J. C. Ejeka, and P. O. Isi

Abstract This chapter summarizes some important applications of magnetic nanomaterials in solar cells. The chapter began with an introduction and then provides a discussion on nanomaterials and their types. A brief discussion on the concept of magnetism and associated concepts were also presented. The chapter finally examined the concept of solar cells and discussed the importance of magnetic nanomaterials in solar cell applications. Magnetic nanomaterials were proven to have a significant impact in improving the efficiency of power conversion in solar cells, increasing transmission of visible light (for applications as window layers in solar cells), and reducing reflection of visible light (for applications as antireflective coatings in solar cells).

Keywords Solar cells · Magnetism · Power conversion efficiency · Nanomaterials · Energy

1 Introduction

Energy is the mainstay of our environment. In our world presently, energy is required for many purposes especially in homes, offices, restaurants, for driving vehicles, etc. Energy could be non-renewable or renewable. Non-renewable energy (NRE) sources include coal, fossil fuels, petroleum products and so on. As the name implies, this form of energy source is not renewable and thus can be used completely over a period of time. Common disadvantages peculiar to non-renewable energy sources include

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the introduction of pollutants into the atmosphere, culminating in the depletion of the ozone layer. Renewable energy (RE) can be renewed, of which one major form is solar energy.

Solar energy emanates from the sun's radiation and can be converted to electrical energy (electricity) with the aid of solar cells by exploiting the photovoltaic (PV) effect. Power plants that rely on solar radiation are very promising, as they are environmentally friendly including the all-time availability of solar radiation [1]. The most familiar solar cells obtainable are fabricated from silicon materials. However, as the limited size of silicon approaches, studies have continued to suggest materials that can serve as a replacement for silicon. One of such possibilities is in the area of magnetic nano-materials.

Nano-materials have one or more dimensions in the nano-range. A nano-range is typically within 1–100 nm. Materials within this range tend to possess extremely unique characteristics in comparison with their bulk phase. Such unique properties have attracted intense research towards this category of materials. Nanomaterials which can be exploited in this area are semiconductors. The introduction of magnetic materials into an otherwise pure semiconductor coupled with the unique nano-range properties is expected to birth new sets of materials for various applications, especially in renewable energy such as solar energy. Semiconductor materials doped with magnetic impurities are termed diluted magnetic semiconductors (DMSs).

In this chapter, brief discussions on nanomaterials, magnetism, solar cells and the importance of magnetic nanomaterials in solar cells are discussed.

2 Brief Review on Magnetism

In the layman's context, when we speak of magnetism, our mind goes to bar magnet. The phenomenon associated with the magnetic field can be termed magnetism. It is the force a magnet exerts either attractive or repulsive on other magnets or magnetic materials. Magnetism has its origin in the motion of electrons in an orbit and on its own axis in the atom and their interactions with one another. In the atom, electrons orbit the nucleus with angular momentum **(L)** known as orbital angular momentum [2]. The motion of electrons in an orbit in the atom creates dipole moments **(m)**. Since matter is made of atoms and electrons are constituent of atoms, all matter is therefore somewhat magnetic (or at least responds to an externally applied magnetic field [2]. The momentum of the electron as it moves round its own axis (spin S) also contributes to the existence of the dipole moment. Spin is a complete quantum mechanical phenomenon and cannot be described quantitatively classically. Magnetism remains a fundamental property of materials.

2.1 Types of Magnetism

Materials respond differently to probes such as optical, electrical magnetic probes etc. Based on the response to an externally applied magnetic field and how their magnetic dipoles (MDs) are oriented with respect to one another, (parallel, anti-parallel or not at all), materials are grouped as diamagnetic, paramagnetic, ferromagnetic, anti-ferromagnetic and ferrimagnetic materials [2–4]. Some materials generate negative magnetization in the presence of an external magnetic field and are called diamagnetic materials. These materials are generally repelled by magnets. Diamagnetic materials are also referred to as non-magnetic materials. Examples are, mono-atomic noble gases e.g., helium, neon, argon etc. are diamagnetic. Others are polyatomic gases e.g., hydrogen and nitrogen, ionically bonded compounds e.g., sodium chloride, magnesium oxide etc., covalently bonded compounds diamond, silicon etc. Atoms of diamagnetic materials do not have permanent MD moment because the MD moment of various electrons in their atoms tends to cancel out, resulting in zero magnetic moments inside the atom. A diamagnetic material placed in an external field has little extra current induced in its atoms and in such a direction as to oppose the external field already present. Thus, in diamagnetic materials, the magnetic moment induced is in opposite direction to the external magnetic field. This explains why diamagnetic materials are repelled by magnets. All materials exhibit this type of weak repulsion to a magnetic field known as diamagnetism. However, it is a very weak magnetism and may be eclipsed by any other magnetic behaviour. Materials that are diamagnetic have negative susceptibility ($\sim 10^{-5}$) [4].

In some other materials, their atoms have permanent MDs moment (Fig. 1a), because magnetic moment resulting from electron spin motion does not cancel but has a net value. In the presence of an externally applied magnetic field, the MDs of such materials are oriented in the direction of the applied field. This phenomenon is known as paramagnetism. Materials that exhibit this behaviour are termed paramagnetic materials. Paramagnetic material acquires a small total magnetic moment along the applied field's direction. Thus, they are slightly attracted to a bar magnet. Examples are oxygen molecules, silicon, bismuth, aluminum, platinum etc. The magnetic susceptibility of such materials is very low in the range of 10^{-4} to 10^{-8}. Diamagnetic and paramagnetic materials are also known as non-magnetic materials, their magnetic dipole does not interact with each other.

Ordered magnetic materials (ferromagnets, anti-ferromagnets and ferrimagnets) have an atomic /molecular structure which makes their dipole moment spontaneously align in certain directions with respect to each other. These materials are strongly attracted to a magnet because they have a permanent magnetic dipole and each dipole interacts with the nearest neighbor. The interactions of dipoles result in a high magnetic response and as such, have high magnetic susceptibility greater than one and up to 10^5 [2]. In these materials, the thermal agitations of the materials are not enough to randomly position the dipole moments and so, they stay in a fixed arrangement. In a ferromagnet (Fig. 1b), all dipole moments couple in a parallel direction, and the dipoles interact in such a way that they tend to orient in the same direction.

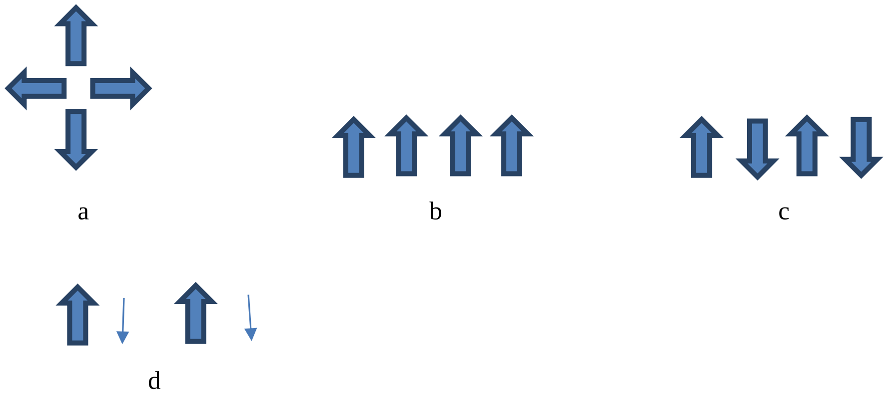

Fig. 1 Pictorial arrangement of dipole moment in materials **a** paramagnetic materials **b** ferromagnetic materials **c** anti ferromagnetic materials **d** ferrimagnetic materials

Ferromagnetic materials retain their magnetism in the absence of the applied field. Examples are iron, steel, cobalt, nickel, etc. Most metals are magnetic materials. Magnetic materials which have dipoles of equal magnitude and their neighboring dipoles orient in a direction opposite to one another are known as anti-ferromagnetic materials (Fig. 1c). Manganese oxide is an example of anti-ferromagnetic material. Anti-ferromagnetic materials are insensitive to the magnetic field at low temperatures. However, above a particular temperature the Neel temperature, they become paramagnetic. Ferrimagnetic materials have dipoles of different magnitude and orient anti-parallel (Fig. 1d).

2.2 *Important Quantities in Magnetism*

(i) **Magnetic Moment Vector (μ).** Magnetism is a result of charges (electrons) in motion. Atoms are made of electrons which are in constant motion around the nucleus in circular orbits. The electron orbital motion constitutes electric current (**I**) given by [2]:

$$I = \frac{ev}{2\pi r} \tag{1}$$

where e is the electron charge, v is electron velocity and r is the orbital radius. The magnitude of the magnetic moment owing to this current is the current multiplied by the area; of which the electron path is a boundary [2, 3]:

$$m = I\pi r^2 \tag{2}$$

$$\mu = \frac{evr}{2} \tag{3}$$

A magnetic moment vector is the capacity to produce and be affected by a magnetic field. The strength of a magnet depends on the magnetic moment vector [3]. The S.I. unit is Am^2.

(ii) **Magnetic field strength/Magnetizing force (H)**. This describes the externally applied field in units of A/m.

(iii) **Magnetization M.** This measures the response of materials to the applied field (H). It is the magnetization induced by the external magnetic field (H). Magnetization equals the magnetic moment per unit volume [3]:

$$M = \frac{m}{V} \tag{4}$$

The unit of M is A/m.

(iv) **Magnetic induction/Magnetic flux density B**. This is the total number of lines of force per unit area due to the magnetization field and the field induced in the materials. Magnetic induction B is the magnetic flux density inside the material. Its S.I. unit is Tesla or $\mathrm{Wb/m}^2$.

(v) **Magnetic susceptibility χ**. This is the readiness with which a material can be magnetized. It defines how a material behaves as a diamagnet, paramagnet and ferromagnet [5]. Thermodynamically, the magnitude of magnetization induced M divided by the external magnetic field H gives the magnetic susceptibility given by Eq. 5 [3, 5]. Magnetic susceptibility has no dimension.

$$\chi = \frac{M}{H} \tag{5}$$

Magnetic susceptibility of materials differs. Diamagnetic materials have very low (negative) susceptibility in the range of $-10^{-5.}$ The susceptibility of paramagnetic materials is slightly higher and is positive approximately $+10^{-5.}$ Ferromagnetic materials have a susceptibility greater than one. The values are orders of magnitude and can vary strongly [2]. Furthermore, there is a pronounced temperature variation for para- and ferromagnetic materials. It should be noted that the above values are consistent only with a static magnetic field and not with a time-varying magnetic field.

(vi) **Permeability μ.** A magnetic material exposed to a magnetic field is induced with magnetism. The magnetization of a magnetic material exposed to an applied magnetic field is due to the concentration of magnetic lines of force within the material. The level of penetration of the lines of force in the material is the material's permeability. Quantitatively, permeability is the ratio of the magnetic induction (B) in the medium to the magnetizing field (H) as given in Eq. 6 [3, 6]. It is a dimensionless quantity.

$$\mu = \frac{B}{H} \tag{6}$$

The magnetization (M) in terms of magnetic field strength (H) and permeability of free space is noted in Eq. 7 [3, 6]:

$$B = \mu_0(H + M) \tag{7}$$

where μ_0 is the permeability of free space. Relative permeability is the ratio of permeability in a medium to permeability in free space as shown in Eq. 8 [6]:

$$\mu_r = \frac{\mu}{\mu_0} \tag{8}$$

(vii) **Retentivity or Residual magnetism:** The capability of a material to retain a specific quantity of magnetism even after the removal of an external magnetic field is called retentivity (or residual magnetism). It is the extent of magnetization present in the absence of the applied magnetic field. Retentivity is measured in Weber per meter square.

(viii) **Coercivity $\mathbf{H_c}$:** Also called magnetic coercivity) is the ability of a material to retain its magnetism in the presence of an applied magnetic field without being demagnetized. A high coercivity corresponds to high resistance to demagnetization. The coercivity of permanent magnetic materials (iron, cobalt) can be as high as 10 MA/m [7]. Coercivity has S.I. unit as Oersted or Ampere/meter.

(ix) **Hysteresis**: When a ferromagnetic material is magnetized slowly by gradually increasing the magnetic field's intensity, magnetic induction starts increasing. A curve describing the magnetizing force (H) versus flux density is regarded as a magnetic hysteresis loop as depicted in Fig. 2. The closed curve is known as the hysteresis curve (or hysteresis loop). The curve shows that the value of B does not become zero in the absence of the magnetizing field The characteristics of the material to preserve its magnetization at the removal of the external field (or the lagging of B behind H) are known as hysteresis. Basically, there are two kinds of the hysteresis loop, one is the B-H loop and the other is the M-H loop [7]. The two hysteresis loops are equivalent. While the B-H loop is used most often in applications, the M-H loop is used in research. The B-H curve is schematically shown in Fig. 2.

3 Thermal Properties of Magnetic Materials

Magnetic materials change their magnetic properties in response to increased or decreased temperature [2] (i.e. they are temperature dependent). Ferromagnetic and ferrimagnetic materials derive their magnetism from the alignment of their magnetic dipoles. The exposure of magnetic materials to increased temperature increases the

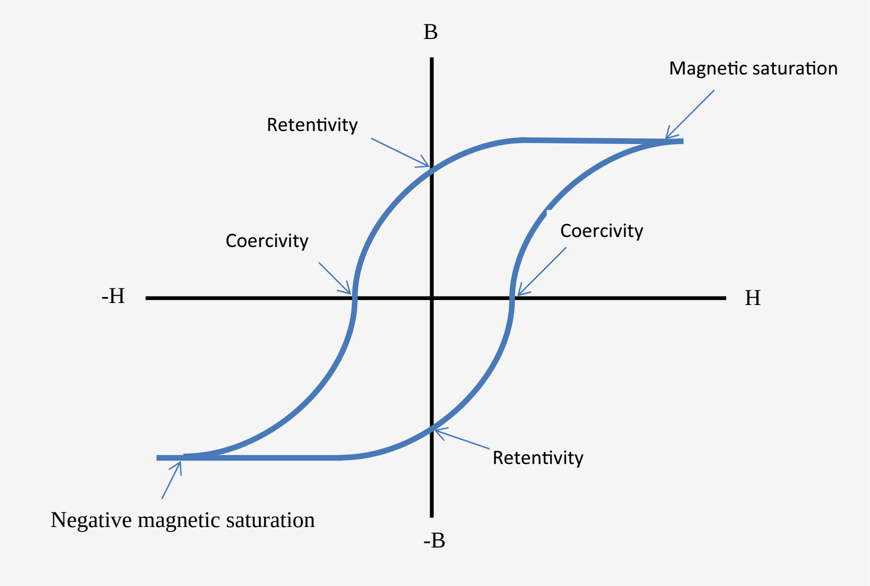

Fig. 2 Hysteresis curve (B-H) for magnetic nanomaterials

intrinsic thermal energy sufficient to overcome the potential energy keeping the dipoles in place. Hence, randomization of magnetic dipoles consequently leads to changed properties occurs. The remanence, coercivity and the maximum energy product of most magnetic materials reduce with increased temperature, except for ferrites whose coercivity increases with temperature. Two temperatures are of importance to the thermal properties of magnetic materials; the working temperature T_w and the Curie temperature T_c. When magnetic material is heated up to the working temperature, the material can recover all of its former magnetizations when cooled and the losses are termed reversible losses. Above the working temperature, the losses are irreversible and hence loss of magnetization is permanent. At the Curie temperature, magnetic material losses its entire magnetization even if cooled afterwards.

4 Nanomaterials

Nano-materials are defined as materials with at least a dimension less than around 100 nm (one-millionth of a millimeter) [8, 9]. It is roughly 100,000 times reduced, compared to the diameter of human hair. Materials at this scale have novel optical, electrical and magnetic properties. Nanomaterials exhibit different characteristics compared to their macro-scale characteristics. A good example is a copper, an opaque substance becoming transparent. Two major factors result in a remarkable difference in the characteristics of materials in the nano- range and their bulk counterpart; increase relative surface area and quantum effect [9]. Characteristics including strength, reactivity; electrical behaviour, optical properties and magnetic properties can be modified by these factors. Nanomaterials have a significantly higher surface area to volume ratio than conventional bulk form.

Also, at the nanoscale, quantum effects come into play in determining the material properties and characteristics which lead to their novel optical, electrical and magnetic behaviour. At the nanoscale, particles are governed by an interesting quantum effect which often makes their characteristics significantly different from their macro-scale counterparts. Properties such as fluorescence, electrical conductivity, and chemical reactivity change as functions of size. The individual atom quantum behaviour and their interaction with one another become relevant. This effect is known as the quantum-size effect (or confinement effect). The wave-particle duality of matter describes a particle as a wave or a particle. In bulk materials, the electrons are assumed as wave-like and free to move within atoms. At the nanoscale, the spatial effect of the wave function of the electron is comparable to the particle size and the electrons begin to feel the presence of particle boundaries thereby adjusting their energies accordingly. In this way, electrons are now confined to quantum levels and are restricted to specific levels.

There are different approaches to classifying nanomaterials. Based on dimensions outside the nanoscale range, nanomaterials can be classified as zero dimensional (0D) nanomaterials [8]. Examples are atomic clusters, filaments, and clusters point like particles which include oxides, metals semiconductors, fullerene uniform particles and arrays, quantum dots, heterogeneous particles arrays, nano lenses etc.

One dimensional(1D) nanomaterials: In one dimensional nanomaterial, at least a dimension is in the range: of 1–100 nm and it includes nanofibers, nanowires, nanorods etc.

Two dimensional(2D) nanomaterials: At least two-dimensional outside the nanometric size range. This class exhibit plate-like shapes such as ultrafine layers, multilayers, nano coatings. graphene etc.

Three dimensional (3D) nanomaterials: These materials are not restricted to the nano-scale in any dimension. They include bulk powders, nanowires and nano tubes.

4.1 Magnetic Nanomaterials

Magnetic nanomaterials are nanomaterials consisting of magnetic elements such as iron cobalt, manganese nickel, chromium etc. and their chemical compounds [9–11]. These materials respond strongly to a magnetic field. Due to their nanoscale size, they are super-paramagnetic which makes them useful in many industrial applications in their original form or coated with functional groups selected for specific applications. Apart from superparamagnetism, magnetic nanoparticles display innovative phenomena, including high field irreversibility, high saturation field and extra anisotropy [4]. Industrial applications of magnetic nano-materials include magnetic recording, media and bio-medical applications.

4.2 Properties of Magnetic Nanomaterials

Magnetic Properties

There are three key issues: (1) fixed size effect (ii) surface effects and (iii) interparticle interactions and their ensembles [12]. The nanoscale size of materials gives rise to the quantum confinement effect which in effect modifies their properties. Surface effects are closely linked to symmetry fracture of the crystal structure at the boundary of each magnetic nanoparticle.

Magnetic nanomaterials may range from 1 to 100 nm and may display super-paramagnetism. Super-paramagnetism is exhibited by ferromagnetic and ferrimagnetic nanoparticles [13]. Due to nanoparticle size, they are single domain particles. Hence, the magnetization of the particles is roughly one giant magnetic moment; obtained by adding an individual magnetic moment of each constituent atom. This is called macro-spin approximation. For a very small particle in the nano-scale, the energy barrier for magnetization reversal which is proportional to grain volume is relatively low compared to thermal energy. Thus, with appropriate thermal energy (large enough), their magnetization can flip direction randomly over a short period of time. The time between two flips is called Neel relaxation time. Super-paramagnetism is caused by the thermal effect; making the thermal fluctuation strong enough to immediately demagnetize a hitherto saturated assembly [9, 13]. Here, the particles have no hysteresis with zero coercivity. An external magnetic field magnetizes the particle with greater susceptibility. When the field is removed, the nanoparticle exhibits no magnetization [14].

Magnetic nanoparticles also exhibit a magnetocaloric effect. The magnetocaloric effect involves heating or cooling magnetic materials when exposed to a varying magnetic field. It is the effect displayed by some magnetic materials; heating up in a magnetic field and cooling down when removed. Magnetocaloric effect results from temperature changes in an adiabatic process and entropy changes in an isothermal process [15]. Magnetic nanoparticles with precise magnetocaloric characteristics are veritable tools to reduce the temperature of nano-sized systems. They are manipulated easily and distributed into distinctive shapes, such as wires or planes.

5 Solar Cells

Solar cells (SCs) are described as devices made from semiconductor materials which absorb incident photons from the sun, utilizing the photovoltaic effect to produce an electric current. The photovoltaic effect creates a potential difference (PD) at

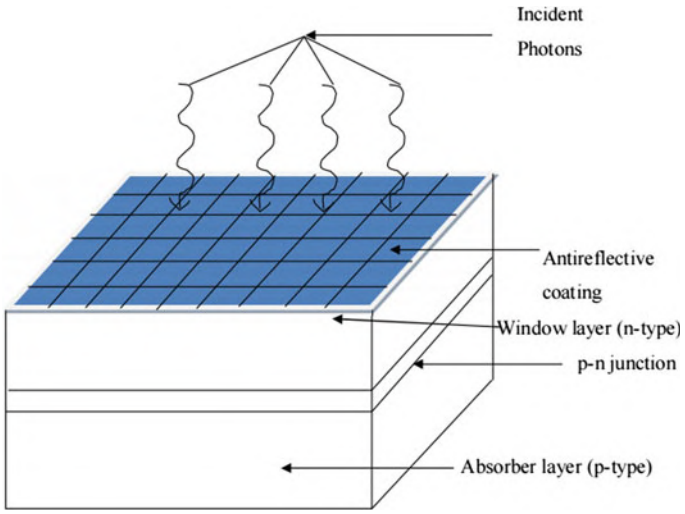

Fig. 3 Diagram of a solar cell

the boundary between a p-type material and an n-type material. This boundary is called the p–n junction. When the photons are absorbed, charged particles in the form of electron–hole pairs are produced, and with the aid of an external circuit, can generate electricity, which can be distributed to power outlets. Solar cells are broadly categorized into two; which are wafer and thin-film SCs. Wafer SCs are characterized by high cost, low absorption coefficient, decreased efficiency in low light and high temperature manufacturing conditions [16]. These drawbacks of wafer SCs are well addressed by the thin film SCs [16].

A typical thin film SC comprises of an anti-reflective coating, a window layer and an absorption layer, and is normally crystalline. Figure 3 illustrates a simplified diagram of a thin film SC.

From Fig. 3, the SC contains an anti-reflective coating which ensures that minimum radiation is reflected from the surface of the cells. With the anti-reflective coating in position, much of the incoming radiation passes through the highly transparent layer (also known as the window layer). This highly transparent layer is generally n-doped. The absorption layer is directly beneath the window layer and is responsible for trapping the incoming radiation from the sun. When a material absorbs an incident photon, the electrons within the material become energized, resulting in their excitation from the ground energy level in the valence band (VB) to an upper energy level in the conduction band (CB) as indicated in Fig. 4.

Once the incident photons are absorbed and the electrons become energized, the electrons escape from the VB into the CB, thus creating holes behind in the VB. These holes created in the VB are positively charged. The existence of the negatively-charged electrons and the positively-charged holes together are referred to as “electron–hole pairs.” This can be illustrated in Fig. 4.

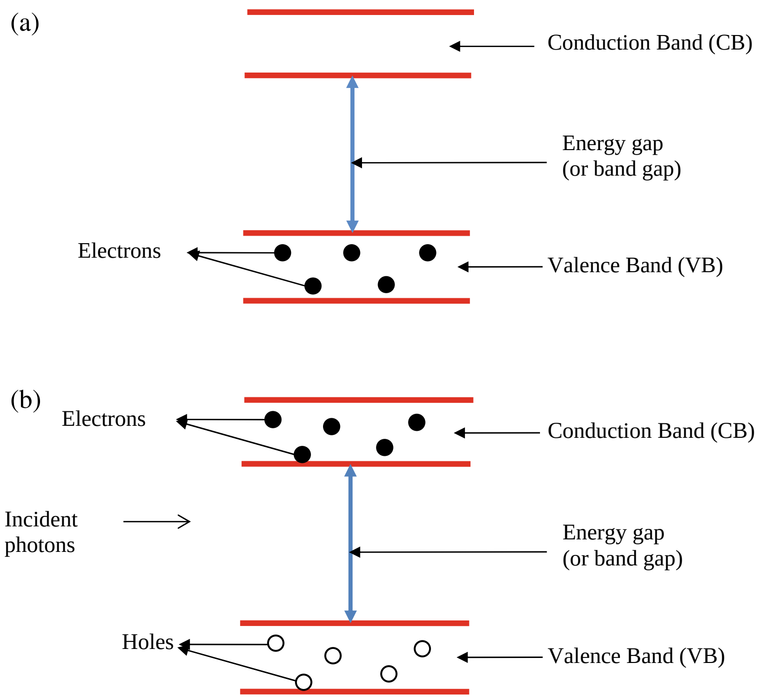

Fig. 4 **a** Schematic illustration of electrons in the ground state. **b** Schematic illustration of the absorption process in a solar cell

In Fig. 4, the difference in energy between the conduction and valence bands is known as the energy or band gap. Within the energy gap, no energy states are permitted to exist.

The charge carriers can be retrieved from the SCs by means of electrical contacts, thus performing work in an external circuit, resulting in the conversion of the chemical energy contained in the electron–hole pairs into electrical energy [17]. After the separation of the charge carriers, they later recombine to form electron–hole pairs in the absorber layer of the solar cell. In the recombination process, the electrons return to their initial state resulting in the release of energy in the form of a photon or transferred to other charge carriers [17]. The former is referred to as radiative recombination while the latter describes non-radiative recombination.

6 Advantages/Applications of Magnetic Nanomaterials in Solar Cells

A typical SC consists of an absorber layer, anti-reflective coatings and a window layer. The absorber layer is responsible for trapping photons to the surface of the solar cell. Absorber layers are semiconductor materials whose interactions with photons result in generating charge carriers (electrons and holes) which in turn helps in the generation of electrical energy. Nanomaterials of course, exhibit unique properties at the nanorange and this fact makes them materials of interest. When magnetic impurities are embedded in semiconductor nanomaterials, they give birth to a new set of materials known as dilute magnetic semiconductors (DMSs). These DMSs play a very vital role in the absorption of photons by a solar cell for energy generation. These DMSs result from combining transition metals and groups II–VI, IV–IV and III–V elements [18].

The incorporation of magnetic impurities into semiconductor nanomaterials has some outstanding advantages in SCs:

(i) **Improving power conversion efficiency (PCE)**

PCE refers to the ratio of the optical power-out to the electrical power-in [16]. One major method to reduce costs for clean solar electricity is by increasing the PV conversion efficiency of the thin film, which implies more sunlight absorption by the PV and subsequent conversion into electricity [19].

Manganese (Mn) doped zinc selenide ZnSe used as a passivative layer exhibited improvement in the PCE (9%) of the solar cell in comparison with the PCE (5.62%) of the undoped ZnSe as reported by [20]. In the literature, improved solar cell efficiency for Mn-doped ZnSe/CdS quantum dots [21] has been reported.

In fabricating poly (3-hexylthiophene) [6]—phenyl-C_{60}-butyric acid methylester (P3HT: PCBM) SCs, [22] reportedly doped these cells with iron oxide nanoparticles (NPs) at varying concentrations with focus on the PCE of the cells. A reference SC fabricated at 0 wt % resulted in a PCE of about 3.05% while the introduction of iron oxide NPs to the SCs resulted in increased PCE to about 3.37% corresponding to an 11% improvement [22].

(ii) **High transmission of visible light**

Light transmission refers to the quantity of visible light allowed to pass through a material. This phenomenon plays a critical function in designing window layers for solar cells. SCs comprise a window layer which allows for the transmission of visible light. Increased visible light transmission by nanostructured europium doped cadmium selenide films when compared with Cadmium selenide materials in the macro-scale has been reported [23]. In the research of [24], a considerable increment in transmission from around 60% [pure ZnO] to about 95% for Eu^{3+} doped zinc oxide nanoparticles were recorded. These results suggest improvement in high transmission of visible light emanating from the addition of magnetic impurities to otherwise pure semiconductors, hence are advantageous for designing window layers for SCs. Such high transmission recorded allows for efficient light transmission through the window layer of solar cells, thus reaching the absorber layer swiftly.

Copper indium gallium selenide (CIGSe) SCs were fabricated using aluminum-doped zinc oxide (AZO) nanorods (NRs) as a window layer [25]. In the cell, pure AZO recorded transmittance of about 89.2% between 400 and 1000 nm, with improved transmittance of about 92.4% for AZO NRs [25], which was attributed to the addition of NR structure on top of the AZO thin film.

(iii) **Reduction in light reflection**

The portion of light in the electromagnetic spectrum that bounces back from a surface is known as reflected light. This phenomenon also plays a critical role when designing SCs. In the design of an SC, it is essential to employ materials that have the capability of decreasing the quantity of light being reflected from the surface. This is because SCs without anti-reflective coatings tend to reflect about 30% of incident radiation [26]. Magnetic nanomaterials have proved to be promising materials in this regard. Jeroh et al. [23] reports decreased reflection of radiation for europium-doped cadmium selenide films in the nanoscale range.

In fabricating CIGSe SC, [25] employed AZO NRs as an anti-reflective coating. The bare (pure) CIGSe cell had a reflectance of about 14.5% between 400 and 1000 nm, whereas the AZO NRs CIGSe SC recorded a reduced reflection to between 2.3 and 7% depending on the height of the NRs [25]. The reduced reflection emanates from the presence of the magnetic nanomaterial (AZO NRs) on the surface of the CIGSe SC. Lower reflection by a cell improves the cell's efficiency.

(iv) **Enhancement of crystal structure**

SCs have been extensively manufactured using single crystal elements such as silicon. The use of compound semiconductors focuses more on polycrystalline materials such as the II–VI, III–V and IV–IV binary compounds. Polycrystalline cells are characterized by low cost compared to single crystalline cells [27]. Due to this advantage, polycrystalline cells are of more interest lately. The incorporation of magnetic elements (especially in the nano-range) into semiconductors has shown improvement in the crystal structure of these semiconductors. Enhanced crystalline structure for europium-doped magnesium selenide (MgSe: Eu) nanofilms has been reported [26, 28] when compared to pure magnesium selenide as prepared by [29].

7 Conclusion

SCs are photovoltaic devices which are employed for converting the sun's radiation into electricity. The use of magnetic nanomaterials in SCs has shown tremendous improvement in the efficiency of the cells over the years. Magnetic nanomaterials have also been shown to reduce reflections of SCs, thereby acting as good antireflective coatings, and of course, they also increase the amount of light transmitted within the material, hence making them good materials for the design of window layers for SCs.

Authors' Contributions **D.M. Jeroh:** Abstract, Introduction, Conclusion.

L.E Esiekpe: Nanomaterials, Types/Classes of nanomaterials, Brief review on magnetism, magnetic nanomaterials.

D.M. Jeroh, J. C. Ejeka and P.O. Isi: Solar cells, Advantages/Applications of magnetic nanomaterials in solar cells.

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Applications of Magnetic Nanomaterials for Wastewater Treatment

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Abstract A key priority field of study over the years has been on the environmental application of nanotechnology (NT) in contaminated water laced with heavy metals (HMs) and dye treatment utilizing sorption techniques. To this end, various magnetic nanomaterials (MNMs) have been fabricated and functionalized to achieve superior nano-sorbents with an improved surface-to-volume ratio and active components to enhance the environmental remediation of industrial effluents containing HMs and dyes. The ideal sorption of various contaminants to MNMs was reported in the studies reviewed to be in the range of pH 2–9.6. Equilibrium sorption data showed that

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the Langmuir (LGR) and pseudo-second-order (PSOR) models mostly defined the sorption processes (SPs) of HMs and dyes to different MNMs. Thermodynamically, the interaction of most pollutants and MNMs were found to be spontaneous, and endothermic or exothermic. The fabricated MNMs were found to be effective in the sequestration of pollutants from an aqueous-medium and could be applied in the treatment of real industrial wastewater.

Keywords Pollutants · Nanomaterials · Sorbents · Sorption · Isotherm · Kinetic

1 Introduction

A vital ecological resource for the sustenance of life expectancy and the biota is water. Water applicability for household or agrarian and manufacturing purposes depends on the key characteristics of the chemical composition of shallow and subsurface water. In safeguarding people's health, access to clean and safe drinking water is a critical necessity for all perfectly functioning societies. The increasingly stringent water quality standards, which are intensified by the changing of contaminants have given an extra comprehensive examination of the existing water supply and treatment methods. Also, global climate change is a focal point of the fluctuating source of fresh water, and this leads to water supply interruption [1].

The increase of a broad scale of pollutants in shallow and subsurface water is a global issue owing to the increased population, swift expansion of industries and extended duration of drought. Pollutants that are enduring in effluents include mineral compounds, HMs, dyes, natural contaminants and several other complicated compounds [2], HMs and organic contaminants in effluents are yielding a frightening biota problem, owing to their acute noxiousness and non-biodegradability. They also cause a menace to human health when amassed in living bodies. Despite the noxiousness of HMs and raw matter, they are a treasured manufacturing chemical used for industrial fabrications. Hence, a huge amount of effluents need innovative treatment and reprocessing of useful materials in effluents before their release into the ecosystem [3].

Contaminants in water are classified into point and non-point sources, where contamination starts from a specific and recognizable source and contaminants are derived from a diversity of sources. Based on their primary physicochemical features, they are also categorized into thermal, nutrient, radioactive, suspended solid and sediment, inorganic and organic and microorganism contaminants. Mineral contaminants comprise of HMs, sulphides, acids, bases, fertilizers, ammonia and oxides of nitrogen. Through conventional and anthropogenic events, water is polluted with contaminants and the concentration of these pollutants in water depends on the aquifer's hydrogeological, geochemical and local geology characteristics. Certain variations in metal ions (MI) noxiousness develop from the change in absorbability, transport, complexes created within the body, chemical reactivity and solubility. HMs are classified based on their noxiousness as biologic essential (copper (Cu), iron (Fe), nickel (Ni), zinc (Zn), and cobalt (Co)) and biologic non-essential HMs (mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr) and lead (Pb)). Biologic essential HMs are not dangerous at modest concentrations, in contrast to biologic non-essential HMs which are extremely noxious even at low concentrations. Cu, Cr, Ni, Hg and Cd tend to create spontaneous radicals, which will lead to the damage of DNA, protein sulfhydryls reduction, lipid peroxidation etc. Table 1 shows the contamination sources [4, 5], their maximum concentration level-MCL (mg.L^{-1}) and the impact of individual HMs on the health of humans [4, 6–8].

HMs can travel via the food sequence through bioaccumulation and their spread in the human body is triggered by crucial disorders such as pancreas disorder, the disorder of heart and brain disorder as well as the prevalent damage of capillary, gastrointestinal inflammation and necrotic vicissitudes in some tissues. HMs can initiate severe noxious and destructive impacts on organisms and the ecosystem even at low concentrations, hence their controlled concentrations by the World Health Organization (WHO) [9].

An organic compound that is employed as a coloured material to fasten the substrate to which it is being put on is the dye. Dye are grouped according to their compositions, colours and uses, of which its utilization is the most conventional practice used to classify dyes. Based on the chemical structure, dyes are classified as azo, phthalocyanine, nitroso, anthraquinone, nitro, triarylmethane and indigoid dyes. Anthraquinone, triarylmethane and azo dyes are highly valuable groups and based on their various functions, dyes are grouped as vat, mordant and disperse dyes. Contingent on the particle charge dissolution in the water-soluble medium, dyes used in fabric production include anionic (acid, direct, and reactive dyes), cationic (the whole basic-dyes) and non-ionic (disperse-dyes) dyes [10].

Currently, they are generally employed in various industries like paper, plastic, textiles, automotive, marine, paint, coating and food industries, rubber, etc. They mostly have a synthetic starting point and a complex formation that makes them relentless to illumination, recyclable and oxidation procedures. Most water-soluble solutions from different industries comprise of a huge volume of pristine dye molecules, which pose a huge hazard to the marine environment, combined with the depletion of oxygen and high biochemical oxygen requirements [11].

It is reported that 0.7–1.6 million loads of dyes waste are produced annually and of this amount, 10–15% is discarded as effluents, thereby making it a general water contaminant. Disproportionate exposure to dye triggers irritation of the skin, respiratory issues and increased threat of tumours in human beings. In addition, it also produces serious damage to the health of humans like vomiting, Heinz body creation, cyanosis, jaundice, enhanced heart rate, quadriplegia, tissue necrosis and shock. Also, certain dyes display carcinogenic activity towards humans either in their natural or degraded structures. Dye's multifaceted structures make them ineffectual in heat, light, oxidizing agents and microbes, making it difficult to degrade them. Their presence in water impacts oxygen solubility and penetration of the sun, which thereby reduced the quality of water and impedes the photosynthesis of marine fauna and flora. Hence, dye production has become a vital vile owing to the improved dye demand for manufacturing development along with its harmful effect and it has

Table 1 Schematics of common sources, impacts and MCL of HMs

HMs	Common sources	Effects on the health of humans	MCL $\times 10^{-2}$ (mg.L^{-1})
Zn	Combustion waste, coal, PVC stabilizers, chemicals and medicine, rubber industry, cans, soldering, batteries, paints, welding fluxes, agricultural use as phosphatic fertilizers, anti-corrosion covering, processing of steel, combustion of waste and mining	Physical dysfunction, hyperactivity, enhanced thirst, depression, neurological signs and lethargy	80
Cu	Plumbing systems in households, occur naturally, pharmaceutical and chemical apparatus, alloys and pigments	Problems with gastrointestinal, damage to the kidney and liver, Wilson's ailment and anorexia	25
Ni	Products of paper, catalysts, components of computers, dental and surgical prostheses, electroplating, arc welding, batteries, paint pigments, rods, ceramic and glass containers mould, and fertilizer plating	Coughing, loss of hair, prolonged asthma, allergic dermatitis, nausea and carcinogenicity	20
Co	Occur naturally, and mining	Vision difficulties, vomiting, nausea, heart issues, thyroid impairment, and asthma or pneumonia	5
Cd	Occurs naturally, utilization for agricultural processes (phosphoric fertilizer), pigments, stabilizers of plastics, anti-corrosive metal covering, different chemical industries, coal combustion and alloys	Damage to the kidney and DNA, irritation to the gastrointestinal, hyperactivity, renal malfunction and carcinogenicity	1
Hg	Luminous light bulbs, electrical and computing equipment, dental fillings, pharmaceuticals, catalysts, precise tools, solders, rectifiers, oscillators, fossil fuel ignition and electronic productions	Damage to the kidney and the nervous system, gingivitis, gastrointestinal problems, stomatitis, abortion and cancerigenicity	0.003

(continued)

Table 1 (continued)

HMs	Common sources	Effects on the health of humans	MCL $\times 10^{-2}$ (mg.L^{-1})
As	Occurs naturally, in agricultural utilization, medicine (veterinary), filters in light, fireworks, antifouling paints, tanning, production of electronics, non-ferrous smelters, electricity generation using coal-fired and geothermal electrical generation plants, pigments, metallurgy and tanning	Damage of skin, coagulation of protein, weakness of muscle, problems of the circulatory system and carcinogenicity	5
Cr	Occurs naturally, in the treatment of wood, chemical industries, refractory, leather and fabric tanning, plating, passivation of corrosion of cooling circuits, pigments, and steel manufacturing metallurgy	Diarrhoea, vomiting, nausea, neurotoxicity, damage to the liver and kidney and allergy dermatitis	5
Pb	Plumbing systems in households, pigments, ceramics, Pb-based products like batteries, solder, sheathing of cables, sheets, glassware, alloys and antiknock agents	Damage to the kidney, decreased development of neural, high blood pressure and carcinogenicity	0.06

become a worldwide interest where every country is devoting a great deal of wealth to find out viable techniques that can bring about the elimination of the unsafe effects of molecules of dyes. Therefore, considerable interest must be given to the eradication of colour effluents to guarantee the viable discharge of treated wastewater into streams [10–12].

Over time, water treatment processes and knowhow have gone through and through innovations and the development of novel NMs, thereby opening up a newfound field for the efficient and cost-efficient prospects for the improved decontamination of industrial wastewater containing HMs, organic and inorganic solutes, dyes, micro-organisms and radionuclides [1, 13]. With the specific importance of water to people in both emerging and highly developed countries, and with a greater fear regarding the viability of meeting the increasing demand for safe drinking water by employing existing techniques, there is a clear obligation for supportable and advanced machineries and materials for the sequestration of contaminants. Though groundbreaking techniques are lower in overall expense, their resilience and effectiveness in comparison to current alternatives for the confiscation of contaminants from water are continually being investigated [1].

In considering and making a decision on the ideal effluent treatment technologies to be explored, the conditions that must be taken into consideration are flexibility of treatment and ultimate effectiveness, treatment agents recycling, eco-friendly and green security and low-cost [2]. To combat water contamination issues, swift and considerable development in the treatment of effluent has been done employing bioremediation, sorption/separation processing, photocatalytic oxidation, ion exchange, reverse osmosis etc. But most of these treatment techniques are constrained by effective technique, the huge prerequisite for energy, cost-effective benefits and treatment effectiveness [2]. Sorption is ideal over other techniques owing to its prospective to confiscate natural and mineral elements from water even at low concentrations [14]. Sorption is categorised as physi-sorption and chemi-sorption. The physi-sorption arises owing to the feeble electro-static interactions relating to the Van-der-Waals and London and dipole–dipole forces. While the chemi-sorption involves the binding of the sorbate to the surface of the nano-sorbent via sturdy covalent or ionic bonds and the effectiveness of the SP is impacted by the temperature, sorbent dose, ionic strength, solution pH, and contact time. To differentiate between the two categories of sorption Freudlich (FRH), Dubinin-Radushkevish (DR), Redlich Peterson (RP), LGR, Sips (SP), Temkin (TKN) and Jovanovich (JNH) isotherm models are utilized [15].

Lately, NT development has promoted a potential offer for water decontamination with exceptional operational effectiveness, cost-efficiency in the exclusion of pollutants and recyclable potential. NT embraces the potential of enormous advancements in electronics, telecommunications, health, ecological remediation and industrial machineries. This comprises of the fabrication and usage of a diverse range of NMs which consist of assemblies and tools with size arrays from 1 to 100 nm and show distinctive properties not noticed in bulk-sized materials [13]. The central theory of NT and nanoscience (NS) is followed by NMs, as its uses comprise of comprehensive inter-disciplinary study space and explosive worldwide growth of its development activity. They are classified into nano-controlled and nano-phase/NPs materials, where the nano-controlled materials refer to particles made of compressed-size material, with the particle size in the scale of a nanometer (nm). The NPs are mostly referred to as dispersed materials. Decreasing the bulk crystalline material's size to the nano-scale, changes their overall behaviour and surface and quantum effects are the two key factors that make NMs' behaviour substantially distinct from their bulk materials. These factors impact the chemical reactivity, electric, optical, magnetic, mechanical and electrical properties of the materials [16].

NMs have been advocated as an operational, cost-efficacious and green substitute for current treatment materials from the resources management and ecological remedy perspective. Owing to NMs' special properties like their huge surface-area, exceptional reactivity, excellent mechanical stability, nano-size, dispersibility, hydrophilicity, hydrophobicity and prevailing solution mobility, they have been revealed by scientists to be an exceptional choice for wastewater treatment in recent times. Most recently, there has been further innovation in the use of NMs such as nano-photocatalysts, nano-sorbents and nano-membrane for the effective treatment of contaminated water [2, 3, 13]. The main contributor to achieving optimum performance in effluent treatment is the size effect of NMs and the size of these materials is carefully linked to their exceptional reactivity surface and elevated surface-area [17].

In the past twenty years, stimulating accomplishment has been put together in innovative NMs advancement for various quality of effluents treatment through the creation of novel materials, the creation of straightforward green or commercial fabrication paths and nanocomposite materials synthesis [17]. The sequestration of pollutants employing sorbents is fascinating owing to the particular material removed from liquid to solid surface. Convectional sorbents have comparatively reduced sequestration capacity and inadequate separation abilities for contaminants. Hence, developing a nano-sorbent such as magnetic nanoparticles (MNPs), which will be applied in the evolving field of water and effluent treatment is indispensable. Based on their nano-structures owing to the simplicity of magnetization direction would fluctuate conditional on the atoms in the magnetic structure ordering, thereby leading to their separation from water-soluble solutions. The utilization of magnetic field (MF) encourages NPs magnetization and hence makes the magnetic force utilization probable. Various materials that are magnetic have been utilized for the confiscation of pollutants from aqueous-medium and due to NP's low sorption capacity (SC) for various contaminants, they are improved [18].

Nanostructure materials construction with multi-components presents very fascinating properties, functions and geomorphologies. MNPs properties such as carrier transportation, adhesion, sorption, surface-area, and reflectance have been utilized for different purposes including effluent treatment. There is a varied category of NMs that comprises of one, two or three metals and their oxides. Structure-regulated, rigid and monodispersed are the attributes of metal-based NMs, which have largely been studied through chemical and physical methods. These valuable attributes and versatility of MNPs contribute to their prospective use in the treatment of effluent as well as sorption, membrane separation, chemical disinfection and photodegradation [17].

Owing to the startling challenge of the growing need for clean drinking water, a multiplicity of effective, cost-efficient and eco-friendly NMs have been created, with each one having a distinctive functionality for potential use in the decontamination of industrial discharges containing HMs and other organic pollutants in surface water, drinking water and groundwater [19]. Within the sorbents family, NPs present more-effective sites and enhanced surface-area for the interface with a variety of pollutants, which leads to effective sorption with straightforward integrated properties [16]. MNPs have been considerably utilized in medicine, ecological study and cleanup in comparison to other NPs [20].

Amongst the existing magnetic sorbents that are capable of removing pollutants from an aqueous-medium, nanosized metal oxides (NMO) like iron (IO or FeO), titanium (Ti), cerium (Ce), aluminium (Al), and manganese (Mn) oxides show extraordinary actions for contaminants treatment, which are activated by their size quantization, extraordinary reactivity, decent surface-to-volume ratio, required mechanical stability, and effortlessness renewal [1, 21]. Also, owing to the significant antibacterial, anti-viral and anti-fungal activities of titanium(IV) oxide (TiO_2), have been explored as water disinfectants for self-cleaning surfaces, water and air decontamination and as photocatalysts in the treatment of water [17]. Current studies have shown that metallic and metal oxide NPs are potentially efficient materials for the sequestration of HMs and dyes from water-soluble mediums [21–23]. Hence, this book chapter deals with the advancement of effective, recyclable and minimal-cost MNMs for the decontamination of industrial waste containing organic and inorganic contaminants discharged into water resources. Also discussed, is the functionalization/modification of the various MNMs with different functional groups for the effective encapsulating of HMs ions and dye molecules. Deliberated in this chapter are the factors impacting the sorption of HMs and dye to MNMs as well as the mechanisms of sorption of HMs and dye to MNMs employing the isotherm and kinetic models.

2 MNMs Fabrication

NMs are considered based on their composition, size, origin and shape. It has been of superb importance in the research area to discover novel forms of NMs with various fundamental designs that can suit innovative functions. However, these materials' distinctiveness ensures that the materials are created with tunable properties, with enhanced properties and performance that are analogous to those of long-recognized equivalents accessible in the market. NMs sizes are impacted by several factors, like the technique employed for the fabrication, pressure, temperature, pH, concentration and time. On the foundation of their functionality, they have been fabricated into shapes and dimensions, which include consistent architectures, spheres, fibres, and sheets [17].

Lately, the fabrication and application of NPs with new properties and functions have been researched greatly, due to their nano-series size, elevated ratio of surface-area to volume and super-paramagnetism. Specifically, the easy synthesis, coating or alteration and the capability to operate or control matter on an infinitesimal dimension, which provides unparallel resourcefulness. The fabrication procedures and surface variation mediums play a serious role in establishing size distribution, surface-chemistry, magnetic characteristics and morphology of NMs. Most scientists have focussed their work on applying biological, chemical and physical procedures for the fabrication of MNPs [2].

Over the centuries, MNPs have been fabricated using bottom-up (reduction of materials components up to microscopic phase with the additional self-fabrication process, which leads to the creation of nano-structures) or top-down (this method originates with macroscopical structures, which control the peripheral process of the nano-structures creation) methods with the application of chemical methods like microemulsions, sonochemical reactions, hydrothermal reactions, co-precipitation, sol–gel, hydrolysis, solvo-thermal, laser ablation, flow injection, electrospray and thermolysis of precursors techniques [4, 24]. While the physical techniques employed for MNPs fabrication comprise of gas-phase deposition, electron-beam-lithography, aerosol, pulsed-laser-ablation, powder-ball-milling etc. For MNPs fabrication employing biological techniques involves fungi, protein and bacteria intervention [25]. Lately, a sturdy effort has been placed on the use of the green fabrication method, where MNPs are obtained from algae, bacteria, plants and fungi, in which a range of metabolites acts as reducing agents in the fabrication of MNPs. The benefit of this method is that they are effortlessly obtainable, reliable and flexible in the kinds of metabolites that could act as reducing and stabilizing agents [24]. Figure 1 depicts the various fabrication techniques employed for MNMs.

With the reduction of the size of NMs to the nm phase, surface-area expansion leads to inevitable feeble stability [16]. NMs instability (colloid NPs) is impacted by the Van-der-Waals and electro-static interactions. Typically, to avoid NMs agglomeration in solutions and give a low deposition rate of NMs, they should be stabilized to ensure their responsiveness and mobility. The stability and size of various NPs are impacted by temperature and pH. NPs surface functionalization is critical for modifying the particle's general properties to suit aimed applications. This gives the materials novel surface chemistry features (reactivity, stability, melting point, electronic assembly and solubility), hence making them homogeneous in size, having a great distribution of shape and controlling their steadiness in water-soluble mediums. To convey stability to the NP's structure, the species present on the NMs surface play a role in the functionalization of the NMs surface and permit the stabilization in a dispersant solution, with enough repulsive forces employed to counterbalance the Van-der-Waals interaction. Achieving NMs stabilization is through the use of stabilizers, electro-static surfactants and steric polymers, to enable NMs with non-explicit moieties, group-precise or extremely precise ligands. To attain stable NPs, various

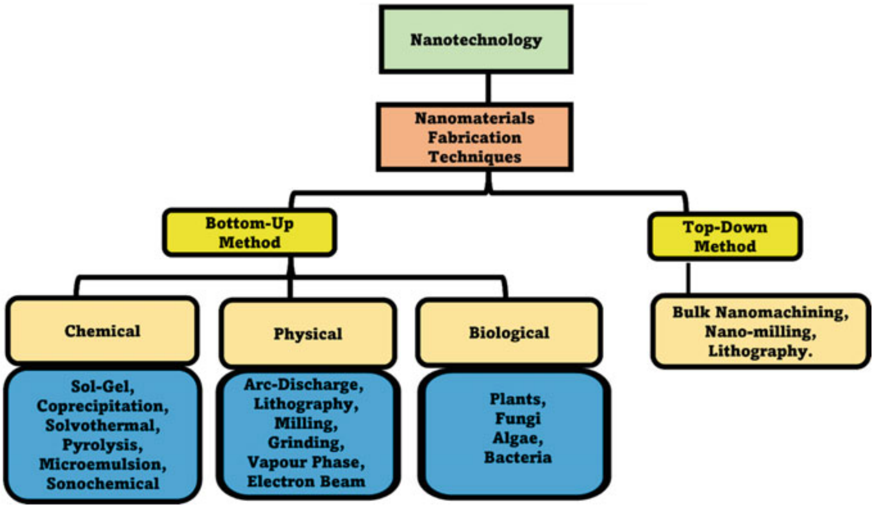

Fig. 1 Shows the various fabrication techniques utilized for the MNMs

covering techniques are employed, which include the use of inorganic (silica, gold, and dextran), polymeric (chitosan, polyethylene glycol, polyvinyl alcohol and alginate) and monomeric (phosphate and carboxylates) stabilizers [2, 4, 16, 25]. MNMs comprises of main magnetic materials and developing part(s) that gives functionality, which is generally referred to as shell(s). The coating and functionalization of MNPs aid to enhance and shielding the core to counter oxidation and instability while offering selectivity for the MNMs [26].

3 Application of MNMs for HMs and Dyes Sequestration

Presently, NMs have continued as an efficient, functional and green choice for existing treatment materials from the perspective of resource protection and ecological remediation. The development of new NMs has been a dynamic development study area in the NT field owing to its enhanced capacity, selectivity and affinity for contaminants. The superior sorption capacities (SCs) for contaminant sorption are associated with their huge surface-area, exceptionally small size, great reactivity and reusability properties, which help to enhance the water quality, water source accessibility and sustainability [16].

In most uses of MNPs, they accept on their surface sorbed molecules like contaminants removed from the water-soluble mediums. Yet, molecules sorbed on the surface of NPs regularly decrease the repulsive colloidal interactions among NPs and could inflame NPs aggregations. Such aggregations in the employed magnetic field (MF) dearth lead to an improvement in the active NPs size (primary aggregates) and with the MF application, the magnetic force (MAF) acting on the key aggregates is sturdily enlarged as compared to the state of individual non-aggregated NPs. In this instance, the sorbed molecules not just achieve their purpose in water treatments but also improves the control of NPs by MF and hence extend the MNPs' field of applications [27].

A well-thought-out flexible kind of material from a systematic and technical point of view is metal oxide-based NMs. They are a fascinating group of materials, which show distinctive properties such as mechanical stress forbearance, high-level optical precision, elevated surface-area and SC, outstanding carrier mobilities etc. MO surface plays a key part in the efficient interaction with various molecules and ions. Recent progress and development of MO-based NMs as well as their extraordinary characteristics have opened new possibilities and opportunities for the utilization of these materials in various fields and especially in the remediation of hazardous environmental pollutants [28]. For the efficient SP, the MNMs' morphology like surface-area, shape, pore-volume, point of zero (pH_{PZC}) and mesoporosity should be critically considered. Inorganic and organic composite properties should be collectively combined and utilized by MNMs, hence making it possible for a broad variety of contaminants sorption [26]. Given the significance of water and the developing uses of NT as an effective nano-sorbents for the sorption of HMs and dyes, NMs present a potential for the advancement of novel and possible solutions for tackling global water pollution using MNMs and their composites, which are characterized by the sorption conditions [22, 29]. Discussed in the next sub-sections are the detailed assessment of the various MNMs employed for the sorption HMs and dyes.

3.1 IO-Based NMs for HMs and Dyes Removal

In current years, nano-structured MO has shown to be the most excellent contender for effluent remediation through the SP. With the general attributes linked with NMs, MO NPs are no exemption owing to the huge pore-volume, surface-area, elevated SC, well-defined pore-sizes and sites functionalized. In the earth's crust, Fe is the fourth most copious element. Their accessibility and fabrication simplicity have ensued in NM's broad studies. NMs have faster sorption rates, superior SC and affinity for contaminants sorption. FeO-based NMs freely employed for noxious contaminants sorption from water and wastewater are maghemite ($\gamma - Fe_2O_3$), , magnetite (Fe_3O_4), hematite ($\alpha - Fe_2O_3$), goethite ($\alpha - FeOOH$), and hydrous ferric oxides (HFO) [15, 30]. IO comprise of anion structure, generally hexagonal or cubic, in which the vacuoles are partly covered with divalent or trivalent Fe, with the coordination prevalent in octahedral FeO_6, but tetrahedral coordination is also detected in Fe_3O_4 structure. IO properties are directly related to their morphologies, structures and size. Table 2 shows the various properties of IO [31]. The exceptionally conventional IONPs are Fe_3O_4 and Fe_2O_3 and owing to their iron oxidation states variance, they depict various physico-chemical features and mechanisms/efficacies towards the sequestration of pollutants [32, 33].

Magnetism is extremely volume reliant as it originates from the cooperative interaction of microscopic magnetic dipoles. With the reduction of the size of ferri or ferromagnetic particles to a critical value of approximately 40 nm, their magnetic properties transform from several domains to specific domains with elevated magnetic susceptibility as well as the thermal energy exceeding the energy barrier. With this size reduction, MNPs become superparamagnetic, losing permanent magnetic moments while reacting to an EMF and this permits straightforward separation

Table 2 Physical properties of various IO

Properties	Fe_3O_4	$\gamma - Fe_2O_3$	$\alpha - Fe_2O_3$
Lattice factors (nm)	a = 0.8396	a = 0.8347	a = 0.5034
Density (g/cm^3)	5.18	4.87	5.26
Colour	Black	Reddish brown	Red
Hardness	5.5	5.0	6.5
Magnetic status	Ferri- or superpara-magnetic	Ferri- or superpara-magnetic	Feebly ferro-magnetic
Crystallographic assembly	Cubic	Cubic or tetrahedral	Rhombohedral or hexagonal

and retrieval using a low-gradient MF. Superparamagnetism is highly reliant on the anisotropy constant and the particle volume. Spherical NMs are desired for effluent treatment owing to their comparatively superior kinetic energy and complementary to their ease of clearance. In addition to the elevated SC, $\gamma - Fe_2O_3$ and Fe_3O_4 can be superparamagnetic [26, 34].

FeO-based NMs are more attractive for the confiscation of contaminants from industrial discharge due to their key characteristics such as miniature size, superior surface-area, chemical stability, less noxiousness and magnetic properties [35, 36]. To enhance IONMs' performance, their blend with other materials and the creation of composites are perfect techniques. These IONMs composites have an additional surface-area, functional groups, stability and SC when equated with IONMs [28]. Existing uses of IONMs in contaminated water can be classified into technologies which employ IONMs as a type of nano-sorbent or an immobilization carrier for the confiscation efficiency improvement and those that utilize IONMs as photocatalysts to breakdown or change pollutants into reduced noxious form. But technologies can use both processes for the decontamination of pollutants. IONMs are presently being explored for organic pollutants sorption, especially for the effective remediation of huge volumes of wastewater samples and rapid separation through the use of sturdy peripheral MF. A great deal of research has been embarked on to assess the confiscation effectiveness of IONMs for organic contaminants [2, 37].

Fabricated polyvinlypyrrolidone layered MNPs (PVP-Fe_3O_4) were employed as a nano-sorbent for the confiscation of different HMs (Cd^{2+}, Cr^{6+}, Ni^{2+} and Pb^{2+}) from artificial soft water and seawater in the fulvic acid presence and dearth. It was reported in this that the % of MI confiscated reduced as the initial MI concentrations were improved from 0.1 to 100 mg/L. Using 0.1 and 1 mg/L concentrations of the four MI, it was noticed that 100% and 80% of MI were confiscated to PVP-Fe_3O_4 using 168 mg/L in artificial soft water and seawater are depicted in Fig. 2. The SP of the four MI was best described using the PSOR model, with general sorption of MI taking place in the first 1.5 h [38].

While in the study by Kera et al. [39], polypyrrole (PPy)-polyaniline (PANI)/Fe_3O_4 (PPy/PANI-Fe_3O_4) nanocomposites (NCs) were examined for the confiscation of Cr^{3+} and Cr^{6+} ions. Study findings show that the sorption of Cr^{6+} to the nano-sorbent was pH reliant, with the ideal removal noticed to pH 2 and credited to the electro-static attraction between the sorbate and the protonated active sites on the sorbent. The SP of Cr^{6+} to PPy/PANI-Fe_3O_4 NCs was ideally described using the Langmuir (LGR) and PSOR models and the optimum SC was 303 $mg.g^{-1}$ at 25 °C. Fabricated NCs based on ligands (meglumine) functionalized on Fe_3O_4 NPs were examined for the elimination of As^{5+}, Cr^{6+} and boron (B) (B^{3+}). The fabricated NCs were characterized employing FTIR, XRD, TGA and SEM spectrometry to ascertain the functional groups, crystalline structure, phase transition and morphology of the NCs. The LGR and PSOR best defined the MI sorption to the nano-sorbent and the determined SCs were 28.2, 12.3 and 23.7 $mg.g^{-1}$ for As^{5+}, Cr^{6+} and B^{3+}. It was also reported in this study that the prepared sorbent could be recycled for up to five-cycles and restored for three-cycles [40]. In this study, trioctyl phosphine oxide (TOPO) layered on Fe_3O_4 NPs was fabricated and utilized for the sequestration of

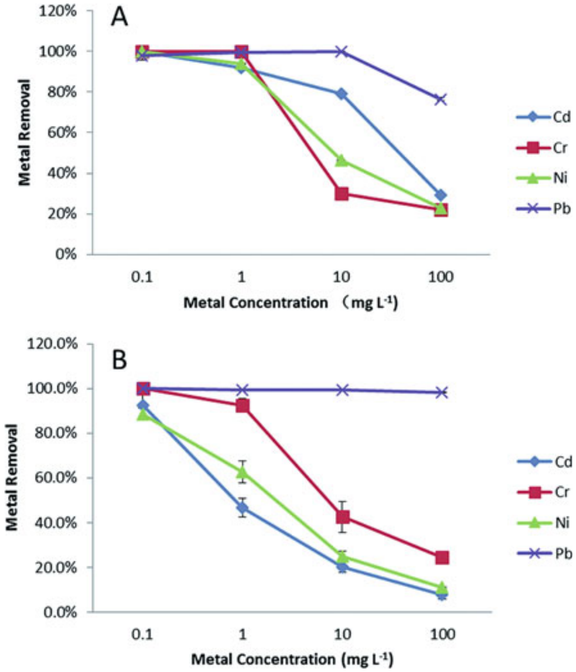

Fig. 2 Impact of MI speciation on PVP-Fe_3O_4 confiscation efficacy in **a** artificial soft water and **b** seawater. Adapted from Hong et al. [38]; Copyright, RSC Advances, 2020. Reprinted with permission from RSC Advances from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

MI of Ni^{2+} and Cd^{2+}. Study results show that the sorption of both MI was pH reliant and optimum sequestration of both MI was observed at pH 8 and 5. LGR model superlative suited the SP for both MI and the FRH model perfectly depicted the sorption of Ni^{2+}. The optimum SCs of both MI were 4.7 and 0.2 $mg.g^{-1}$. While the PSOR model ideally defined the SP of both MI. It was concluded in this study, that the prepared nano-sorbent could be used effectively for effluent remediation [41]. Ferric oxide (Fe_2O_3) was encapsulated with Co and Ni and used to confiscate Pb^{2+} ions. Study results show that the SP was perfectly defined using the pseudo-first-order (PFOR) and LGR and FRH models using Fe_2O_3 and Co@Fe_2O_3 and Ni@Fe_2O_3. The optimum SCs using the various nano-sorbents were 136.00 $mg.g^{-1}$ (Co@Fe_2O_3), and 97.5 $mg.g^{-1}$ (Ni@Fe_2O_3) [30]. While 3-aminopropyl)triethoxysilane (APTES) and glutaraldehyde (GA) encapsulated on MNPs were utilized for the elimination of Cu^{2+}. The best possible elimination of Cu^{2+} was detected at pH 6 and the SP was best defined using the LGR and PSOR model. The optimum SC was assessed to be 19.26 $mg.g^{-1}$ [42]. Mesoporous carbon capsules were captured on Fe_3O_4 NPs through the continuous and subsequent coating of silica and silica/carbon coating on the Fe_3O_4 NPs, which was trailed by chemical etching using NaOH. The prepared NCs were categorized by SEM coupled with BET to have a rattle-like structure with a particular surface-area of 1570 m^2/g and a total-pore-volume of about 3.02 cm^3/g. The prepared NCs were employed for the confiscation of different pollutants and it was found that the prepared nano-sorbent was effective for the sequestration of the various pollutants, with high optimum SCs of 608.04, 1656.90 and 108.38 $mg.g^{-1}$ for methylene blue (MB), congo red (CR) and phenol [43]. In the study by Qurrat et al. [44], where CoFeNPs were encapsulated with various amino regents (hydrazine and dodecylamine) to produce CoFeNPs1 and CoFeNPs2. The produced nano-sorbents were explored for the confiscation of azoic dyes (acid orange 7(AO7), naphthol blue black (NBB), reactive orange 16 (RO16), reactive red-P25 (RRP25), acid orange 52 (AO52) and amaranth (AMH)). The SPs for all dyes were perfectly depicted applying the PSOR model, while the LGR model depicted the interaction between RO16 dye and the nano-sorbents. The determined SCs from the LGR model were 65.57 and 74.07 mg.g^{-1} using CoFeNPs1 and CoFeNPs2. Thermodynamically, the SP of RO16 dye was spontaneous and exothermic as well as slight randomness at the solid–liquid boundary. Alkali cation was encapsulated into IONPs and employed for the efficient removal of methyl blue (MB). MB sorption to IONPs was explained by the PSOR model. It was reported in this study that the functional groups of -OH, -Cl as well as alkali cations present on the NPs surface substantially impacted the sorption of MB [45]. While chitosan encapsulated on Fe_3O_4 and was used to confiscate Evans blue dye. It was reported that the sorption of this dye was pH reliant, with ideal elimination detected at pH 4, which was promoted due to the electrostatic interaction between the sorbent and negatively charged sulfate groups on the sorbate. The sorption of this dye was ideally defined using the LGR model, which was indicative of the monolayer sorption of dye molecules to the sorbent surface and the assessed SC was 243.90 mg.g^{-1}. A subsequent test of the prepared sorbent for the confiscation of other anionic dyes shows the sorbent to be effective in capturing the various dye molecules [46]. In this study, Purpureocillium lilacinum was employed to mycosynthesize Fe_2O_3 and employed as a sorbent for the basic blue 41 (BB41) dye. The prepared nano-sorbent was found to be effective in the decontamination of dye molecules [47]. While Fe_3O_4 functionalized with activated carbon (AC), β-cyclodextrin and alginate polymer NCs (Fe_3O_4/AC/CD/Alg) were fabricated and employed for MB sequestration. At above pH 3, the sorption of this dye was improved and ascribed to the electro-static interaction between the positive dye molecules and immobilized negatively charged sites on the sorbent. The LGR model best-depicted dye molecules sorption to the sorbent and the assessed optimum SC was 2.08 mg.g^{-1}. While the PSOR best modelled the SP and the SP was thermodynamically spontaneous, endothermic and with high randomness [48]. Sarojini et al. [49] and Zhao et al. [50] fabricated PPy/IO-seaweed NCs and $ZnFe_2O_4$ and applied the fabricated sorbents for the effective confiscation of CR and MB, and auramine O (AO) and Cd^{2+}. The sorption of CR dye was pH reliant and with optimum sorption taking place at pH 3. Both SPs using the various prepared sorbent were ideally defined using the LGR and the PSOR model. The assessed optimum SCs for CR, MB, AO and Cd^{2+} using PPy/IO-seaweed NCs and $ZnFe_2O_4$ were 500, 256.76, 201.29 and 152.48 mg.g^{-1}. Thermodynamic results for CR sorption show that the process was spontaneous, endothermic, and with enhanced randomness. Table 4 gives a summary of the non-exhaustive list of IONMs and their effectiveness in the confiscation of diverse HMs and dye as well as their various SCs.

3.2 Ce-Oxide Based NMs for HMs and Dyes Elimination

Cerium(VI) oxide (Ceria-CeO_2) is a lanthanide, an extremely valuable rare-earth material with a face-centred cubic structure owing to its sturdy ability to store, release and transport oxygen (O_2), confiscate pollutants from mediums, non-noxiousness, minimal cost, and effective in the performance of the electrocatalytic process. It has greatly been explored in sensors, supercapacitors, fuel cells etc. CeO_2 attributes are generally associated with the relationship between its valence state Ce^{3+} and Ce^{4+} (with sturdy redox capacities) and their morphology and structure. Also, when the medium is distinctive with O_2, it is transformed back into CeO_3. Currently, CeO_3 has been studied as a material having excellent features and which has been utilized in various functions such as catalytic-reactions, biologic purposes, and treatment of wastewater containing various pollutants. It is applied in wastewater treatment owing to the occurrence of various anions from O_2 and cations from Ce on its key structural surfaces. However, CeO_2 contains specific O_2 vacancies on its surface and this has an impact on the SP and sorbent reactions [51–53]. CeO_2 performance is derived from the chemical effect at their surface and their reactivity is associated with the defects on the surface. The elevated surface-area of CeO_2 blendes with flexible geomorphologies presents a plus for pollutant sequestration. Morphology tailoring and size of particles are critical in creating huge surface-areas and innumerable sorption sites for capturing pollutants from water effectively [54].

NCs of CeO_2/ZnO and CeO_2/ZnO were fabricated and used as a sorbing material for Cr^{6+} in this study. The optimum sequestration of Cr^{6+} ions was reported at pH 7 and the process of Cr^{6+} sorption to both nano-sorbents was defined using the PSOR and the monolayer LGR models [55]. CeO_2/corncob NCs were prepared and applied as a nano-sorbent for the effective confiscation of Cd^{2+} and Cr^{6+} ions. Optimum sequestration of these MI was noticed at pH 9. SPs for each MI were defined by the PSOR and intraparticle diffusion (IND) models [51]. While CeO_2 NPs coated to reduced graphene oxide (rGO) (CeO_2/rGO) were obtained via in-situ growth and self-assembly technique and were explored as a useful sorbent for the capturing of Cd^{2+}, Pb^{2+} and Cr^{6+} at pH 5.56. Pb^{2+} sorption was best-defined using the LGR model, while Cd^{2+} was perfectly described utilizing the FRH model. The assessed SCs for Pb^{2+} and Cd^{2+} were 95.75 and 31.26 using various fabricated CeO_2/rGO-HMT and CeO_2/rGO-AM [56]. In the work of Fouda-Mbanga et al. [57], nitrogen-doped carbon NPs were layered on CeO_2 to create N-CNPs/CeO_2NRsnC and were employed for the confiscation of Cd^{2+}. The prepared nano-sorbent was found to be effective in the treatment of Cd^{2+} contaminated aqueous solution at pH 8. The SP was also discovered to be thermodynamically spontaneous and endothermic at ambient temperatures. Through the impregnation technique, ZnO/CoO_x/CeO_2 NCs were fabricated and utilized for the confiscation of CR via sorption-photocatalysis cooperation. Under ideal settings, 98.8% of CR dye molecules were confiscated and the stability test of the prepared materials shows that the prepared material upheld nearly the same confiscation after 4 cycles of the SP [58]. Employing hydrothermal and sol-precipitation techniques,

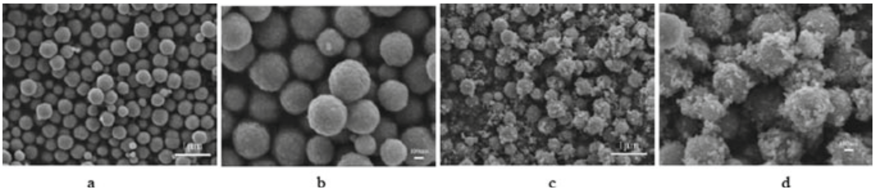

Fig. 3 SEM images (**a** and **b**) Fe_3O_4 and (**c** and **d**) Fe_3O_4/CeO_2 NCs. Adapted from Zhihao et al. [59]; Copyright, Materials Science, 2022. Reprinted with permission from Materials Science from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

magnetically separable Fe_3O_4/CeO_2 NCs were prepared and used for the eradication of acid black 210 (AB210) dye. The morphology from SEM (Fig. 3a, b) shows uniform distributed spherical particles of Fe_3O_4, with a mean diameter of 400 nm. While from Fig. 3c, d, limited openings on the Fe_3O_4 surface are noticed, which was indicative of non-uniform covering of CeO_2 on the Fe_3O_4 NPs. While the saturation magnetization (M_s) of the Fe_3O_4 NPs and Fe_3O_4/CeO_2 NCs were determined to be 69.1 and 22.9 emu/g. The reduction in the M_s value in Fe_3O_4/CeO_2 NCs was ascribed to the coating of CeO_2 on the NPs, which reduces the magnetization of the NPs (Fig. 4). The SC for AB210 dye was reduced with growing pH and was heightened with improving dye concentration and temperature. The SP was effectively specified utilizing the PSOR and the LGR model. The assessed SC of the sorbent was estimated to be 124.5 $mg.g^{-1}$ [59].

While self-assembled Mxene-CeO_2 NCs prepared via the hydrothermal technique were used for the elimination of rhodamine B (RhB) and MB dye molecules. The fabricated NCs were shown in this study to be effective in the elimination of RhB and MB dye molecules and could be employed in the degradation or treatment of dye molecules [60]. Also, AC improved by bimetallic Fe and Ce NPs was employed for the use of MB and RhB sequestration. The fabricated NCs were found to be effective for the sorption of MB and RhB dyes and the sorption equilibrium was reported to fit the LGR and PSOR models, with an established SC of 324.6 $mg.g^{-1}$ for RhB dye [61]. Table 4 gives a summary of the non-exhaustive list of CeO_2 and their NCs' effectiveness in the sequestration of different pollutants as well as their diverse SCs.

3.3 Ti-Oxides Based NMs for HMs and Dyes Elimination

One of the most valuable MO-based NPs is TiO_2, which has been utilized in various disciplines, particularly in industrial productions [28]. TiO_2 NPs are largely employed in putrefying organic matter in effluents, skincare and cosmetic products, paints, and antibacterial and cleaning air products [62]. Owing to their photocatalytic, ingrandness, chemical stability, and simplicity of fabrication of TiO_2 NPs, they are a prospective contender for the elimination of noxious pollutants from effluents

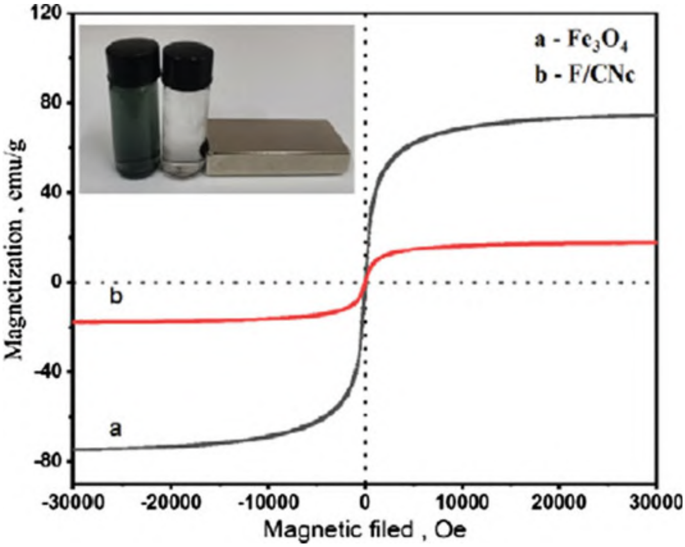

Fig. 4 Hysteresis loops of Fe_3O_4 and Fe_3O_4/CeO_2 NCs. Adapted from Zhihao et al. [59]; Copyright, Materials Science, 2022. Reprinted with permission from Materials Science from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

and artificial aqueous-mediums. The generally employed phase structures which are important for manufacturing use are anatase and rutile, which is distinct from brookite [15].

A new NC N–TiO_2-α-Am.Ph, fabricated by the surface modification of nano TiO_2 (N-TiO_2) with α-aminophosphonates (α-Am.Ph) was applied for the uptake of Cu^{2+} and Pb^{2+} ions. Optimum confiscation of MI was reported at pH 7 and the PSOR and LGR models best define the SP between Pb^{2+} and Cu^{2+} and the NCs. All four isotherm models appropriately described the process of sorption involving Cu^{2+} and the NCs. Exploring the NCs in the sequestrating of MI from drinking water and industrial effluents, it was found that 90–94% recovery was achieved by employing the micro-column system [63]. Employing the sol–gel techniques, TiO_2 NPs were fabricated in this study. The prepared TiO_2 NPs were evaluated for Pb^{2+} ions confiscation. The TEM image shown in Fig. 5, shows aggregated NPs with a mean diameter of 21.1 nm. pH 6 was found to improve the removal efficiency of Pb^{2+} using the NPs and kinetic data show that the PFOR and PSOR models define Pb^{2+} sorption to the NPs. While the LGR model perfectly defines the SP and the optimum SC of 7.41 $mg.g^{-1}$ was determined at 25 °C. Outcomes from this research show that prepared TiO_2 was effective in the confiscation of Pb^{2+} ions [64].

While TiO_2/GO NCs were prepared and employed for Cu^{2+} and Pb^{2+} elimination. The result from the batch experiments carried out showed that MI was efficiently removed from an aqueous-medium using the prepared NCs, with optimum elimination of 69.36 and 89.00% noticed for Cu^{2+} and Pb^{2+} ions in ideal circumstances [65]. Employing the hydrothermal method in this study, TiO_2 NPs were fabricated. The

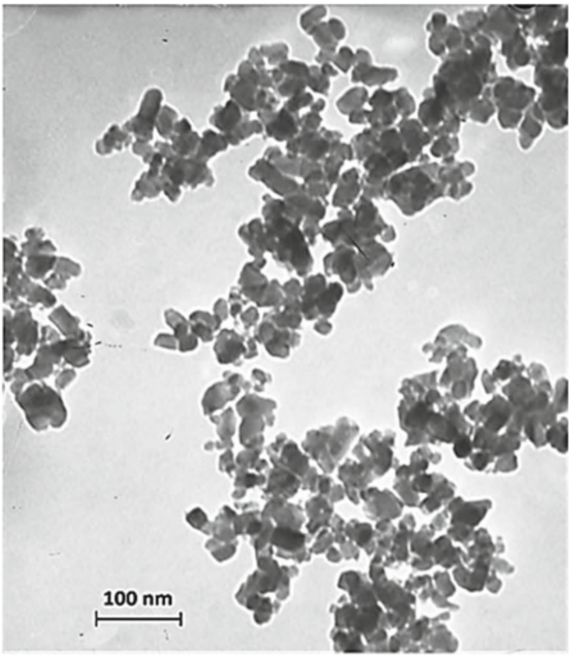

Fig. 5 TEM image of prepared TiO_2 NPs. Adapted from Poursani et al. [59]; Copyright, Scientific Research, 2016. Reprinted with permission from Scientific Research from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

fabricated NPs were tested for the effective confiscation of various MI (Pb^{2+}, Cu^{2+}, Fe^{3+}, and Zn^{2+}). The fabricated NPs were discovered to be useful in the sequestration of various MI from an aqueous-medium [66]. Also, prepared TiO_2 coated with MWCNTs (TiO_2/MWCNTs) was found to be effective in the confiscation of Pb^{2+} ions. The PSOR and LGR models efficiently define the SP involving Pb^{2+} ions and the NCs. The determined SCs using the NCs were 137.0 and 33.0 $mg.g^{-1}$. Thermodynamically, the interaction between Pb^{2+} and the NCs was spontaneous [67]. Nickel ferrite/TiO_2 ($FeNi_3/TiO_2$) NCs were created and evaluated as a prospective sorbent for Cr^{6+} elimination. Study findings show that the sorption of Cr^{6+} ions to the NCs was reliant on the contact time, pH, sorbent dosage, and initial Cr^{6+} concentration. The FRH and PSOR models define the SP of Cr^{6+} and the SC was assessed to be 76.34 $mg.g^{-1}$ [68]. While the efficiency of prepared TiO_2 and γ-Al_2O_3 nanosorbent was explored for Cu^{2+} confiscation under various chemical factors. The FRH and PSOR models were found to describe Cu^{2+} ions sorption and the determined SCs 9288 and 3607 mg/kg at solution pH 8. Thermodynamically, the interaction of Cu^{2+} to the NPs was spontaneous [69]. Employing chitosan beads (CS) cross-connected with glutaraldehyde (GLA), GO and TiO_2, two nano-sorbents were fabricated (CS-TiO_2-GLA and CS-GO-TiO_2-GLA) and which were utilized for the decontamination of FD and C Red 40 (CR40). The optimum sequestration of dyes molecules was reported at pH 1.73 and the sorption of both dyes was defined using the IND model. This study showed the possibility of employing the prepared sorbent for the sequestration of anionic dyes [70]. CR and phenol red (PR) dyes were confiscated from an aqueous-medium using TiO_2 coated with AC (TiO_2/AC NCs) made from watermelon rind (WR). The results of the SPs of both dyes were effectively defined by the LGR and PSOR models [71]. While TiO_2 doped with PANI was used as a sorbent for methyl orange (MO) confiscation from an aqueous-medium. It was found that the sorption of this dye was reliant on the contact time, dosage, initial MO concentration and pH. The LGR and PSOR models were found to best define the sorption of MO dye to NCs. The determined SC was 136.9 $mg.g^{-1}$ [72]. Table 4 gives a summary of the non-exhaustive list of TiO_2 and their NCs' efficiency in the confiscation of diverse contaminants as well as their various SCs.

3.4 Al-Oxides-Based NMs for HMs and Dyes Elimination

In light of the relentless growth in the NT field and its usage in environmental contamination remediation/treatment, there has been growing attention to the use of MO such as sorbents for the sequestration of contaminants from the ecosystem especially Al-oxide NPs owing to their low-cost, elevated surface-area, the reactivity of their surface, better SC, surface acidity and thermal stability [73]. Amongst the different MO NPs, Al-oxide-based NMs have economical construction costs and elevated decontamination effectiveness. Most importantly, Al-oxides NMs were reported as the most excellent existing tools for the sequestration of As by the United Nations Environmental Program (UNEP) agency [28]. Alumina (Al_2O_3) appears in various structural forms naturally like α-Al_2O_3, γ-Al_2O_3, θ-Al_2O_3, η-Al_2O_3 etc. It is distinguished by its non-noxious, easy usage, chemical stability and many OH^- groups, all these properties make it an effective sorbent for the sorption of contaminants [21].

Fabricated Al_2O_3 NPs altered with humic acid (Al-H), 1,5-diphenyl Carbazon (Al-C), and walnut shell extractant (Al-W) were used to confiscate MI such as Cd^{2+}, Cu^{2+} and Ni^{2+}. The sorption of these MI was relatively reliant on the solution pH and the PSOR model best defines the sorption kinetics of these MI. While the LGR model matched well with the sorption kinetic data from the study and the assessed SCs using Al-H, Al-C and Al-W were 92.0, 63.8 and 97.0 $mg.g^{-1}$ [74]. While carbon dots layered on Al_2O_3 (CD/Al_2O_3 NCs) were assessed as a possible sorbent for effective sequestration of Pb^{2+} ions. Pb^{2+} ions sorption to the NCs was best defined by the FRH and PSOR models. The assessed SC was 177.83 $mg.g^{-1}$. The interaction between the sorbate and sorbent was determined thermodynamically to be spontaneous and endothermic. Six sorption–desorption cycles were reported using these NCs for Pb^{2+} ions sorption, which showed decent stability and reusability of the prepared nano-sorbent [75]. Al_2O_3 modified with GO (Al_2O_3/Mn/GO) was explored for the elimination of Cd^{2+} ions. The ideal elimination of this MI was reported at pH 7 and the maximum sorption assessed at this pH was 120.48 $mg.g^{-1}$. The LGR and PSOR models ideally described the SP between Cd^{2+} and the NCs [76]. Produced Al_2O_3 nanofibre via electrospinning techniques (stable spinning voltage of 17–20 kV and flow rate of 0.5 ml/h), was explored for Ni^{2+} sequestration in this

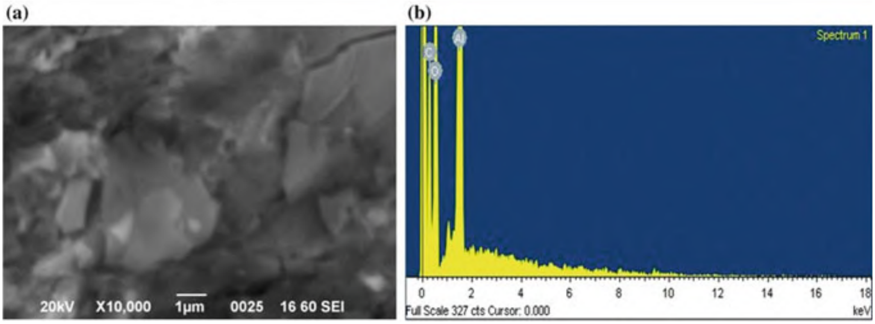

Fig. 6 **a** SEM image of Al_2O_3 and **b** EDX analysis of Al_2O_3. Adapted from Bhargavi et al. [78]; Copyright, Springer Nature, 2015. Reprinted with permission from Springer Nature from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

study. The behaviour of the sorbent was best defined by LGR and PSOR models [77]. Fabricated Al_2O_3 NPs utilizing the solution combustion method were employed for the sequestration of Zn^{2+} and clour black G (CBG) dyes. The SEM image in Fig. 6a depicts a clear surface required for sorption. It also shows the accessible nano-size pores and cavities on the sorbent surface, which are evident in the significantly enhanced SC of the prepared sorbent. Analysis of the EDX result shows that the major components of the prepared nano-sorbent were C, Al and O atoms as depicted in Fig. 6 (b). The optimum confiscation of Zn^{2+} and CBG dye was at pH 7 and 2. The LGR and PFOR models best define the SP and the assessed SCs were 1047.83 and 262.16 $mg.g^{-1}$ for Zn^{2+} and CBG dye [78].

While Al_2O_3 coated with various doping ions was explored for the effective confiscation of indigo carmine (IC) dye. It was found that the LGR and PFOR and liquid film diffusion (LMD) models best fitted the sorption of IC dye to the NCs. The assessed SC was 456.3 $mg.g^{-1}$ and the interactions were thermodynamically spontaneous and endothermic [79]. Al_2O_3 layered with ZnO was found to be very effective in the treatment of water-soluble medium with MO and CR dyes in the studies of Tajizadegan et al. [80] and Bello et al. [81]. The SP for CR sequestration was ideally described by applying the LGR and PSOR and the assessed SC was 33.39 $mg.g^{-1}$. Thermodynamically, the reaction between the sorbate (CR) and sorbent was spontaneous and endothermic. Table 4 gives a summary of the non-all-inclusive list of Al_2O_3 and their NCs' efficiency in the confiscation of diverse pollutants as well as their various SCs.

3.5 *Mn-Oxides Based NMs for HMs and Dyes Elimination*

Mn-oxide (MnO_x) is a common MO NMs that has fascinated a lot of interest. They have distinctive catalytic activity, high energy and magnetic nature. One of the MO-based NPs, which is inexpensive and environmentally friendly is MnO_2. Exceptional features such as extraordinary surface-area and SC of MnO_x-based NMs, make them outstanding applicants in gas sensors, energy storage, catalysts and decontamination of various pollutants [28]. This metal oxide shows structural suppleness and occurs in different polymorphic attributes like α, β, γ (having chain-like tunnel-form), δ (layered type) and λ (spinel-type) based on the inter-associating of MnO_6 octahedra configuration. δ form has an encrusted structural form (birnessite) and is recognised as one of the highly reactive polymorphs. Mineral pyrolusite, which is the natural source of MnO_2 is a poor sorbent and oxidizing reagent, hence its functionalization is imperative [82].

MnO_2 is preferred among other MO in diverse processes owing to their cost efficiency, eco-friendliness and their unique characteristics like the ability to make various morphological structures, elevated surface-area, minimal renewal costs, elevated oxidative degradation effectiveness, and distinctive crystal structure. Their polymorphs and polyvalent properties make them excellent catalysts in organic contaminants sequestration. Owing to the elevated surface energy in MnO_2 they tend to amass and have low resolution. To avert this and increase their affinity and SC for contaminants, MnO_2 surfaces are functionalized or modified [83–85]. The exceptional SC, and minimal cost. modest noxiousness, great availability and green behaviour offered by Mn-oxide make it a good sorbent for pollutants remediation [86]. CdO/MnO_2 NCs created by a modest chemical technique was utilized for the sequestration of methylene orange (MO) dye. The sorption of this dye was found to be ideally defined by the LGR and the PSOR models. The interaction between the dye molecules and the NCs was also found to be non-spontaneous and endothermic [87]. While GO embedded on CS was layered on MnO_2 to create α-MnO_2/GO-CS NCs and employed for the amido black 10B (AM10B) and MB dyes in this study. The TEM images in Fig. 7a–d were assessed to verify the size and morphology of the prepared NCs. Figure 7a, b shows rod-like shapes with an identical size of MnO_2 NPs. While Fig. 7c, d confirms the formation of α-MnO_2/GO-CS NCs with an approximate size of 700 nm length and 15.5 nm thickness. It was found that NCs were effective in the elimination of both cationic and anionic dyes. MB sorption to the NCs was best described by applying the LGR and PSOR models. The assessed SCs for MB and AB10B were 328.9 and 150.6 $mg.g^{-1}$. The prepared NCs were also found to be stable after 10 successive recyclability tests [88].

In the study by Omorogie et al. [89], Terminalia ivorensis biomass was improved by MnO_2 and employed for MO and CR confiscation. The ideal removal of both dyes was found at pH 2 and the sorption of both dyes (MO and CR) was defined by the LGR-FRH model and the SCs were 81.32 and 92.84 $mg.g^{-1}$. The mixed 1, 2 models (PFOR and PSOR) described the SP of both dyes. At 298 K, the interaction between the sorbent and dye molecules was non-spontaneous and above this

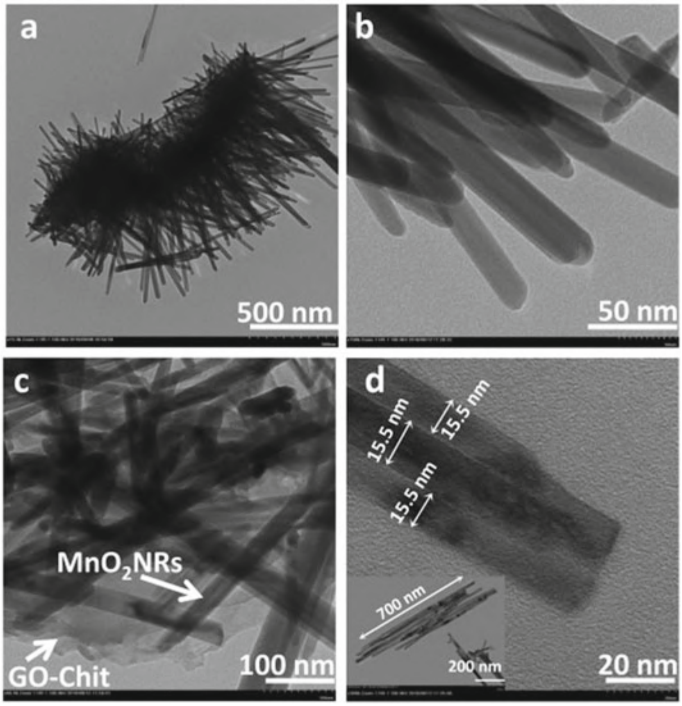

Fig. 7 TEM images (**a**, b) of α-MnO_2 NPs and (**c** and **d**) α-MnO_2/GO-CS NCs. Adapted from Rajendiran et al. [88]; Copyright, Elsevier, 2022. Reprinted with permission from Elsevier from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

temperature, the interactions were spontaneous and endothermic. While copolymer beads coated on MnO_2 were employed for the elimination of MB and RhB dyes. The prepared NCs were found to be effective in the elimination of both dyes and the LGR model fitted more to the sorption equilibrium results for both dyes. The assessed SCs were 18.45 and 3.13 mg.g^{-1}. The findings indicated that the prepared NCs were an effective material for the sequestration of organic pollutants [90]. Multi-functional magnetic sorbents composed of MnO_2 and PANI (Fe_3O_4/PANI/MnO_2 NCs) were utilized in the sequestration of Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+} ions. The sorption of Cd^{2+} was highly reliant on the solution pH, with optimal sequestration of Cd^{2+} ions noticed at pH 6.3. The equilibrium sorption data fitted the LGR model and the assessed SC was 154 mg.g^{-1} [91]. While polythiohene (PTh)/MnO_2 NCs were prepared through the green fabrication procedure and utilized for the elimination of Pb^{2+}, Cu^{2+} and Zn^{2+} ions. The sorption of all MI was explained by the PSOR and LGR models. The assessed SCs for Pb^{2+}, Zn^{2+} and Cu^{2+} were 82.10, 30.72 and 60.79 mg.g^{-1}. The prepared NCs were shown by experimental data, DFT calculation and characterization to be effective towards the sequestration of MI. They were also found to be stable after five cycles of reusing NCs [92]. A redox precipitation technique was employed to fabricate MnO_2 loaded on biochar (BC) which was pyrolyzed from invasive hyacinth (BC/MnO_2), which was employed to assess the sorption of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}. The sorption of the various MI was perfectly defined using the LGR and PSOR models. The optimum SCs for Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} were found to be 216.22–351.37, 66.48–151.43, 48.90–103.91, and 31.25–68.36 $mg.g^{-1}$ [93]. While a magnetic sorbent was fabricated with Fe_3O_4 layered on MnO_2 and assessed as an effective sorbent for the confiscation of Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+} ions. The removal efficiency using the NCs was reported to be within the range of 83.23–99.81% for all MI at a pH of 6.5. The PSOR and the LGR did describe the sorption of all MI to the NCs and the SCs were determined to be 498, 439, 416.5 and 490 $mg.g^{-1}$ for Cu^{2+}, Cd^{2+}, Zn^{2+}, and Pb^{2+} [94]. Table 4 gives a summary of the non-all-inclusive list of MnO_2 and their NCs' efficiency in the confiscation of diverse pollutants as well as their various SCs.

4 Effects of Various Factors on the HMs and Dyes Sorption to MNMs

Normally, the SP of various HMs and dyes to different nano-sorbents is generally impacted by various environmental parameters like sorbent dosage, sorbate initial concentration, rate of agitation, pH, contact time, temperature and the used sorbent material's physical features comprising of the sorbent surface-area and the size of the particles. The SP is assumed to be attained when equilibrium is realized between the contaminants and the sorbents. The impacts of these various factors on the SP of HMs and dyes are discussed in the next sub-sections [7, 11, 95, 96].

4.1 Impact of pH

The pH is a key factor that influences the sorption of HMs and dyes and controls contaminants speciation and surface charge of the sorbents as well as directly impacts the SCs [7, 16, 21, 96]. Solution pH variation can precisely impact the effectiveness of the SPs owing to the surface of materials protonation, the altering of the sorbent surface properties and the charge of the pollutants [97]. The surface charge and potential are critical in forecasting the creation of surface complexes, ion transfer, surface reaction etc. [4]. The pH_{PZC} is a mutual way to estimate or describe the electro-kinetic features of a solid surface by assessing the pH at which the net surface charge of the solid surface is zero/null. It is entirely employed to denote pH_{PZC} in systems where the primary determining ions are H^+ and OH^- [95]. With increasing pH higher than the pH_{PZC}, the active surface sites on the sorbent become deprotonated and the active sites on the surface of the sorbent become more negative and consequently improve on the electro-static interaction with the positively charged contaminants. But at pH values lower than the pH_{PZC}, the active sites on the sorbent surface become protonated and they become positively charged. This consequently improves the interaction between the positively charged active sites on the sorbent and the negatively charged contaminants electro-statically [98].

Distinctive water pH levels are because of ecological changes, hence, it is crucial to ascertain the ideal pH values for elevated confiscation of HMs and dyes from contaminated water [21]. Researching the impact of pH is important for HMs and dyes sorption/decontamination. The sorbent material's surface charges and acidic and basic compound's ionization degree are delicately impacted by pH. Hence, the rate of pollutant uptake might be improved or reduced based on the primary pH value. As a consequence, hydroxyl (OH^-) and hydrogen (H^+) ions are sorbed with excellent efficacy, thereby improving the capability of the SP as the operational groups of the sorption sites split and which leads to a variation in the kinetics of the reaction and the equilibrium attributes. Normally at low pH values, dyes uptake rates are impacted and are reduced and enhanced for cationic and anionic dyes [95]. HMs ions mostly exist in species of Me^{2+}, $Me(OH)^+$ and $Me(OH)^2$ (where Me refers to Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}) at various values of pH in an aqueous-medium. At low pH, Me^{2+} is the main species, which may be hydrolyzed to create $Me(OH)^+$ and $Me(OH)^2$ with enhancing pH values. A key role is played by the precipitation ($Pb(OH)^2$ (precipitation constant (PC)- 1.2×10^{-15}), $Cu(OH)^2$ (PC-2.2×10^{-20}), $Zn(OH)^2$ (PC-1.2×10^{-17}) and $Cd(OH)^2$ (5.27×10^{-15})), when the $pH > 9.7$, $pH > 7.4$, $pH > 8.0$ and $pH > 11$ corresponds to MI concentrations [94]. As observed in Table 4, the sorption of most MI species was enhanced with increasing pH, with the sorption of most pollutants taking place with the pH range of 2–9.6. The mechanism of MI uptake varied at different pH values as the solution pH impacts the structure of the sorbent surface and the sorbate structure present in an aqueous-medium [99].

4.2 Influence of Sorbent Dose

In studying the sequestration of contaminants from industrial effluent, a key factor is the sorbent dose, which is required to select the ideal sorbent dose to decrease the treatment process cost [98]. The extent of contaminants confiscated by the SP is directly proportional to the amount of sorbent utilized [21, 100].

As reported in the studies of Babudurai et al. [101], Horst et al. [6], Nodeh et al. [102], Kataria et al. [103], Safari et al. [104], Wen et al. [105], Zhao et al. [50], Oukebdane et al. [106], Kumari et al. [107], and Panahadeh et al. [40], improvement in the sorbent dosage led to an increase in the number of active sites on the sorbent surface for sequestrating HMs and dyes, thereby causing a considerable increase in the percentage (%) of confiscation of pollutants. With a subsequent rise in the sorbent dosage, there is a reduction in the active sites owing to the decrease in the sorbent surface-area, which is heightened by the enhancement in the number of NPs present owing to aggregation, and this greatly decreases the % of pollutants removed. Research papers reviewed showed that improvement in the sorbent dose led to an improved confiscation of contaminants owing to the improvement in the surface-area of the sorbent and hence an enhanced number of accessible active sites available on the sorbent surface for the SP.

4.3 Influence of Contact Time

Another critical factor in the SP which is employed to predict the mechanism of sorption is the contact time that is mandatory for the confiscation of different contaminants from effluents onto the sorbent material [98]. From the commercial and technological point of view, sorption time as a performance factor is important. Hence, contact time optimization will lead to the creation of an applicable technique for contaminants treatment and can also be efficient in assessing water and effluent treatment costs [97]. Generally, the extended contact time of the SP enhances the SC and the efficiency of pollutant confiscation. At the beginning of the SP, the quantity of pollutants sorbed to the surface of the sorbent increases fast and slows down and achieves equilibrium after some time. This is attributed to the quantity of the sorbed pollutant at the dynamic equilibrium phase. The critical contact time to attain the stability state is known as the stability time and the quantity of the sorbed pollutant at the stability time mimics the ultimate sorbent material sorption rate under the operational requirements [21, 50, 95, 100, 102, 103, 106].

4.4 Influence of Initial Sorbate Concentration

A vital energetic force that is delivered to enhance mass transfer resistances of pollutant molecules between the water-soluble medium and the solid phase is the initial concentration. At minimal concentrations, the proportion between the preliminary quantity of pollutants molecules to the accessible sorbent surface-area is low and hence, the sorption rate is not affected by the preliminary pollutant concentration. However, the unoccupied sorption sites become fewer at higher pollutant concentrations and thus, the rate of pollutants confiscation depends on the initial pollutant concentration [95]. Normally, the stability of the SC enhances with rising contaminant concentration, which is suggestive that a higher preliminary contaminant concentration will improve the SP. But the percentage of pollutants confiscated reduces with improved initial contaminant concentrations [50, 98, 103, 106, 108–110].

5 Isotherms and Kinetic Models for the SP of HMs and Dyes to Various MNMs

Kinetic models define the association between the sorbed sorbate amount (q_t) and the contact time (t) for the SP. Because of chemical reactions' existence, kinetic projections are important for the design of the sorption system and reaction rate controlling step determination. Furthermore, the nature of sorption changes with the physio-chemical classification of the sorbent and the condition of reactions like pH, ionic strength, dosage, and temperature. The most used kinetic models consist of the PFOR and PSOR, Elovich (ELH) and IND models [15].

The sorption reaction model regulates the sorption functioning and mechanisms. The PFOR was introduced by Lagergren in 1898 to define the process of liquid–solid phase sorption of oxalic acid and malonic acid to charcoal. It is considered as the most basic model relating to the sorption rate based on the SC. While in 1998, Ho define the process of the sorption of divalent MI to peats, in which the chemical bonding between the divalent MI and polar functional groups on peats is liable for the peat cation-exchange capacity. This fundamental theory is that sorption may be second-ordered and the rate limiting steps may be chemical sorption connecting valent forces via sharing or interchange of electrons between the peat and divalent MI. Also, Ho's second-order rate equation (PSOR) is employed to distinguish kinetic equations on the SC for solution concentration. Weber and Morris in 1962, hypothesized that the IND rate changes comparably with the half power of time. According to the theory by Weber and Morris, the limiting step rate is IND, a plot of the solute sorbed against the square root of the contact time will produce a straight line passing via the origin of the graph. However, the rate constant for IND is gotten from the curve incline [111]. The PFOR model is relevant when the percentage of sorption sites occupation is relative to the amount of sorbents' unoccupied sites. While the PSOR processes are hugely impacted by the number of sorbate ions on the surface of the sorbent and the equipoise concentration of the sorbate ions [98].

The sorbate and sorbent interaction is suggestive of the sorption isotherm and the factors resulting from these different models give facts about the SP. An isotherm is also a critical tool for evaluating the distribution of sorbent over liquid solid borders and their SC assessment. Hence, isotherm research data are employed to create an applicable sorption system [97]. The use of sorbents with a high particular surface-area involves achieving sorption equilibrium at a rapid time owing to the quicker kinetics for the pollutants' confiscation. While in the SP, the SC of the nano-sorbents is determined by employing different isotherm models. The most common models that are generally employed to assess the SC are the LGR and the FRH models. The LGR model is essentially associated with the idea that sorption happens on a monolayer and with no additional sorption taking place after saturation [112].

The LGR model was created by Irving Langmuir in 1916 and is the top extensively utilized isotherm model for studying sorption. While the FRH model was proposed in 1991 by Freudlich to explain the mathematical model to a non-linear isotherm, which will result in a clean empirical formula for sorption on multiple sites [41, 98].

Table 3 Kinetic and isotherm models

Models	Linear expression	Parameters
PFOR	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}$	$q_{e,}$ q_t and k_1 indicate the SC at equilibrium ($mg.g^{-1}$), SC at time t ($mg.g^{-1}$) and PFOR rate constant (min^{-1})
PSOR	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2 is the PSOR rate constant (g/mg.min)
IND	$q_t = k_F t^{1/2} + c$	k_F and C denote the IND rate constant ($mg.g^{-1}.min^{1/2}$) and the intercept of IND
LGR	$\frac{1}{q_e} = \left(\frac{1}{Q_m K_L}\right)\frac{1}{C_e} + \frac{1}{Q_m}$ (Type 2)	Q_m, K_L, and C_e indicate the monolayer SC ($mg.g^{-1}$), sorption equilibrium constant (L/mg) and sorbate equilibrium concentration (mg/L)
FRH	$\ln q_e = \left(\frac{1}{n}\right)\ln(C_e) + \ln(k_f)$	n and K_f indicate the FRH constants

The LGR model symbolizes one of the dependable laws of physics regulating the SP, which is centred on the theory that the sorbate is particularly layered and consistent, sorption bonds are flexible and sorption energy is the objective of the sorbed amount of sorbate on the sorbent. While the FRH model adopts that sorption happens on diverse sorbent surfaces and making it appropriate for modest and elevated concentrations and relatively ineffective at reduced concentrations [113–115]. The linearized forms of both models are depicted in Table 3. One of the critical factors in the choice of sorption isotherm and kinetic is the square of correlation coefficient (R^2) and the closer the value of R^2 to 1, the more reliable the acquired experiment data with the respected models [113]. Table 4 shows a summary of research performed for kinetic and isotherm model applications for the sequestration of pollutants using MNMs [15]. The SP of various pollutants to MNMs was mostly ideally defined in the order of PSOR > PFOR and LGR > FRH > LGR-FRH > Koble-Corrigan. The PSOR model is interrelated with the experimental data from reviewed studies, with the chemisorption mechanism being the rate-determining phase, which is considered a chemical reaction between the sorbate and the sorbent. While the LGR model predict the monolayer SP and the surface of the sorbent was homogeneous [1, 98].

6 Thermodynamics

The parameters of thermodynamics are extremely considered in defining the SP and achieving an equilibrium state. To ascertain the SP's spontaneity and feasibility, thermodynamic considerations for sorption research are mandatory. The parameters of thermodynamics comprise of the change in entropy (Δs°), change in Gibb free energy (ΔG°) and change in enthalpy (ΔH°). The Van't Hoff equation is employed to determine Δs°, ΔG° and ΔH°, which gives an understanding of the SP's nature and mechanism [116].

Table 4 A summary of the non-exhaustive list of MNMs and their efficiency in the confiscation of different HMs and dyes as well as their various SCs

Nano-sorbents	Contaminants	pH	Kinetic model	Isotherm model/Qm (mg.g^{-1})	Thermodynamics	References
IO-doped methyltrimethoxysilane (Fe_2O_3-MTMOS)	Pb^{2+}	5	PSOR	FRH/105.50	–	[102]
$\alpha - Fe_2O_3$	Pb^{2+}	9	PSOR	LGR/70.42	Spontaneous and endothermic	[118]
Alginate-Based Fe_3O_4–MnO_2 xerogel	Cr^{6+} and Cd^{2+}	6	PSOR	FRH/7.24 and 7.79	Spontaneous and exothermic	[119]
Unmodified (Fe_3O_4 NPs), and modified with poly(sodium acrylate) (Fe_3O_4/PSA NPs)	Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, and Cr^{6+}	3–7	PSOR	LGR/4.83,14.24, 5.26, 3.34,45.71, 23.65, 35.22/16.93, 33.44, 17.65, 34.61, 129.10, 39.71, and 39.99	–	[120]
Silica-reinforced IO NCs	Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}	5 (Pb^{2+}, Cd^{2+}, and Cu^{2+},) and 6 (Ni^{2+}, and Zn^{2+}	PSOR	LGR/19.67, 20.56, 22.06, 19.85, and 22.34	Spontaneous and endothermic	[121]
MNPs@SiO_2@GOPTSLys	Cr^{6+}, Zn^{2+}, and Cu^{2+}	Alkaline pH	PSOR	17.2, 4.8, and 3.9	–	[122]
Polycationic/di-metallic Fe/Al (PDFe/Al) NCs	Cr^{6+}	3	PSOR	LGR/6.90	–	[123]
Hyperbranched polyglycerol (HPG)-MNPs	Ni^{2+}, Cu^{2+} and Al^{2+}	9	PSOR	LGR and FRH/0.451, 0.700, and 0.790	–	[124]
Fe_3O_4	Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+}	6	PSOR	LGR/85, 79, 83, and 66	–	[125]
Macroporous IO NCs cryogels	As^{3+}	6.5	PSOR	LGR/118	–	[126]

(continued)

Table 4 (continued)

Nano-sorbents	Contaminants	pH	Kinetic model	Isotherm model/Qm (mg.g^{-1})	Thermodynamics	References
Magnetic Fucus vesiculosus (brown algae)	MB and crystal violet (CV)	5 and 3	PSOR	LGR/577 and 1062	–	[127]
SDS-coated MNPs	Methyl violet (MV)	3	PSOR	LGR/416.7	–	[128]
γ-Fe_2O_3–Al_2O_3	CR	7	PSOR	FRH/498.00	–	[115]
Nanosized metal oxides—modified AC	Malachite Green (MG) and RhB	9.6 and 2.38	ELH	Koble-Corrigan/4.31 and 2.88 mmol g^{-1}	–	[129]
Graphene oxide-mesoporous iron oxide nanohybrid (GO/m-Fe_3O_4 hybrid)	RhB and MB	8	PSOR	100%	–	[130]
Fe_3O_4/activated carbon	Bismarck brown (BB)	7	PSOR	LGR–FRH/224	–	[131]
Magnetic NCs hydrogel (PVAcMAn/Fe_3O_4/Me)	CR	5	PSOR	LGR/48.6	–	[132]
MNCs	Acid Yellow 42 (AY42) and Acid Red 213 (AR213)	2	PSOR	LGR/62.36 and 77.99 62.36	Spontaneous and endothermic	[133]
Fe_3O_4@SiO_2@Kit-6/NH_2	Sunset Yellow (SY), RhB, Ponceau 4R (P4R) and Brilliant Blue (BB)	2	PSOR	LGR/8.41, 10.89, 6.26, 5.41 and 7.14	-	[134]
Zeolite-IO MNCs	MG	8	PFOR	FRH/21.05	Spontaneous and exothermic	[135]
MnF/ZrO-MNCs	RO 16	2	PSOR	LGR/409.84	–	[136]
Fe_3O_4 or γ-Fe_2O_3 NPs	CR	–	LGR/48.1 and 105.3	–	–	[137]

(continued)

Table 4 (continued)

Nano-sorbents	Contaminants	pH	Kinetic model	Isotherm model/Qm (mg.g^{-1})	Thermodynamics	References
PANI/CeO_2 (PANI/CeO_2-1 and PANI/CeO_2-5)	Remazol Red 133 (RB-133)	6.5	PSOR	FRH/18.6 and 13.9	Spontaneous and endothermic	[138]
CeO_2	Naphthol green B dye (NGB)	3	PFOR	LGR/41	Spontaneous and endothermic	[139]
Bare and surfactant-functionalized CeO_2 NPs	Methyl orange (MO), victoria blue (VB), RhB 6G (RhB6G), direct red (DR), brilliant blue, (BB), (CR), fast green (FG), eriochrome black-T (EBT)	5	PSOR (EBT)	FRH/75112,4-171.3 (EBT)		[140]
Binary NCs (BNCs)	Pb^{2+}	5	–	LGR/68.37-70.01	Spontaneous and endothermic	[141]
TiO_2	Pb^{2+}	7	PSOR	LGR/55.04	Spontaneous and endothermic	[142]
TiO_2/CS and TiO_2/CS-CMM NCs	Thymol violet (TV)	7	PSOR	84.32 and 97.51	–	[143]
Acid-activated kaolinite clay (AAC)/TiO_2	Mn^{2+}, Fe^{3+}, Cu^{2+} and Pb^{2+}	–	PSOR	LGR/0.678, 3.989, 0.169, and 0.002	Spontaneous and endothermic	[144]
SiO_2–TiO_2	Acid Yellow 219 (AY219)	–	PSOR	FRH/9.69	–	[145]
CuO/TiO_2 NCs	As^{5+}	3	–	FRH/90	–	[146]

(continued)

Table 4 (continued)

Nano-sorbents	Contaminants	pH	Kinetic model	Isotherm model/Qm (mg.g^{-1})	Thermodynamics	References
γ-Al_2O_3	Cr^{6+}, Pb^{2+}, Cd^{2+} and Ni^{2+}	3 (Cr^{6+} and 5 (Pb^{2+}, Cd^{2+} and Ni^{2+})	PSOR (Cr^{6+}, Pb^{2+} and Ni^{2+}) and PFOR (Cd^{2+})	LGR and FRH/13.3, 6, 1.1 and 0.33	–	[147]
Fe_2O_3/Al_2O_3 microboxes (MBs)	Hg^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+}	7 (Hg^{2+})	PFOR (Hg^{2+})	LGR/216	–	[148]
Poly (Vinyl Alcohol)/Al_2O_3 (Al_2O_3-PVA)	Ni^{2+}	5.3	PSOR	–	–	[149]
Al_2O_3/GO/HNT NCs	CR and MB	3 and 9	PSOR	FRH and LGR/329.8 and 258.4	Spontaneous and exothermic	[150]
Fe_3O_4/MnO_2	Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}	6.3	PSOR	LGR/53.2	–	[151]
Biochar-impregnated MnO_2 NCs	Cu^{2+} and Zn^{2+}	7	PSOR	LGR/1,124 and 995	Spontaneous and endothermic	[109]
CeO_2 NPs supported on $CuFe_2O_4$ nanofibers	Pb^{2+}, Ni^{2+}, and V (V)	7 and 6	PSOR	LGR–FRH/972.4, 686.1, and 798.6	–	[108]
GO-MnO_2	Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+}	–	PSOR	LGR/490 (Pb(II))	Spontaneous and endothermic	[152]

For considerable sorption to take place, the ΔG° of the SP must be negative and it is defined by Eq. 1.

$$\Delta G^{\circ} = -RT\ln K_D \tag{1}$$

R, T and K_D signify the gas constant ($8.314*10^{-3}$ kJ.mol^{-1} K^{-1}), the absolute temperature and the equilibrium constant which is provided by $K_D = \frac{q_e}{C_e}$.

The ΔH and ΔS were evaluated utilizing the following association in Eqs. 2 and 3. Their values are estimated from the intercept and slope of the plot ln K_D against 1/T [117].

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}$$

Positive and negative values of ΔH° signifies the endothermic and exothermic nature of the SP of contaminants to the MNMs. A positive Δs° values show enhanced unevenness/randomness across the interface of the solid solution during the SP, making slight structural changes to both sorbent and sorbate. While negative Δs° values signify a reduction in the irregularity of sorption. When ΔG° is negative and positive, the SP is spontaneous or favourable and non-spontaneous or unfavourable [114]. As observed from Table 4, determined thermodynamical parameters show that the sorption of most pollutants (HMs and dyes) to the MNMs were spontaneous, endothermic and in some case exothermic.

7 Conclusions and Future Prospective

The development of customized NPs with magnetic features as well as their high sorption ability present a new means to deal with effluent decontamination. Also, their functionalization has lately been assessed as a capable tool for the detection and decontamination of industrial wastewater. The confiscation of HMs and dyes was found to depend on the pH, sorbent dosage, initial contaminant concentration, contact time and temperature from the research reviewed. The optimum sequestration of various contaminants to MNMs was noticed in the range of pH 2–9.6. Equilibrium sorption data showed that the LGR and PSOR models generally described the SPs of various pollutants to different MNMs. Thermodynamically, the interaction of most pollutants and MNMs were found to be spontaneous, and endothermic or exothermic. The fabricated MNMs were found to be effective in the sequestration of pollutants from an aqueous-medium and should be applied in the treatment of real industrial wastewater. Nevertheless, before industrial use from a laboratory level, research on their general fabrication, with precise morphology, biocompatibility, stability and surface functionality optimization should be considered in the future.

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Magnetic Nanomaterials for Decontamination of Soil

Onyedikachi Ubani, Sekomeng Johannes Modise, and Harrison Ifeanyichukwu Atagana

Abstract Several persistent organic and inorganic pollutants enter the environment accidentally or deliberately due to diverse advances in industrial activities, causing adverse alterations in the ecosystem and threatening human health. The quest for unique technologies to remediate environmental pollution is paramount. Consequently, nanotechnology, an evolving scientific approach, has been used in diverse fields, and nanoremediation (NNR) an engineered nanomaterial purposely for environmental remediation, proved effective, rapid, and efficient in the treatment of contaminated soil due to its diversity and versatility in applications. Thus, magnetic nanoparticles (MNPs) are superparamagnetic because of their nanoscale size, which has excellent potential in various applications. They have become an efficient tool for soil remediation due to their intrinsic qualities, providing target specificity and cost-effectiveness compared to conventional treatment methods. The techniques are essential to separate the polluted negligible particles from the residual materials in any soil remediation approach, thereby reducing the accretion of pollutants while controlling their spread from one medium to another. Hence, nanoremediation using MNPs is a new option that treats soils contaminated by organic, heavy metals (HMs) and metalloid pollution.

Keywords Heavy metals · Magnetic nanoparticles · Nanoremediation · Soil contamination

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1 Introduction

The rapid industrial development and suburbanization globally have caused a heavy compromise and contamination of soils. Soil pollution is due to the deliberate dumping, improper treatments, management and disposal of untreated toxic waste from different sources, including agricultural activities, into the soil [1, 2]**.** For instance, metals and persistent organic pollutants (POPs) are organic contaminants which threaten soil quality because they are toxic and accumulate in soil for a long period. They are pesticides, deliberate or accidental byproducts of industrial waste like polycyclic aromatic hydrocarbons (PAHs), HMs, polychlorinated biphenyls (PCBs) and many more (Fig. 1) [3].

They are one of the soil's contaminants, which are non-biodegradable and persist in soil for a lengthy period from the point of entering into the soil. These pollutants are toxic and hazardous materials, and if not properly managed, they create significant adverse conditions and environmental concerns. These materials are harmful derivatives often produced by building sites, industries, farms, laboratories, garages, and various production and manufacturing plants, many of which end up in the soil. Due to their nature, their disposal is by specially approved amenities. Because their accumulation in soil (persistent toxic wastes) has adverse effects on the soil, affecting the soil layer strength in the topsoil, and consequently reducing the fertility and biological activity of the soil. Soil pollution threatens life on Earth by substantially causing various health problems with severe conditions such as kidney and liver damage, neuromuscular blockage, and several types of cancer (Fig. 2 a**s** adopted and modified from [2, 4]).

Therefore, searching for safe disposal or treatment of such complex pollutants generated by many industries entering the soil at concentrations high enough to endanger the environment has been challenging [5–7]. Because of the consequences of soil pollution on the ecosystem, research on innovative methods to treat or manage

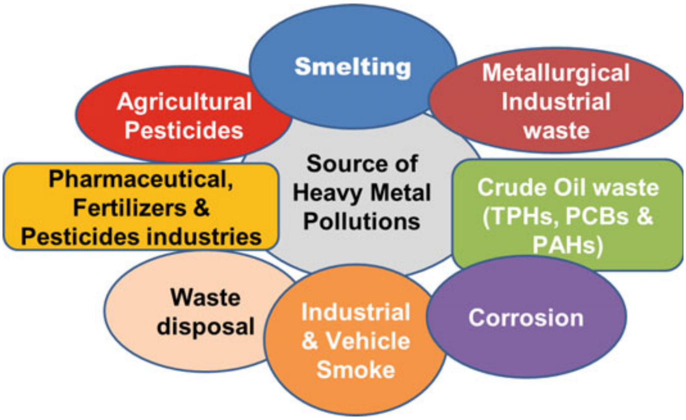

Fig. 1 The sources of HMs pollution in soils

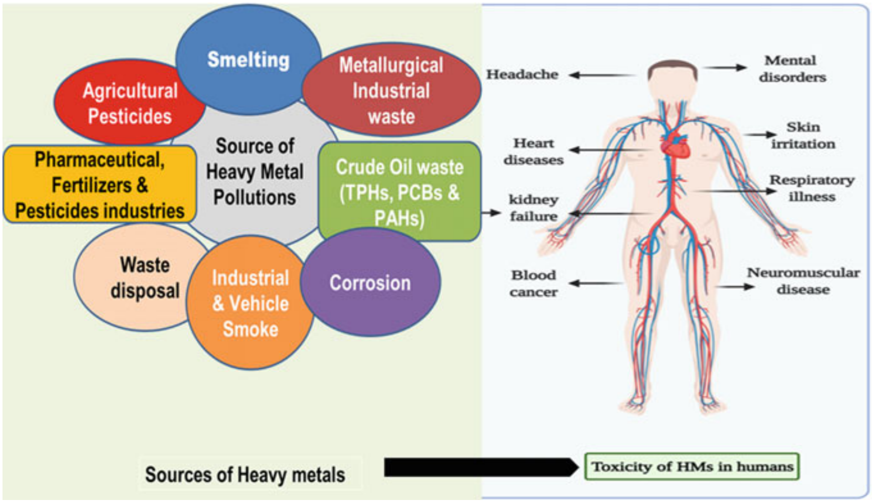

Fig. 2 The sources of HMs in soil and their toxic consequences on humans

soil pollution and its hazardous impact on the environment is needed because the confiscation of contaminants from the soil should be linked with ecological remediation [8]. However, the remediation of polluted soils could be challenging because of the interfaces of contaminants, including variations in solubility, evolution, phylogenesis and bioavailability, contesting for adsorbents on the binding sites (Bss) and inhibition of microbial metabolism may cause synergetic and aggressive impacts on the remediation process [3].

In recent years, a branch of science, nanotechnology, has played a significant role in solving different environmental challenges. Nanotechnology in the environment has progressed impressively in biological, chemical, and physical remediation methods in treating polluted soil through nanoscale fragments to eradicate or diminish contaminants from soil [9]. Lately, the application of nanomaterials (nms) in soil remediation has drawn massive attention because of the superior reactivity, extraordinary surface-to-volume ratios, surface-functionalization, and physical properties modification like chemical composition, morphology, porosity, and size. These properties possessed by nms are helpful in their selectivity and efficiency in removing contaminants. The introduction of NPs in soil permits the clean-up of broad areas and minimizes costs and intervals because of the in situ application [1].

The core benefits of nms for soil remediation, particularly for general cleaning contaminated soils, are cheap cost and cleanup time interval, degradation of pollutants, needless disposal of polluted soil or transfer of the soil [8]. Nanoremediation applications are the use of combative NPs for the transformation and decontamination of pollutants. The primary functions of NPs in remediation are catalysis, chemical reduction, and sorption because NPs possess excellent surface area-to-mass ratios, diverse allocations of active sites (Ass), and increased sorption capacity [9]. Furthermore, NPs could disperse and enter the minute spaces in the subsurface, and NPs are versatile and can move long distances and accomplish more excellent spatial distribution [9]. Remarkably, small-sized NPs of 1–100 nm scale can be injected in small spaces and their activation with time enhances enzymatic activities. Thus, their advanced applications have led to various synthesized NPs, such as Fe-based in polluted soils [10].

An example is magnetite (Fe_3O_4), an iron oxide (FeO) comprising iron in its bivalent or diatomic state, Fe(II), though, in this form, it is a mixed oxide containing Fe(III) and Fe(II) with an inverse spinel structure. In Fe_3O_4, FeO has been discovered to act as a catalyst that increases Fenton oxidation, that improves electron transfer in the degradation of organic pollutants**,** and then, an adsorbent (ADBs) with organic coatings, and stabilizer for surfactant foams [10]**.** Adsorbents are widely applied to treat HMs contamination due to their suitable fabrication, straightforward regeneration and excellent mechanical strength [11]. Recently, MNPs is known as higher adsorbents for eliminating polluting environmental composites. Nevertheless, its allured capacity is not the only specific reason for its usage. Their amazing surface charge and redox activity features are the conspicuous bases for their criterion of why they are preferred over other materials [12]. Magnetic separation is a remedy used by industries for HMs treatment, primarily for separating pollutants from soil to enable the reduced volume of waste or polluted soil. Even though magnetic separation techniques have shown promising effects, there are still commercial limits: the application of surface-modified MNPs raises the rate of partitioning procedure as a result of its complicated synthesis via the coating of functional materials on bare Fe_3O_4 NPs [13].

2 Magnetic FeO NPs (MFeONPs) Synthesis

MFeONPs have been described in many reports with versatile compositions and levels. The most outstanding quality of MFeONPs is synthesized by adaptable synthetic methodologies, including thermal breakdown, coprecipitation, micelle creation, magmatic and beam pyrolysis procedures (Fig. 3) [14, 15]**.**

2.1 Biological Synthesis

Green chemistry in nanotechnology is the manipulation of chemicals to reduce or remove toxic materials from the environment, which has drawn the attention of many scientists worldwide. Biologically, plant-mediated metallic nms are syntheses using different plant parts such as tissue, extracts, and exudates. These biological nms are environmentally friendly, safe and nontoxic in applications because they comprise reducing agents such as Cit A, Vit C (AA), $C_{15}H_{10}O_2$, and raw enzymes such as DHs, SDRs and EESs. These components play a vital part in the biological production of

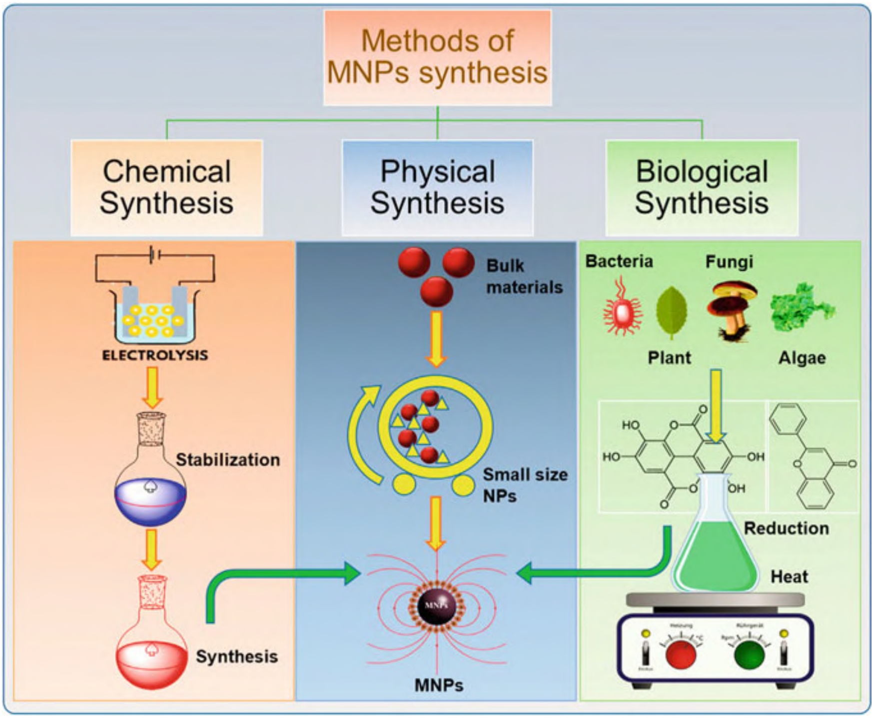

Fig. 3 The synthesis of MNPs with different methods. Diverse synthetic techniques have been used for MNPs of preferred sizes, morphology, stability, and biocompatibility; most techniques in synthesizing MNPs comprise the ball milling method, co-precipitation, thermal decomposition, hydrothermal, microemulsion, sol–gel method, and biological method. Adapted from Ali et al. [15]. Copyright, Frontiers publishers, 2019. Reprinted with permission from Frontiers publishers from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

NPs. The use of leaf extracts has been swift, nontoxic, and facile in synthesizing FeO magnetic NPs.

An example is the Carob leaf extract in one reaction with iron(III): iron(II) and NaOH solutions [9]**.** This process takes place at a lower-temperature level in a one-vessel reaction via a typical radius of the monodispersed NPs (4–8 nm) covered in R – COOH of Amide-I and II chains of the amino acid in the extract [14]**.** The drawback in the bio-synthesis of NPs using plant parts is the production of small amounts of secreted proteins by plants leading to a reduced synthesis rate. Because the biological products of NPs are an absolutely novel methodology and are emerging, there are definite drawbacks related to it. For instance, plants yield low amounts of secreted proteins leading to a reduced synthesis level. Another disadvantage is that all plants cannot be used for nanoparticle synthesis [14].

Interestingly, the capability of MNPs to remediate pollutants in soils has been tested, predominantly using a mixture of the starch-stabilized MNPs with amended soil and actual contaminated soil, which showed that the greater the dosage, the better the immobilization of the pollutant [14]. Previously, it was applied to decontaminate Cs-contaminated very small particles from bigger soil particles and accomplished significant separation. Nano-Fe/Ca/CaO/[PO_4] compounds have been applied to immobilize Cs-sorbed clay and were separated from contaminated soil by a modest pulverized technique in dry conditions: Eighty percent of the harmful Cs made up 27 wt.% magnetic soil particles [13]. An experiment also confirmed that cationic polymer-coated MNPs could separate Cs-polluted clay selectively from polluted soil. The smaller particles were separated successfully into magnetic portions using polyethyleneimine-coated MNPs [13]. Several NMs have been employed to remediate soil and groundwater, mainly MeOx, Z-NZVI, enzymes, CNTs and fibres, TiO_2, and noble metals. However, the commonly used nanomaterial for the remediation of soil and groundwater is zero-valent iron (nZVI) because it is regarded as the best electron donor and extremely reactive [9].

2.2 *Zero-Valent Iron NPs (ZVI-NPs)*

Several studies were centred on removing pollutants by zero-valent iron (ZVI) because of its naturally nontoxic, sufficient, cheaper, simplicity in synthesis, and bioavailability. Pollutants were removed by a mechanism involving the transference of electrons from ZVI to pollutants, converting pollutants to nontoxic or less toxic species. Also, Zero-valent iron could be used to degrade and oxidize some organic compounds with DO-producing H_2O_2. Then, H_2O_2 could be condensed to water by the transportation of two-electron from ZVI. Thus, this Fenton reaction takes place via blending iron (II) and H_2O_2, producing OH· which has the strong dissolving ability for some organic compounds. Metallic iron NPs have the potential for magnets, and their use is anticipated to stimulate the magnetic reclamation steps. N-ZVI shows tremendous surface activity. As such, ZVI NPs are widely used to remove contaminants (HMs), by creating an oxidation state. The hydrogen produced during the oxidation state on the ZVI NPs surface effectively eliminates pollutants.

Furthermore, various active sites on the surface of ZVI are helpful for the removal of contaminants [11]. However, the NPs dimension and the compact condition of ZVI-NPs could promptly interact with environmental media, which causes agglomerates in the synthesis process, decreasing the reactivity of ZVI-NPs, causing slow movement of ZVI-NPs to the pollutants, which limits the comprehensive usage of ZVI-NPs. Therefore, to decrease ZVI-NPs aggregation, it is usually mixed with a coat such as Gr, Si, clay, or a membrane [11]. Furthermore, ZVI-NPs as a reducing material gained attention because of their outstanding benefits like specific large surface area, inexpensive, and amazing reactivity with HMs. An example is an improved removal of Cr^{+6} with amino-functionalized vermiculite-supported ZVI-NPs (AVT-ZVI-NPs), which was stable [11].

2.3 *FeO(s)*

FeO NPs have shown their sorption activities because of their specific large surface area, permeability configuration, and strong magnetic reaction attributed to their excellent sorption capacity. They have been in different structures, such as hematite (a-Fe_2O_3), Fe_3O_4, and maghemite (c- Fe_2O_3). The magnetic effects of a-Fe_2O_3 are determined by many factors like crystallinity, sub-particle structure, particle size, exchange interfaces, and cation doping. Although the photocatalytic activity of a-Fe_2O_3 is limited due to its lesser separation efficiency and poor conductivity, it mixes with diverse semiconductor constituents to create a heterostructure. For instance, the synthesis of a-Fe_2O_3 with graphitic carbon nitride-based Z-scheme heterojunction via simple solid condition reactions improved the efficiency of photocatalytic degradation of organic pollutants/dyes and HMs ions such as Cr (VI) and Cd^{2+} and Cu^{2+} with elevated pH. Once more, the synthesis of a-Fe_2O_3 and aluminium oxide composites has shown a large specific area, sorption effect and permeable configuration of a-Fe_2O_3 and aluminium oxide with extraordinary removal proficiency on Hg^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} cations [11].

2.4 *Fe_3O_4*

Fe_3O_4 comprise Fe^{2+} and Fe^{3+} ions. The adsorbent effect of Fe_3O_4 is determined by its effective surfaces and morphological features. The degradation efficiency increased by an enhanced catalyst dosage because of the increased surface area of the catalyst, which improved the Adpt of photons. Fe_3O_4 can remove HMs from the environment example is the synthesis of CMC-immobilized Fe_3O_4 NPs (CMC-Fe_3O_4), which displayed better sorption capability for Pb^{+2} and HMs removals like Cd, Cu, Fe, Zn, and Ni than other pure Fe_3O_4 NPs [11].

2.5 *c-Fe_2O_3*

c-Fe_2O_3 NPs have large chemical stability devoid of any decrease reaction due to their magnetization saturation, facilitating the proficient separation of contaminants from the environment. In contrast, it is commonly utilized because of its nontoxicity and cheaper synthesis than most materials [10]. Several pollutants could be removed using c-Fe_2O_3 polymers by electrostatic interactions, such as the elimination of Cr^{+6} and Cu^{+2} by PPY/c-Fe_2O_3 and PANI/c-Fe_2O_3. Thus, c-Fe_2O_3 NPs could be better adsorbents for arsenic(V) As^{5+} than Fe_3O_4 because concrete/c-Fe_2O_3 nanocomposite (CM nano) has been shown to be an excellent adsorbent for the decontamination of As^{5+} [11].

2.6 Spinel Ferrites and Their Composites

Spinel ferrites and their composites have been applied in the decontamination of polluted environments because of their magnetic behaviour, stability, and biocompatibility. However, their catalytic reaction is determined by their polymerization process, which is the adjustment of the crystalline, crystallite size, and particular surface areas by several calcining temperatures and diverse pH values. The spinel ferrites removed aromatic nitro compounds from the environment because they are not complex but simply synthesized, including their high resistance to strong acidic and basic conditions. The magnetic reclamation effect of MFe_2O_4 (M=Zn, Co, Mn) spinel ferrite NPs was effective for the decontamination of nitroarenes composites because they possess huge pore capacity area as an advantage to the other ferrites NPs. The spinel ferrite configuration shows greater ferromagnetism, nontoxic effects, and outstanding photochemical stability; thus, their application is like a catalyst to remove soil pollutants.

Furthermore, $AgI/CuFe_2O_4$ composite revealed excellent magnetization and cycling performance separation from pollutant mixture because of their distinctive magnetic effects, stability, and sustainability. Therefore, the recyclable heterojunction composites combining the magnetic spinel ferrites and photocatalysts capability is a promising approach to removing contaminants [11]. On the other hand, carbon materials such as graphene (Gr), chitosan (CH or CS) and MWCNTs drew substantial awareness because of their distinctive configuration and effects. They are viable in the elimination of HMs and radioisotopes (RxList). However, MWCNTs are incredibly hydrophobic and aggregate in solution because of the reaction that occurs in them, which could hamper the compelling sorption efficacy and drop the sorption effects; thus, to improve their sorption efficiency, which should occur in a combination of magnetic ADBs such as the spinel ferrites. In addition, the sorption approach's mechanism and kinetics are determined by features like superficial configuration, magnetic effects of the ADBs and treatment parameters which may include pH, adsorbent concentration, contamination period, temperature, and pollutant concentration. However, magnetic adsorbents reportedly encountered several challenges requiring further research and development to enable multiple pollutant solutions [11].

3 The Fate of NPs in Soil

The use of NPs for decontaminating pollutants from the soil may lead to their accumulation or increased constituent concentration in the soil, thereby altering the soil's properties. The addition of NPs in soils can adjust the soil pH, and pH is an essential parameter that regulates soil nutrient availability, microbial dynamics, general soil health, and plant growth and development. When soil pH is altered or adjusted due to the presence of NPs, it could cause adverse effects on soil microorganisms and nematodes because NPs can attack mycelium and significantly destroy the functioning of microbial cells. The adverse effects caused by NPs in soil could be attributed to their concentration and type, soil type, and the enzymatic activity of the soil. For instance, higher concentrations of NPs in soil may lower dehydrogenase activity. As such, the equilibrium of the soil nutrient and fertility levels is disrupted. The sorption of NPs in soil could be mostly by surface complexation, hydrophobic partitioning, and ion exchange, and the colloid-facilitated transference of pollutants also follows these procedures [10]. The elimination efficacy increases as the concentration of nano adsorbents increases; this is assisted by the availability and functionality of active surface sites, viable attraction, and extent of surface charge (positively or negatively charged) on NPs for the sorption of metal ions, thereby developing chelate complexes for pH. This occurs because the removal of metal ions improves with a higher pH level of the solution resulting in the complete elimination of metal ions [13, 16]. Therefore, nanoscale particles significantly impact metal transference, maybe slowly trapped in soil or speeding up their movement. As such, the application of NPs in decontaminated soil should be deliberate and tailored to encourage its viable applications because the removal efficacy of metal ions from the soil is tremendously reliant on the pH of the solution [16, 17].

4 Decontamination of Soils Using NPs

Most soils are contaminated by organic and inorganic pollutants at higher concentrations; this type of soil pollution becomes a challenge in terms of making the right choice of remediation technologies suitable for removing the contaminants. The typology of pollutants and soil biogeochemical properties adds to the complexity of the challenge because either of them impacts or limits the removal of soil contaminants. In soil, these contaminants could be in particulate forms, adsorbed, absorbed, or disintegrate in soil pores. Each behaves differently because of soil parameters such as pH, OMC, and CMC which impact their mobility and availability in soil [18]. For instance, As, in its oxidized state, particularly at acid-neutral pH, adsorbed to Fe and Al oxides, to a reduced scale. In Na-contaminated soils, As becomes mobile and is free from the compact phase to soil dissipation, like $AsO_4{}^{-3}$. In plummeting surroundings, As also takes the form of an AsO_3, which could be absorbed by the clay segment via added energy than the $AsO_4{}^{-3}$. Indeed, As^{+3} are more toxic than As^{+5} because it forms more stable multiplexes with the Sulfhydryl groups (SH) enzymes. The oxidative ability of MnO_2 is adequate to dissolve the AsO_3 to $AsO_4{}^{-3}$. Then, regarding Cr, it is established that in the normal state, particularly in tri- and pentavalent forms. The trivalent form produces stable multiplexes with organic and inorganic ligands comprising O_2 or N. In soil, these metals penetrate quite a few depths. Overall, typical soil environments favour the Cr^{+3} form, in which residues are fixed, and absorb on the surface of O^{-2} and $SiO_3{}^{2-}$, creating stable links straight at acidic pH. At pH beyond 5, $Cr(OH)_3$ is discharged as an OH^-. In alkaline pH media,

Cr^{+3} dissolved into CrO_4^{2-}, which is a poisonous formation of Cr. The presence of MnO favours this oxidation. The Cr^{+5} type is extra motile than Cr^{+3}, particularly in organic matter (OM).

The OM performs as a reducing agent, and, furthermore, it is complex, withholding the production of Cr^{+3} in the process [18]. Also, PAHs are oily wastes that are substantial sources of organic hydrocarbon pollutants in the environment, like oil-derived fuels [18]. Polycyclic aromatic hydrocarbon (PAH) gained significant attention in ecological studies due to its high resonance energies and dense clouds of pi electrons of the benzene rings, making them POPs, recalcitrant to degrade in the environment [18]. The behaviour of PAHs is determined by their specific environmental exposure. They could be absorbed into the soil's OM; and their bioavailability is limited, making them less susceptible to remediation. Numerous procedures have been applied, with different outcomes, trying to degrade these recalcitrant complexes; such procedures were chemical degradation, biodegradation, phytodegradation and a combination of degrading techniques. The success achieved depends on the environmental factors, the microbial populations and class, and the kind and pollutants configuration [8].

Thus, the use of nZVI for the remediation of polluted soils is motivated by electron transfer and sorption as well as fixation effects. Such that nZVI are more active in the immobilization of HMs and metalloids in soils. The PCBs degradation in polluted soil was tested using nZVI; however, it was noticed that soil properties affected the nanoparticle efficiency for PCBs degradation, but at three hundred degrees Celsius in the air combining FeO and V_2O_5/TiO_2, nZVI acted as a catalyst for remediating PCB contaminated soils**.** Furthermore, nZVI-Pd showed positive results in degrading PCBs contaminated in soil; again, it was noticed that soil properties affected the nanoparticle efficiency for PCBs degradation. Then, applying MFeO-NPs, like nFe_3O_4, in soil amended with As and PAH yielded positive results in pollutant immobilization and reduced soil toxicity. This may be because of its elevated sorption abilities and magnetic effects that improved the decontamination from the medium by magnetic energy**.** Then, the application of nFe_3O_4 as a catalyst in a Fenton procedure was mixed with a dissolving agent, such as H_2O_2 or $K_2S_2O_8$, which degraded PCBs in sand amended PCBs at > 69%, though, in naturally polluted soil, degradation capacity with the same treatment was limited to 7–8%. Once more, iron NPs such as nZVI, nZVI-Pd and nFe_3O_4 were evaluated to remediate industrial Cr and PCBs contaminated soils, which aimed at comparing the effectiveness of Fe-NPs for the reclamation of soil polluted with Cr and PCBs, indicating positive degradation [3].

4.1 PAH Remediation Using Activated Carbon-Based Nanomaterial

Activated carbon-based nms are novel NPs because of their properties and applicability. They have been used in PAHs remediation, which included fullerenes, SWCNTs, MWCNTs, as well as graphitic materials. Carbon nanotubes (CNTs) drew massive attention because of their distinguished structures, like advanced biological strength, heat resistance, sorption ability, and stable pH ranges. They are the utmost favourable NMs for remediating contaminants as adsorbents. Their large surface-active site-to-capacity ratio and controlled pore size dispersal of customary adsorbents make them unique for remediation. However, the challenge in using CNTs is the option of accumulation, a drawback in the decontamination procedure, but the solution is integrating a functional group [19].

4.2 MNPs

MNPs were applied to decontaminate As -polluted soil. magNPs reduced As concentration in an extractable stage because of the sorption of contaminants onto MNPs [20]. The capability of magNPs (ZVI NPs and Fe/Cu NPs) to fixate As in soil and decrease its movement via immobilization was established. However, the sorption of As is influenced by soil pH because alkalinity promotes condensation of As^{+5} and $Fe(OH)_2$ and promotes As immobilization [21]. Thus, NPs of binary oxides (Fe–Mn binary oxide NPs) were also prepared and applied to immobilize As in soil as an *in-situ* method [22, 23]. Metal NPs have been used to decontaminate and restrain pollutants in soil, and metal NPs (SiO_2 NPs) reduced the concentrations of Zn, Ni, as well as Cd to a reasonable extent [24]. Notably, NPs composites such as biochar with iron phosphate NPs and sodium carboxymethyl cellulose improved immobilization of Cd in soil via reduced bioaccessibility and filtration, suggesting the augment of NPs composites (nGoethite and nZVI) for the remediation of contaminated soils [25].

Furthermore, applying the NPs composites (nZVI) in soil remediation did not alter the soil parameters at a lower dosage; instead, the reduction in soil phytotoxicity occurred, but the soil phytotoxicity rose as the EC of the soil rose at a higher dosage. The application of MNPs in remediating polluted soils is viable because of their simplistic partitions via their magnet and distinctive metal-ion ADPT. Nevertheless, eliminating non-magnetic HMs such as Cd and Pb by chelation as well as separation by magnetic force using MNPs (core–shell $Fe_3O_4@SiO_2$ NPs and iminodiacetic acid chelators) from contaminated soil was successful. However, the application altered only the soil's organic content and not the soil's chemical composition [9, 26].

5 Environmental Effect of Magnetic NMs in Soil Remediation

The application of NMs in soil remediation has been successful, but NMs may have a harmful impact on humans and the environment. The route and features prompting ecological toxicity are complex. Thus, lots of factors may influence the impact of synthesized-NPs on organisms, such as dissolution perspective, particle surface effects, accumulation potential, contact with environmental materials, and physiological, biological, and microbial behaviour in contact with NPs [9]. Exposure to nms impacts negatively the environment and humans, like FeO-NPs with mutagenic effects because they could destroy organisms' growth capacity or replicate [27]. The impact of nZVI in ranges of 1 to 20 mg L^{-1} in concentration on soil microbial mode was examined in sandy-loam (SLS) and clay-loam (CLS) soils. It indicated that soil type has affected the amount of possible toxic effects on soil microbial populations by nZVI. The effect could be attributed to the mass organic content (OC) in CLS, which acted as a defensive mediator in addition to nZVI to the soil, thus, making nZVI inactive by hindering interface with soil microbial cells. During the remediation of SLS using nZVI, microbial biomass and aryl-sulphatase activity, heterogeneity, and richness in the soils were adversely altered, and there was no exact concentration responsible for the influence on the soil. This implies that more research may be necessary with a variety of soil types and proprieties for a better understanding of the influence of soil properties and type on the effect of nZVI on soil microbial populations. This is because composites of nZVI have shown different effects in different studies, which may be attributed to the colloidal stability of nZVI properties and dosage, soil type and properties/parameters, contaminants type and their concentration and soil bacteria communities [9, 28–39]. In addition, the chemical conversions of nms in the environment are tremendously complex, which include the reduction, oxidation, dissolution, sulfidation, biodegradation, ADPT of macromolecules, and degradation of the surface-coated materials [34–36].

Nevertheless, the application of nZVI in the remediation of contaminated soils is encouraged as a viable nanoremediation devoid of ecotoxicity effects [40]. Though, anecdotal evidence recommends that the reactivity of nZVI in contaminated soil could be influenced by combinations of complex elements, such as contaminant types, nZVI properties, the soil geochemical conditions (pH, EC, temperature, NOM, moisture, DO), soil phytotoxicity and the ageing soils [10, 35, 41, 42]. However, there are several advantages to applying nanoremediation, such as reduced temperature changes, extra tunable pore dimension, smaller inter-particle distribution, and different surface interfaces [43, 44]. Remarkably, NMs retain larger surface spaces due to their distinctive features and radical sorption sites, leading to their exceptional absorbent [45]. Therefore, NMs have been considered a promising technology to remediate soils polluted with hazardous chemicals such as chlorinated organic solvents, organochlorine pesticides, HMs, PCBs and PAHs. NNR methods have been classified as economical, eco-friendly, viable, and rapid remediation techniques;

these make NPs and NMs outstanding in the reduction/oxidation, catalytic degradation, precipitation, and co-precipitation of chemicals, as well as catalysis in degradation that could alleviate the absorption/sorption of targeted pollutants in soil [35, 44, 46, 47]. Furthermore, the latest finding on the relations between photo-catalysts and microbes has unlocked a broad path for long-term environmental pollution remediation, focusing on the long-term improvement of photo-catalysts [44, 48].

6 Conclusions

Magnetic nms for the decontamination of co-contaminated soil focus on the transformation and detoxification of the contaminated soils. Nevertheless, the components and varying properties of the soil environment impact Magnetic nanomaterial's performance physically, chemically and biologically, which leads to the harmful effect of Magnetic nms on organisms that induce contrary effects on the soil bioremediation process. Coating magnetic nms could reduce the toxic impact on soil microorganisms. The key benefits of applying NMs in soil remediation are a decrease in cleaning period and total expenses, reduced contaminants to virtually nothing in sites, thus, needless disposal of polluted soil. The extensive application of NMs in environmental remediation is because of their pronounced reactivity and extraordinary capacity to immobilize HMs such as Cd, Ni, and Pb. It has been revealed that using nZVI to immobilize As and Cr in the soil could efficiently reduce the concentration of the pollutants. Granting that the diffusion in concentrations of analytes and pollutants suggests that the stability of the treatment and relations between HMs and the soil components have to be examined. Several studies revealed that magnetic separation by uncoated Fe_3O_4 NPs in an acidic condition effectively eliminates polluted soil. This is because a decrease in pH raises the positive charge on the surfaces of MNPs, which causes a strong bond with negatively charged clay particles because of their ferromagnetic attraction. Considerations of dosages during the applications of NPs (below or above 1%) via sorption processes are essential in soil remediation because dosages of NPs enable complete immobilization of pollutants concentration such as As, TPH and PAHs in the soil. Soil remediation with MNPs is viable because of its exceptional separation mechanism. However, the combination of NNR and other remediation technologies seems to be better for soil remediation because the combination procedure improves sustainable remediation practices for green environmental protection practices. For instance, using the magnetic effects of the NPs in combination with other remediation technologies could efficiently help improve pollutants adsorbed on the NP surfaces. As such leads to increased pollutant immobilization and a decrease in soil toxicity with suitable effects of the magnetic NPs such as size, sorption mechanisms, and magnetism. Though numerous remarkable achievements have been recorded with magnetic NPs for the remediation of contaminated soil, thus, studies regarding magnetic NPs or in combination with other bioremediation technologies are essential to improve the remediation systems.

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Magnetic Nanomaterials-Based Sensors for the Detection and Monitoring of Toxic Gases

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Abstract Magnetic nanomaterials (MNMs)-based sensors have found a growing interest in the detection and monitoring of toxic gases. Since the development of MNM-based sensors, magnetic materials have become an integral part of electronic sensor fabrications. The MNMs are easily embedded into the transducer materials, and their interaction with the surface is easily recognized by an external magnetic field. The chapter focuses on the various MNM-based sensors, considering their principles, types, applications, strengths, and demerits. The discussed MNM-based sensors are electrochemical, optical, piezoelectric and magnetic. An overview of the recent literature is given, and their various applications are also presented therein.

Keywords Electrochemical · Magnetic nanomaterials · Sensors · Transducers · Piezoelectric

1 Introduction

Nanotechnology is one of the newly emerged research trends in science and technology that is based on material science, quantum mechanics, microelectronics, computer science and molecular biology [1–5]. The term "nanotechnology" refers to a scientific way of synthesizing new materials on nanoscale levels (1–100 nm) [1, 5]. On the other hand, nanomaterials (NMs) describe generally materials which are produced by nanotechnology or materials that possess a single unit in dimension measuring one to one-hundredth nanometers [3]. NMs have remarkable advantages over non-NMs or traditional materials in their physical and chemical characteristics due to the quantum size effect [6–8]. Besides, features such as small sizes and wide surface areas will essentially improve the functionality of NMs greatly [2, 5]. NMs

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can appear naturally, or be purposely developed through engineering to carry out certain tasks [9]. It has numerous uses in a wide range of industries, including agriculture, medicine, transportation, and manufacturing extremely durable materials with high mechanical qualities [8, 10].

On the other hand, magnetic nanomaterials (MNMs) are groups of NMs that could be influenced via incident magnetic fields. The magnetic materials (Fe, Co and Ni) and the chemical components with functionality are usually two components of such material [1–3, 7]. Over the years, magnetic and superparamagnetic materials have been employed for a range of industrial uses in treatments like hyperthermia, magnetic resonance imaging and gas monitoring [7, 11]. The application of their various properties (chemical, electrical, thermal and magnetic) in various analytical processes of detection and chromatographic processes helps in the improvement and advancement of new diagnostic approaches with excellent precision, improved extraction recoveries, selectivity and overall detection speed [7, 11]. The fabrication of these nano-materials requires the application of various (metallic) magnetic materials such as iron (Fe), nickel (Ni), and cobalt (Co), as well as their various derived complexes [12]. From these metallic-magnetic materials, iron oxides, (ferric oxide and ferrous oxides) and their various ferrite derivatives (Cobalt Iron Oxide and Manganese Ferrite) are majorly employed in the fabrication of MNMs. This is suitably due to their excellent chemical properties, comparatively high magnetic moments, and ease in the preparation process when weighed against metallic alloys, such as Iron–platinum, Ni, Co and Manganese oxide [7, 13].

Usually, iron (Fe) oxides easily decompose under acidic conditions in addition to degrading in organic compounds [7]. It also effortlessly reacts with oxygen and, thus, modifies the functionalities of the material surface characteristics. [14]. These functionalities of the fabricated MNMs surface introduce various physic-chemical properties to the fabricated materials and improve the analytical abilities of the materials [14, 15].

MNM exhibits beneficial characteristics when compared to traditional materials or non-MNMs. Such characteristics like high surface area and possible functionalization or modifications for improved specificity, adsorption efficiency as well as ease of separation [7]. Additionally, MNMs are usually reusable/recyclable and cost-effective. Notwithstanding their countless merits, MNMs have some limitations. One of such limitations is the superparamagnetic or ferromagnetic properties which cause a reduction in their intrinsic magnetism due to agglomeration and aggregation in media [7]. This abnormality is overcome by modifying the MNMs with different materials. Such modification or functionalization could improve the rate of electron transfer within MNMs due to their conductivity. Other limitations of MNMs include ease of oxidation and the formation of hydrated oxides in an acidic environment [7]. These limitations of MNMs at high temperatures could reduce the accuracy or precision of the analysis [7].

2 Magnetic Nanomaterials-Based Sensors

Generally, sensors are machines or subsystems that detect changes within the surroundings and launch the signals into a computing workstation. In another word, sensors are devices or modules that generate a signal (output) to sense a physical phenomenon [16, 17]. Sensors are constantly used with an electronic machine or a computer. They have been greatly employed in the detection of toxic and damaging gases as well as for natural gas leakage [1]. Remarkable improvement has been recorded in the accuracy and sensitivity when determining the definite nature of gas due to the change from single metallic oxide to combined metal oxide [16–18]. Various sensors are widely applied in our everyday activities [1, 16]. These applications include robotics, medicine, machinery, aerospace, cars, and many other facets of our everyday life. Other sensors determine the physio-chemical properties of materials, including, vibrational, optical and electro-chemical sensors for various monitoring purposes [17, 19]. The improvement of electronic devices (sensors) in recent times has brought about integration as well as miniaturization and micro-miniaturization of devices [2]. NMs are increasingly significant to the development of gas-sensors. Various benefits are derived, in terms of analytical figures of merit recognized [1, 2]. Such benefits include a short boundary of detection, improved sensitivity, and a reduced phase of analysis than traditional materials [1, 20].

Since MNM-based sensors are specific in function, it is imperative to note that a particular gas detector cannot detect every kind of noxious gas. They are manufactured to detect some low levels of oxygen which is crucial for industrial gas detection and sequentially to prevent fire outburst accidents [16–19]. The specific sensor would simply detect the exact gases for which it is proposed. Though each sensor comes with capabilities and limitations, one has to be careful when selecting a particular sensor for a specific application [16]. The following functional requirements should be considered when choosing any MNM-based sensor: high sensitivity, reproducibility, specificity, response linearity, stability as well as short response and recovery time [16, 17]. At room temperature, the development of reliable and low-cost sensing mechanisms for the detection of gases, has continued to pose a significant challenge to the technological and scientific world [17]. However, different MNM-based sensors could be grouped according to their detection methods. These sensing methods include diverse variations in optical, electrical, acoustic, calorimetric and chromatographic properties [1, 16–19]. Gas interaction usually occurs as soon as the surface of a sensing material is exposed to the environment, and, thus changes the main physical parameters of work function, conductivity and permittivity, as indicated in Fig. 1. An important element in sensor structure, the transducer, is responsible for the conversion of physical parameters from one form to another. Hence, in an electrically transduced sensor (chemical) where the gas particles relate to the sensing material, the interactions define the nature (stability, sensitivity as well as biocompatibility) of the sensing devices [17, 21].

The sensing material should be modelled in a way to have a wide surface for interaction with the related gas particles and, efficiently convert these required actions into

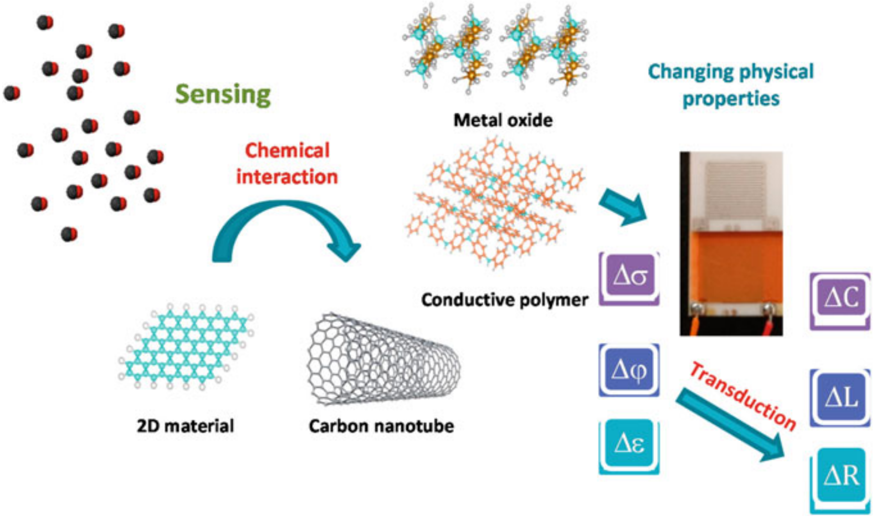

Fig. 1 The detection method of sensing materials as adapted by Nikolic et al. [17]; Copyright, MDPI publishers, 2019. Reprinted with permission from MDPI publishers from open-access articles distributed under the terms of the Creative Commons Attribution License (CC BY)

measurable information. Additionally, the sensing material should exhibit suitable properties for easy processing of signals [6, 22].

By and large, sensors are being used to measure harmful gases as a result of technological and monitoring advancements [1, 2]. Sensor systems have a significant advantage over conventional sampling and analysis approaches for measuring harmful gasses accurately. The majority of these devices can be generically categorized into (1) electrochemical sensors, (2) optical, (3) piezoelectric sensors based on piezoelectric materials, and (4) magnetic sensors. MNM based-sensors are sensors that have at least one nano-material sensing dimension that is no larger than 100 nm. The MNM based sensors are essential in the field of nanotechnology because they can (a) monitor physical and chemical processes in hard-to-reach areas, (b) detect biochemical in cellular organelles, and (c) quantify micro particles in the environment [16, 17]. The major application of MNM based sensors in the detection of hazardous gases have been elaborately presented in the 2019 review article [16], which gives the hazardous gases to include acetylene (C_2H_2), carbon monoxide (CO), carbon dioxide (CO_2), Hydrogen (H_2), hydrogen sulphide (H_2S), nitrogen monoxide (NO), nitrogen dioxide (NO_2), chlorine (Cl_2) as well as ammonia (NH_3), and the various MNM-based sensors employed. Subsequently, the recent progress in this area is a comprehensive analysis of the various MNM-based sensors (electrochemical, optical, piezoelectric and magnetic) types, transducers and analytes types, their detection ranges and limits as well as their analytical figure of merits and applications [1, 2]. Recipes for these studies exemplified the applications of the MNM based sensors and their mode of operation in detecting hazardous gases. In this chapter, emphasis is placed on the overview of the different MNM-based sensors for the detection and monitoring of toxic gases.

3 Electrochemical Sensing Devices

Electrochemical sensors are sensors that can provide accurate and timely information about the structure of a system by merging an electronically specific layer (the acknowledgement component) with an electrochemical transducer [19, 23]. Modern electrochemical sensors use a variety of features to distinguish between different limits, whether they are physical, chemical, or natural boundaries, in our everyday lives [2, 20]. They are well-established and reliable tools for obtaining constant cycle control messages through on-the-spot predictions of compound structure. The mid-1950s saw the commencement of electrochemical detecting innovation [18, 23–26]. The most common approach for detecting oxygen and dangerous gases, such as carbon monoxide and hydrogen sulfide, is being used today [19, 26]. This method is not used to calculate flammable gases; however, it is the greatest option overall for monitoring ecological toxic gases. For on-site monitoring of priority pollutants in addition to addressing other environmental needs, electrochemical sensors and detectors are particularly convincing [16]. Many of the parameters for on-site environmental analysis's needs are met by such devices. They feature constructed sensitivity to and selection against electro active species, are quick and precise, small, transportable, and affordable [1–3, 19]. Decentralized clinical analysis has already been greatly impacted by such capabilities. Broad electrochemical sensor applications for pollution management are still in their infancy, despite their enormous promise for environmental monitoring [1, 8, 27, 28]. In electrochemical sensors, the target analyte and the recognition layer interact to produce an electrical signal that contains analytical information [28]. Environmental monitoring can be done using a variety of electrochemical instruments (a subject on the sensitivity needs and the make-up of the analyte). The bulk of these procedures can be divided into two groups: amperometric and potentiometric sensors [26–28].

The foundation of amperometric sensors processes is based on the detection of biochemical recognition methods of electro active species [28]. The working electrode's potential is fixed (relative to a reference electrode) during the signal transduction process, and the current is monitored as a function of time. The electro active species' response to transfer electrons works as a result of the applied voltage [19, 26, 28]. The L.C. Clark oxygen cathode was the first amperometric sensor [28]. The oxygen that enters the framework via a gas-porous layer is condensed to water on an honorable metal-cathode. The composition of the working anode has a significant impact on the yield of amperometric sensors. The calculation of the current delivered by an anode surface enzymatic or bio affinity response with a constant working voltage similar to the reference terminal is what drives the amperometric sensor standard [27, 28].

In potentiometric sensors, the whole detection process is turned into a potential signal that is logarithmically proportional to the various activities (concentrations) of species generated in the process [1, 2, 28]. This potential signal is then used to generate the analytical information. Ion selective electrodes are used in these devices to capture the potential signal. The electrode's tip is equipped with a perm selective ion-conductive membrane that is intended to produce a potential signal that is largely caused by the target ion. Potentiometric sensors provide a high degree of selectivity, are easy to use, and are inexpensive, making them particularly appealing for field operations. However, they are frequently slower and less sensitive than their amperometric counterparts. Potentiometric instruments have historically been more extensively utilized, but as amperometric probe research grows, this balance should eventually shift [27, 28].

3.1 Principle of Electrochemical Sensor

Electrochemical sensors are controlled by introducing the target gas into the sensor, which results in the production of an electrical signal corresponding to the convergence of the gas. In exchange, the sensing electrode oxidizes or reduces the diffused gas [28]. A typical electrochemical sensor consists of a counter terminal separated from the detecting cathode (or working anode) by a thin layer of electrolyte (Fig. 2 as adapted from [27, 29]). This technique allows a suitable quantity of gas to react to the detecting anode and generate an appropriate electrical indication. The gas joins at the exterior of the detecting cathode with either an oxidation or a decrease instrument after diffusing through the blockage. Exceptionally well-planned cathode materials for the target gas stimulate these reactions. When a resistor is connected over the terminals of the anode and cathode, a current proportional to the gas fixation flows between them, and the current can be computed in order to calculate the centralization of the gas [26–29]. Due to the simultaneous creation of a current, the electrochemical sensor is sometimes referred to as a small power device or simply an amperometric gas sensor [27–30].

The maintenance of constant and reliable potential is crucial for detecting anode for a sensor with an external driving voltage. The detecting terminal potential fluctuates because of the constant electrochemical reaction that takes place on the anode surface. It results in deteriorating sensor performance over time. In order to support the sensor's effectiveness, a reference anode is included. Within the electrolyte, this reference anode is located close to the detecting cathode [26, 31]. When a constant voltage is connected to the detecting terminal, the estimation of this constant voltage at the detecting terminal is maintained at the reference anode. Thus, allowing zero current flows from or to the reference terminal. The particles (gas) react at the detecting anode, and the current flows are calculated between the detecting and the counter terminal, and the grouping of gas is typically easily recognized [29]. When the voltage applied to the detecting cathode is estimated, the sensor becomes explicit to the target gas. For electrochemical sensors of the small energy unit type,

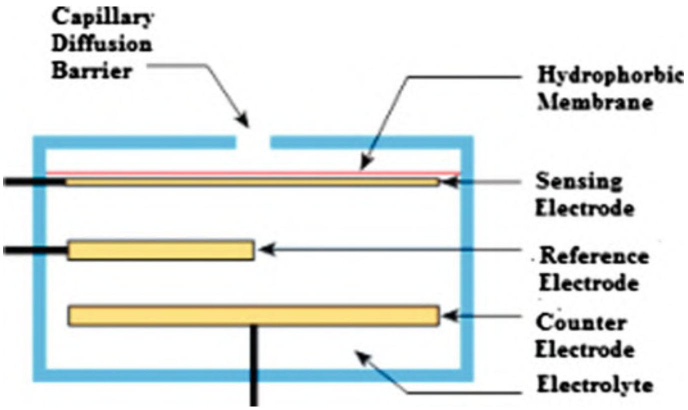

Fig. 2 The working principle of electrochemical sensors

an external driving voltage is not necessary. For instance, an oxygen-specific electrochemical sensor uses a Pb or Cd anode to supply electrons for cathode oxygen reduction [26–32].

Pros of electrochemical sensors

- The range could be specific to a certain gas depending on the type and concentration of the intended to be detected.
- Outstanding accuracy and repeatability. The sensor will consistently and accurately measure a target gas after the calibrated to a specific concentration.
- Does not become contaminated by other gases. Other environmental vapors won't reduce the sensor's lifespan or make it shorter.

Cons of electrochemical sensors

- Life expectancy decreases with increasing exposure to the target gas. Typically, the maximum life expectancy of three years is mentioned. High temperatures and low humidity might dry out the electrolyte in the sensors. The electrolyte is also depleted by target gas or cross-sensitivity gas exposure.
- A brief or restricted shelf life.
- Other gases' shared sensitivity can cause interference with some sensors. This has its benefits, but it can also have its drawbacks [28–35].

4 Optical Sensing Devices

Light rays are transformed into electronic signals by an optical sensor [36]. It measures the actual amount of light and converts that measurement into a form that the instrument can read, much like a photo resistor [34–36]. The capacity to measure changes from one or more light beams is one of an optical sensor's properties. Most frequently, this change is brought about by changes in the light's intensity. The single-point approach or dispersion of points can both be used by optical sensors. A single-phase change is necessary for the sensor to be activated using the single-point approach. As far as the distribution notion is concerned, the sensor reacts along a broad array of sensors or a single fiber optic array [36, 37].

The Benefits of Optical Fiber Sensors over Traditional Sensors devices (TSD) now have a wider range of uses thanks to advancements in research and development, including in telecommunications and medical science [37]. Their productions were made to function with a wide range of physical characteristics. However, TSDs are more dependable and stiffer than conventional electrical and electronic sensors for performance in challenging conditions, where they struggle [36].

The benefits of Optical fiber sensors over other forms of sensors include the following [36–39]:

- Are non-electrical devices that provide sensitivity to a variety of environmental factors and call for light cable weights and sizes.
- Allow access to ordinarily inaccessible locations
- Allow remote sensing, and frequently do not require contact.
- Are immune to rust and do not contaminate their surroundings.
- High sensitivity, resolution, and dynamic range are provided.
- Data transfer systems can be interfaced.

The operational principle of an optical sensor is based on the transmission and reception of light; the item to be detected interrupts or reflects a beam of light from the emitting diode. The resulting reflection of the beam is evaluated based on the equipment used. This enables the detection of things irrespective of the material used by the manufacturer [36, 37]. Many kinds of optical sensors exist today. Figure 3 as adapted from [34], describes the most common configurations of an optical sensor.

In a through-beam sensor, the transmitter and receiver (which are situated across from one another), make up the system's two individual parts. A beam of light is

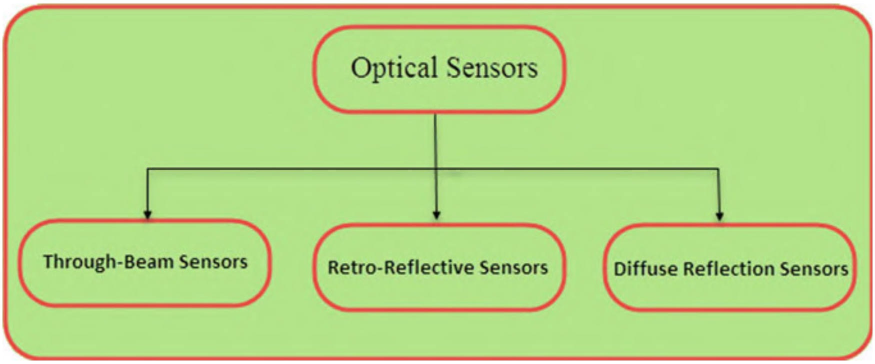

Fig. 3 Optical sensors configurations

directed toward the receiver by the transmitter. When the light beam is interrupted, the receiver interprets it as a switch signal [37]. For the Retro-Reflective Sensors configuration, the transmitter and the receiver are located in the same compartment. However, in Diffuse Reflection Sensors, one compartment contains both the transmitter and the receiver, and, the transmitted light is reflected by the intended target object [36, 37, 40].

4.1 Optical Sensing Applications

Research on optical-materials sensing is ongoing worldwide, and these sensors are finding more and more uses in environmental monitoring, medicine, biomedicine, and chemical analysis. Although absorption and fluorescence are the primary physical phenomena utilized for optical chemical sensing, chemical luminescence as well as Raman scattering, and Plasmon resonance have also been reported [36, 40, 41], Undoubtedly, the application area that appears to have the most room for growth is healthcare. For several reasons, optical biosensors are finding more and more uses in various fields of medicine [36]. Optical sensing can help with several difficulties associated with monitoring electrical power generation, production, distribution, and conversion systems. Whether a hydroelectric turbine needs a special resistant system or a windmill needs a lightweight solution, optical sensing offers special features that precisely match with these formerly challenging applications [40, 41].

5 Piezoelectric Sensors

By definition, piezoelectricity refers to a material's capacity to produce electrical charge as a result of mechanical deformation [42]. The term "piezein," which means to "squeeze" or "press," is where the name originates from. The brothers Pierre and Jacques Curie first identified it in 1880 when they showed that different crystals, including zincblende, tourmaline, cane sugar, topaz, and quartz, exhibit piezoelectricity [42, 43]. After a few decades, the first real-world uses emerged. Using a quartz-based piezoelectric transducer, Langevin created an ultrasonic submarine detecting method in 1918. After that, during both World Wars, this strategy—known as sonar—was employed. The field of frequency control was introduced in the 1920s when quartz was used to stabilize oscillators, which is also widely acknowledged [43–45]. The electrical dipole serves as the foundation for piezoelectricity's fundamental theory. A piezoelectric substance often has an ionic bonded crystal structure at the molecular level. Due to the symmetry of the crystal structure, the positive and negative ion dipoles cancel each other out while the system is at rest, hence an electric field cannot be seen. The crystal deforms under stress, loses its symmetry, and develops a net dipole moment [44]. Over the crystal, an electric field is created by this dipole moment. The direct piezoelectric effect, which causes electricity to be generated when stress is applied, is unique in that it is reversible, meaning that materials that exhibit it also do so in reverse, causing stress to be generated when an electric field is applied.

The direct piezoelectric effect, which causes a material to produce electricity when stress is applied, is one of the special features of the piezoelectric effect. The material can also produce the opposite effect [44, 45]. In order to ensure that the directed pressure selectively loads the elements in a specified direction, pressure sensors are constructed with a thin membrane and a large base. The crystal components of accelerometers have a seismic mass associated with them. The way forces are applied to the sensing elements is the primary distinction between these two examples' functioning principles [44]. While a connected seismic mass applies the forces in accelerometers, a thin membrane is employed in pressure sensors to transfer force to the environment. It is common for sensors to be sensitive to multiple physical parameters. When subjected to vibrations, pressure sensors provide erroneous readings. Therefore, advanced pressure sensors use acceleration correction components in addition to pressure sensing components. The correct pressure information is obtained by carefully matching those elements and subtracting the acceleration signal (released by the compensation element) from the combined pressure and acceleration signal. Vibration sensors can also be used to recover energy from mechanical vibrations that would otherwise be lost. To achieve this, mechanical strain is converted into useful electrical energy utilizing piezoelectric materials [43, 45, 46].

5.1 Working of Piezoelectric Sensor

The basic principles of a piezoelectric sensor are as follows:

- Charges in a piezoelectric crystal are perfectly balanced, even when arranged in an asymmetrical manner.
- Because the effects of the charges cancel each other out, the crystal faces won't have any net charge.
- The crystal's charge falls out of equilibrium as it is pressed.
- As a result, from this point on, the effects of charge do not cancel one another, causing net positive and negative charges to emerge on the crystal's opposing faces.
- As a result, when the crystal is squeezed, voltage is generated over the opposing face; a phenomenon that is termed as piezoelectricity [44, 45].

In automotive applications, sound creation and amplification, liquid and fluid level measurement, and ultrasonic applications, piezoelectric sensors with a disc form are frequently used [43]. To detect changes in vibration or pressure and produce a usable electrical output, rings of piezoelectric sensors are used. Piezo ring sensors are frequently used in ultrasonic equipment for welding, cleaning, and dental purposes. Piezoelectric cylinders are another name for tube-shaped piezoelectric sensors. Piezo tube sensors are frequently used in the level, flow, and fiber optic sensors in sonar, mechanical, automotive, and scientific applications [44]. For vibration and pressure sensors, piezoelectric sensors with a plate or block shape are frequently utilized. Plate and block piezo sensors are frequently used in accelerometers and ultrasonic applications in a variety of sectors, including aerospace, automotive, and medical [45, 46].

6 Magnetic Field Sensing Devices

Nowadays, magnetic sensors based on NMs are explored as promising sorbents in sample preparation techniques, such as food samples and the extraction of food components as well as the determination of pollutants levels in industries [19], due to their main advantages of; (i) reduced size (ii) ease of operation (iii) maintenance free and (iv) protection of contacts from oxidation, dust and corrosion owing to the glass bulb (hermetic) and inert gas [19] The various contacts are activated via magnetic field rather than mechanical parts. Magnetic devices are developed into Hall Effect (HE), Tunnel Magnetoresistance (TMR), Giant Magnetoresistance (GMR), Electromagnetic induction, Giant Magnetoimpedance (GMI) and Anisotropic Magnetoresistance, based on their physical phenomena [47]. The utilization of magnetic sensors with corresponding NMs manufacturing techniques makes it practical to integrate computing circuitry and sensing capability simultaneously [1, 2]. This makes the resultant chip-like systems very smart for internet applications. Additionally, the magnetoresistance and Hall sensors comprise ninety-eight of the magnetic sensor markets [7]. In the environment, various flexible magnetic sensors have been developed for healthcare and diagnostic purposes by applying novel approaches to investigating organisms, cells and chemical phenomena [48].

HE as a form of the magnetic sensor is a transducer determining magnetic fields that are built on the principle of the Hall Effect. It is the direct outcome of the magnetic Lorentz force (MLF), which deflects a moving charge carrier in a magnetic field. The MLF deflects the incident current when a field (magnetic) is applied perpendicularly to the current flow. As a result, opposite charges accumulate at the surface of the anode orthogonal to the flow of current, causing a Hall voltage at the equilibrium point [19]. The carrier mobility of the semiconducting MNMs is the leading factor determining the sensitivity of HE-sensors. Recently, silicon based HE-sensors with the robust and efficient monolithic fabrication of sensing elements are ubiquitous [49]. HE-sensor comes with some advantages [19]:

- uncomplicated device architecture,
- low cost;
- ease in construction
- ease of integration with other circuits and scaling down;
- linear response;
- excellent robustness.

However, the sensor, like other NM-based sensors [50], also suffers a number of shortcomings. HE-sensors usually have weak output signals when compared with other sensors, like magnetoresistive sensors. Additionally, finite offset signals and drifting with temperature in HE-sensors are major problems [19]. A good number of commercially available HE-sensors have an architecture with sophisticated electronics to overcome these problems [19] and amplify their output voltage. HE-sensors have been widely applied in devices such as power supply protection, flow-meters, pressure diaphragms, damper controls, rotary encoders, ferrous-metal detectors, tachometers, vibration sensors, etc. [49]. Typically, HE-sensors are generally rigid and thick, therefore limiting their applicability in the field of flexible and wearable electronics [19].

7 Conclusion

Gas detection sensors will continue to be built on the foundation of MNM-based sensors since they are based on dependable technology. Robust and small MNM-sensors have always been useful for personal and industrial gas detection and monitoring systems due to their dexterity. Electrochemical and optical sensing devices are still in their early stages of development, and new applications are being developed quickly. A significant portion of research continues to focus on the blending and joining of certain materials, both organic and nanoscale. This is likely to continue since the development of sensors with greater precision and sensors capable of making synchronous decisions has been a long-standing focus of research on sensors with the ability to operate in complex systems.

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Application of Magnetic Nanomaterials as Drug and Gene Delivery Agent

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Abstract Magnetic nanomaterials are characteristically biocompatible and superparamagnetic thus promising as drug carriers. They guarantee a controlled release of therapeutic materials to targeted sites, guard drugs from metabolization and mitigate their potential toxicity/side effects to healthy cells. Equally, they synergically work with thermotherapy and imaging (magnetic resonance imaging, near infrared optical imaging and magnetic particle imaging) through both local (hydrolysis, pH, conjugation of biomarkers etc.) and external (external magnetic fields, ultrasound, light etc.) stimulus in advancing medical treatment and therapy. Therefore, these materials are extremely important in biomedical applications, more especially in drug delivery systems. Based on the aforementioned, this chapter offers a brief introduction to magnetic materials, their synthesis and surface modification, stimuli-responsive control of drug release and a conclusion based on the reviewed research work.

Keywords Magnetic nanomaterials · Drug delivery · Targeted sites · Local stimulus · External stimulus

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1 Introduction

Nanomaterials (NMs) and their formulations have exclusively been explored by researchers and scientists in novel and varied applications (solar cells, catalysis, biomedical, material filters water treatment, etc.) owing to their physiochemical properties [1, 2]. Particularly, magnetic NMs have drawn unrivalled research interest due to their exciting properties which include small area, superparamagnetism, simplistic functionalization and large surface area. These properties have been exploited in the fabrications of magnetic inks [3], catalysis systems [4], magnetic fluids [5], gyroscopic machinery [6] environmental remediation [7] and biomedical fields [8]. In biomedical applications, magnetic NMs have been used extensively as therapeutic agents (drug delivery carriers) [9], magnetic separation [10], photo-hyperthermia [11], tissue engineering [12], biosensing [13] and in transfection of numerous vectors (both viral and non-viral) and magneto-infection [14] thus transforming medicine and pharmacology greatly.

Therapeutic/drug delivery using magnetic NMs as nano-carriers/nano-vehicles has momentously gained interest over years. Importantly, drug delivery involves the release of conjugated therapeutic agents either encapsulated, physisorbed or grafted/bounded onto NMs. The application provides an efficient and improved therapeutic effect of drugs by maximizing on biological and (super)magnetic properties of these materials. Drug release occurs in two main routes namely; (1) locally activated and (2) externally activated. Locally activated occurs through chemical or biochemical stimuli such as hydrolysis, pH, enzymatic activities etc. Conversely, externally activated requires the use of external stimuli such as light, ultrasound, external magnetic fields etc. [15].

The use of magnetic NMs over traditional administration as gene and drug delivery systems are many. For instance, they offer the possibility of use in procedures coupled with diagnosis and treatment of diseases which otherwise is unattainable in traditional administration. For example, controlled drug delivery can be used in tandem with hyperthermia. During magnetic hyperthermia, cancerous cells can be destroyed due to the low tolerance of elevated temperatures (42–49 °C) [16] and thermal stimulus can ensure the release of loaded drugs to the targeted site thus synergically providing efficient treatment procedures [17]. Equally, a combination of drug systems with imaging capabilities like MRI, MPI and NIR provides excellent theranostics (combination of therapy and imaging) [18]. This is made possible due to their many characteristics (pharmacokinetics, drug release, solubility of drug, penetration and retention, biodistribution and cytotoxicity) which are advantageous over conventional methods (Fig. 1).

It is worth-noting that conventional/traditional drug administration is ordinarily administered through parental, oral, transdermal or pulmonary routes thus demands for many doses for optimum efficiency. Nevertheless, the use of nanomaterials as control drug release agents ensures a reduction in the quantity of drug administered, minimizes toxicity and maximizes the available dosage thus overcoming the shortcomings of conventional routes. In particular, this system is crucial in the treatment of

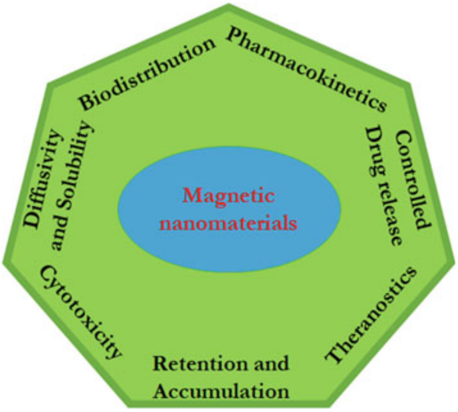

Fig. 1 Advantages of Magnetic NMs as drug carriers over conventional methods/systems

diabetes or persons using anti-inflammatory medicines since insulin will be readily released on demand for the former and the availability of drug concentration in the blood stream guarantees no pain in the latter [8].

Until now, multiple magnetic NMs have been synthesized and are typically consisting of pure metals (Co, Ni and Fe), metal alloys (FePt, CoPt), ferrites, or metal oxides. Notably, iron-based oxide NMs have been the most explored. They include the Fe_3O_4-crystalline magnetite or $\gamma - Fe_2O_3$-maghemite. In the fabrication of nano-systems for drug delivery, their surface charge, intrinsic magnetic properties, size, toxicity and degree of stability in aqueous substance must be considered. Normally, small-sized NMs (<20 nm) of ferromagnetic and ferrimagnetic materials exhibit a single magnetic domain with a huge magnetic moment. Consequently, NMs portray superparamagnetic characteristics of huge magnetic moments, fast response to external magnetic fields, negligible coercivity and remnant magnetization devoid of external magnetic fields [19]. With the withdrawal of external magnetic fields, a superparamagnetic material loses its magnetism thus this forms the basis of their usage in drug delivery since safe removal is guaranteed. Due to their small sizes coupled with a huge surface-to-volume ratio, these materials tend to aggregate because of the great surface energy. Equally, pristine and uncoated iron oxide NMs get oxidized in the air hence losing magnetism and lending them unstable. Therefore, their physiochemical properties are retained and their stability is enhanced through coating or surface modification.

2 Conjugation of Magnetic Nanomaterials

Like other novel nanomaterial applications, drug delivery systems require well-engineered and innovative materials with exceptional physiochemical properties. To achieve this, various innovative synthesis approaches with a high degree to control nucleation mechanisms and growth have been employed thus leading to the production of NMs with desirable and controlled magnetic, catalytic, crystalline and structural properties. Physical and chemical synthesis has been widely used thus far. The physical methods include ball milling, sputtering (metal evaporation) and electrode deposition. Despite the fact that large quantities and relatively high-quality production of NMs are realized by these methods, exact control of their physiochemical properties remains a challenge.

Conversely, chemical methods guarantee measured control size, composition, shape and structure of NMs. These methods include gas-phase deposition, oxidation, co-precipitation, microbials, flow injection, thermal decomposition, laser pyrolysis, herbal plant extract, sol–gel, microwave and biosynthesis via herbal extract (Fig. 2) [20]. Among the listed methods, co-precipitation is the most commonly used because of its simplicity, the possibility of easy scale-up and its mild conditions [21]. Detailed discussion on the methods of synthesis can be found in Chap. 2.

The surfaces of as-synthesized magnetic NMs ought to be modified to attain long-lasting stability and biocompatibility more particularly in biological media. Lack of surface modification results in agglomeration due to high surface energy, van der Waals and attractive forces which are ubiquitous among particles. Therefore,

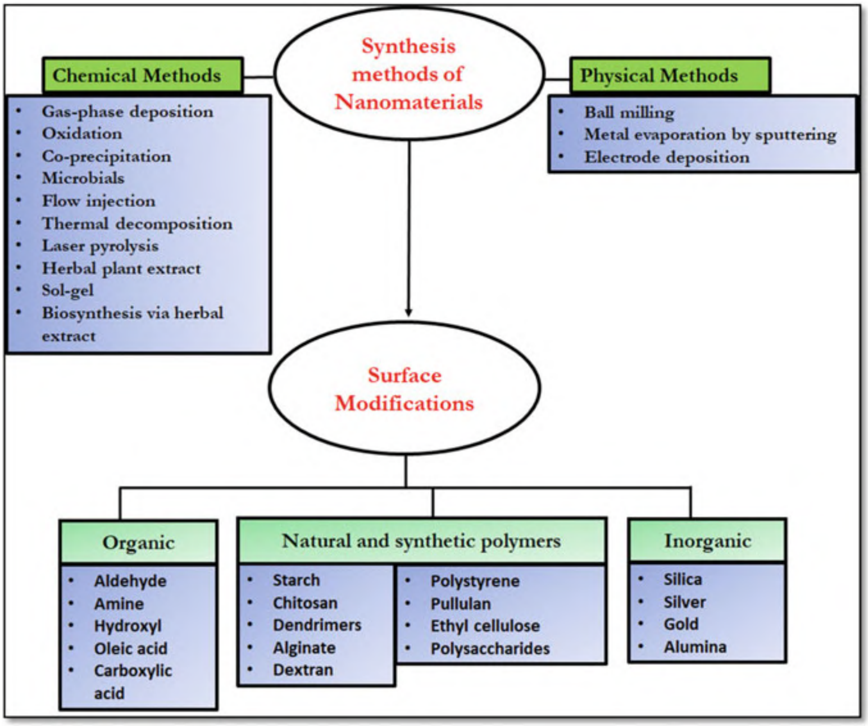

Fig. 2 Different types of conjugation and coating of NMs

different stabilizing matrices such as organic and inorganic substances and synthetic and natural polymers have been employed as modifiers (Fig. 2).

Surface-modified NMs show improved saturation magnetization, act as anchoring sites for better drug binding and can as well as catalysts in the synthesis of aromatic compounds [22], biocatalysis [23]and photocatalysis [24]. For instance, surface coating of iron oxide magnetic nanoparticles (NPs) can be conducted through adsorption and encapsulation. Adsorption entails the grafting of NPs surfaces using small molecules through anchoring moieties (organophosphorus or carboxylate and silanes). Also, magnetic nano-vehicles are fabricated through encapsulation in self-assembled amphiphilic structures such as polymers, lipids and vesicles thus exhibiting excellent biocompatibility and good dispersibility [25]. For example, Maryam Rajabzadeh et al. [26] reported on the CuI immobilized on tricationic ionic liquid anchored on functionalized magnetic hydrotalcite (Fe_3O_4/HT-TIL-CuI). The produced nanocatalyst showed promising performance for C-N coupling reactions among a variety of aryl halides and N(H)-heterocycles (benzimidazoles, pyrazoles and triazoles) in the presence of 2.5 mol% of nanocatalyst and under air atmosphere revealed high yields in absence of any additives. Equally, due to the magnetic nature of this system, recovery from a mixture of reactions is possible with the use of a permanent magnet.

Equally, Ghasemi-Ghahsareh et al. provided a novel approach for designing Fe_2O_4@SiO_2-L- tryptophan as a strong inorganic–organic hybrid catalyst. The catalyst was found to be eco-friendly, highly reusable and embodied high catalytic activity to manufacture spiro[indene-2,2′-naphthalene]-4′-carbonitrile derivatives. The motivation behind the use of L- tryptophan was due to the presence of both carboxylic and amino moieties of which various catalytic transformations can be conducted [27]. Additional, recent studies cover on $AlCl_3$@nano Fe_3O_4–SiO_2 multi-layer magnetite nanocatalyst for the one-pot synthesis of spiro[benzochromeno [2,3-d] pyrimidin-indolines] through a three-component condensation in refluxing C2H5OH of different naphthols, isatin derivatives, and barbituric acids [28]. The catalyst recyclability in 4 test-runs performed without activity loss coupled with a simplistic preparation procedure provides some of the advantages of this route. Other groups researched various metal oxide NPs (CeO_2, γ-Fe_2O_3, $\propto - Al_2O_3$, TiO_2) coated with statistical copolymers [22]. The functional groups in copolymers necessitated noncovalent binding to oxide surfaces and poly(ethylene glycol) polymers to achieve colloidal stability. The functional groups are organically derived from phosphorous acid compounds R-H_2PO_3 that have undergone screening for their robust affinity to metal and their multidentate binding ability.

3 Stimuli-Responsive Control of Drug Release and Translation Into Clinics

Based on the available reports from 2018, nearly 9.6×10^6 deaths were ascribed to cancer-related complications [29] and by 2030, projections allude a daily deaths of 30×10^6 as a result of the same disease [30]. Noteworthy, radiotherapy, chemotherapy and surgery account for the chief therapeutic and treatment procedures for this deadly disease. Clearly, radiotherapy and surgery are used in localized treatment while chemotherapy is considered the most ideal for all forms of tumor treatment. However, chemotherapy lacks specificity hence leading to serious side effects which include damage to healthy cells and unguided obliteration of tumorous cells. This drawback can be remedied through the use of targeted magnetic NMs since they offer excellent tumor selectivity.

Therefore, voluminous research based on the production of magnetic NMs and their application as drug-delivery agents has been conducted and reported (Table 1). Figure 3 shows a step-wise process involving the fabrication of a drug delivery system from the initial point of formulation to the clinical approval stage and finally commercialization. The entire process takes between 12 and 18 years. After the formulation phase which involves composition and physicochemical evaluations, preclinic research studies which involve in *vitro* as well as in vivo are conducted to verify the efficacy, bioavailability and safety of nano-vehicles prior to their administration in patients. Before approval for clinics, phase I to phase II clinical studies must exhibit bioequivalence, similar efficacy when compared to the standard drug and safety profile [31].

3.1 Magnetic Nanomaterials in MRI-Assisted Drug Delivery

A study on the synthesis of nanocomposite meant for MRI contrast agent and drug loading/realize has been reported [47]. The PEGylated magnetite/hydroxyapatite (PMHA) nanocomposite was produced and an MTT assay was conducted to determine the A549, MCF-7 and MRC-5 and cell toxicity of curcumin-loaded nanocomposite. It was established that PMHA showed high cytocompatibility whereas curcumin-loaded nanocomposite exhibited substantial cytotoxicity for A549 and a greater toxic effect on MCF-7 cancer cells. Also, the latter registered a drug loading capacity of 1.9 mg/g and a pH-dependent release.

The chemical co-precipitation synthesis method was used to produce cobalt-substituted ($Mg1\text{-}xCoxFe_2O_4$) NPs meant to be employed as an MRI contrast agent and hyperthermia. The NPs were then coated with Chitosan. It was observed that T_2 and r_2 values increased with the value of x due to an increase in anisotropy, susceptibility and magnetic moment. On the other hand, in vivo results exhibited 29.2 and 41.6 drops in intensity [37]. Also, clinical nanophores have been showcased as drug nano-vihicles in a procedure that depends on electrostatically weak interactions to

Table 1 Type, of MO, Synthesis, functionalization, drug and targeted disease

MO	Synthesis technique	Surface modification	Drug	Targeted disease	References
Superparamagnetic iron oxide (Fe_3O_4) nanoparticles (SPIONs)	Co-precipitation	Conjugated by Folate (FA)	Camptothecin (CPT)	Prostate cancer	[32]
Fe_3O_4 superparamagnetic nanospheres	Emulsion-solvent evaporation	Conjugated by vitamin C	Carboplatin	Breast cancer	[33]
Magnetite nanoparticles	Modified co-precipitation	Nanoparticles intercalated by curcumin-encapsulated SA/PVP-co-VAc microbeads	Curcumin	Cancer	[34]
Fe_3O_4	Chemical co-precipitation	Coating with polyethylenimine-graft-poly (maleic anhydride-alt-1-octadecene)	Curcumin	CUR delivery and MRI contrast agent	[35]
Magnetic hydrogel- Fe_3O_4	Co-precipitation	Functionalization and copolymerization with methacrylic anhydride and methacrylate respectively	Doxorubicin	Hyperthermia and breast cancer	[36]
$Mg_{1-x}CoxFe_2O_4$	Chemical co-precipitation	Surface functionalization with chitosan	HeLa cells	MRI imaging and hyperthermia	[37]
Fe3O4@SiO2@SBA-15	Co-precipitation	Coating with SiO_2 silica	Doxorubicin	Drug delivery (MCF-7 cell)	[38]
Magnetic nanoparticles (MNPs)	Co-precipitation	Coating with carboxymethyl chitosan	Doxorubicin	Drug release	[39]
Fe_3O_4-paramagnetic	Monte Carlo simulation and molecular dynamic	PEG-ylation	5-fluorouracil	Drug delivery and cancer treatment	[40]
MNPs (Fe)		Encapsulation of graphene	Ferulic acid	Drug release	[41]

(continued)

Table 1 (continued)

MO	Synthesis technique	Surface modification	Drug	Targeted disease	References
MNPs (Fe3O4)	Chemical co-precipitation	Coating with Silica-thiol	Methotrexate and cysteine	Drug release	[42]
Iron oxide nanoparticles	Standard co-precipitation	Functionalization with lactobionic acid	Ceftriaxone	Controlled drug release	[43]
$\mathrm{NixCu}_{1\text{-}x}$ -silica nanoparticles	Sol–gel	SiO2 silica	PTX	Skin cancer	[44]
MNPs (Magnetite Fe3O4 NPs)	Co-precipitation	Coating with PEG	Doxorubicin	Anticancer activity, in vitro drug release	[45]
Magnetite Fe_3O_4	Simple ionotropic gelation	Sodium Alginate/Magnetite NPs Microbeads, doped with Mg2+ and Al3+ ions	Doxorubicin (DOX)	Drug delivery	[46]
Magnetite Fe3O4	PEG coating	Hydroxyapatite	Curcumin	Drug release and MRI	[47]
NiFe2O4	Core–shell strategy	Silica coating	Curcumin	Drug delivery	[48]
Magnetic microspheres (MMS) based on Fe_3O_4	Co-precipitation	Polymer coating	5-fluorouracil	Drug release and cancer therapy	[49]
Fe3O4	Glutaraldehyde and Tripolyphosphate stabilizers	Polyvinyl alcohol/collagen	Polyvinyl alcohol/ collagen	Drug release	[50]

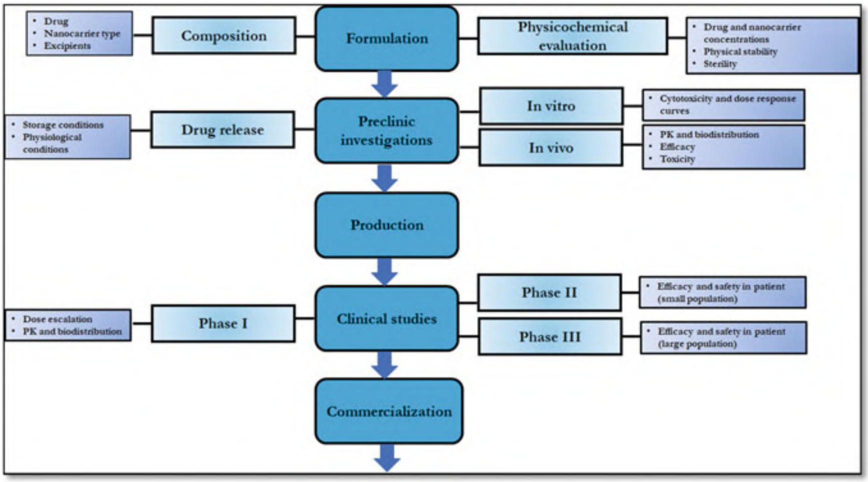

Fig. 3 Transition from formulation to clinical and commercialization of drugs

keep the drug and nanoparticle structures intact. They investigated whether Ferumoxytol could be used as a magnetic drug carrier capable of carrying multiple drugs after facile loading through the use of coincubation and enhancing their therapeutic efficacy without changing the NPs or drugs and the results were promising [51].

3.2 Magnetically-Engineered Drug Delivery

Externally localized magnetic fields have extensively been used to guide MO and deliver drugs to specific sites by capitalizing on their magnetic properties. The practice has gained traction due to its efficiency and accumulation of MO in specific pathologies like inflamed and tumorous sites [52]. Importantly, the physiochemical properties of MO dictate their magnetic response. For instance, the higher saturation magnetization of nano-vehicles ensures proper control of MO in the bloodstream and well-engineered accumulation to targeted locations [53].

In a study carried out by Pan and co-workers, they fabricated bovine serum albumin (BSA)-based plasmonic and magneto-luminescent multifunctional nanocarriers (MFNCs) by incorporating gold nanorods, gold nanoclusters and ion oxide nano particles for the delivery of the anticancer drug doxorubicin to the cervical cancer cells (HeLa cells). To make the MFNCs, gold nanorods, IONPs, and BSA-stabilized gold nanoclusters were mixed well first, and then drop-wise addition of acetone to the mixture was performed [54]. The self-tracking capability of the synthesized multifunctional nanocarriers (MFNCs) was demonstrated in vitro using single and two-photon imaging, as well as the possible usage in magnetic targeting. Additionally, significant T_2 -relaxivity was investigated, with the MFNCs' findings indicating good conditions for MRI. Furthermore, Dox-loaded multifunctional nanocarriers (MFNCs) effectively transported the drug to cervical cancer cells, leading to effective cell death while simultaneously exploring the drug release from the Ncs [54]. As a result of their therapeutic and multimodal imaging characteristics, the discovered nanocarriers offer tremendous prospects for passive targeting in vivo, making them suitable candidates for cancer theranostics.

To use superparamagnetic Fe_3O_4 NPs (average size $= 21 + 4$ nm) as magnetic target delivery, 3(trimethoxysilyl) propyl methacrylate (TMSPM) and tetraethoxysilane (TEOS) was used and the creation of C=C double bonds formed for further polymerization of glycidyl methacrylate (GMA). For possible use in boron neutron capture therapy, an immobilization of NPs by isopropyl-*o*-carborane was conducted. To examine the cytotoxicity effect, various cells such as MCF-7, Hela, L929 and BxPC-3 were used during in vitro studies. Interesting, the results exhibited an effective immobilization of carboranes on NPs, low cytotoxicity and superparamagnetic nature preserved [55]. Similarly, magnetically Fe_3O_4 NPs (poly-nanocrystalline, dispersed and spherical in shape) were grafted with chitosan for possible use as a nanocarrier for Telmisartan (Tel) which is an anticancer drug with poor solubility. Drug loading was made possible via an amide bond with a loading capacity of ~50% which was attributed to a great BET surface area of 134 m^2/g. The nanocarrier (MNP-CS (MNP–CS–TEL) exhibited pH responsive features and cytotoxicity which was dependent on the dose. An analysis of magnetization showed that chitosan coating has no effect on magnetic properties thus it can serve as an excellent magnetic nanocarrier [56] Through chemical precipitation, superparamagnetic graphene oxide (SPMGO) was synthesized and then functionalized cyanuric chloride (CC) acting as a linker for drug loading. For the treatment of cancer, methotrexate (MTX) was immobilized on both SPMCO and SPMCO/CC. In vitro studies revealed that SPMGO/MTX and SPMGO/MTX as drug carriers are hemo-compatible and have increased effectiveness of MTTX against cells (Caov-4, MCF-7 and Hela) with excellent large loading of drug and controlled release [57]. Furthermore, the coprecipitation synthesis method was used to produce nano-magnetite particles which were then coated with poly(butylene adipate-co-terephthalate) (PBAT) followed by a second coating using a mixture of PBAT and poly(butylene adipate) (PBA). These NPs produced exhibited biodegradability, and re-usability and can be used in the absorption of phthalates from aqueous solutions [58]

3.3 Vectorized Nano-vehicles Drug Delivery

Conjugation of MO with moieties such as antibodies, small organic molecules or peptides provides a promising therapeutic targeting agents delivery system. The enhancement of therapeutic effects and specificity on disease sites is achieved by uniquely selecting targeting agents capable of interacting with disease markers through antigen–antibody or ligand-receptor [59]. In the recent past, numerous research studies have focused on vectorized magnetic nano-vehicles and examined their drug-delivery abilities. For instance, Mu et al. [60]fabricated HER2/neu peptide using paclitaxel-loaded iron oxide NMs to treat breast cancer. The process involved the use of stable iron oxide conjugated with both peptide and carboxymethylated-β-cryclodextrin thus ensuring proper loading of paclitaxel hydrophobically. Importantly, in vitro studies of these nano-vehicles exhibited breast cancer targeting potentialities.

Similarly, Leach et al. [61] designed A10-3-Ji PSMA specific aptamer and hybridized DNA_RNA which was used to conjugate iron-oxide NMs and doxorubicin as drug delivery agents for prostate cancer. It was established that the agent was capable of enhancing the cytotoxicity of targeted cells whereas reducing damage to non-targeted cells. Therefore, it indicates that the drug delivery system can provide substantial efficacy because of it being cytotoxic to targeted cells when compared to non-targeted cells. A drug delivery nano-vehicle with double receptors was effectively developed, bound and internalized by LHRH-R-and uPAr-overexpressing PC-3 cells. The studies show a successful loading and release of anticancer drug PTX upon it being absorbed by iron oxide NPs which were polymerically coated. Due to the superparamagnetic nature of iron oxide NPs, the LHRH-AE 105-IONPs showed a meaningful MRI contrast effect. The improved efficiency of double-receptor-targeting LHRH-AE-IONPs-PTX led to about 2 times greater cell cytotoxicity when compared to single-receptor-targeting IONPS. Therefore, this drug delivery system offers a novel and potential therapeutic route for PCa hence improving patients' quality of life [62].

Also, Rao and co-authors performed a transdermal administration of Epirubicin-loaded iron-oxide (superparamagnetic) NPs meant for skin tumor treatments. Epirubicin(EPI) was added to superparamagnetic operationalized iron-oxide NPs (SPION) leading to the formation of EPI-SPION via covalent linkage of the reaction between $-NH_2$ and –COOH groups on EPI and SPION, respectively, producing a strong peptide bond. The brown aqueous SPION solution turned red after it was linked with EPI [63]. The in vitro transdermal investigations revealed deep penetration into the skin of external magnetic field-driven EPI–SPION composites. The magnetic field-assisted SPION transdermal vector was able to bypass the stratum corneum via follicular routes, indicating that a SPION-based vector could be used for effective transdermal skin cancer therapy.

3.4 Stimuli-Responsive Drug Delivery

The introduction of stimuli-functional groups or coatings provides another strategy employed to increase targeted drug release. For instance, the variations of pH between healthy (normal) cells and non-healthy cells can be exploited in this strategy. Therefore, through pH-sensitive coatings or pH-sensitive bonds in formulations like liposomes and polymers, the delivery of drugs embedded in nano-vehicles can be achieved due to pH variations [64].

Obireddy et al. fabricated a pH-responsive nanocomposite by using amine-functionalized magnetic NPs (amine-MNPs) with carboxymethyl chitosan (CMC). The produced MNPs-CMC was loaded with doxorubicin (DOX) to obtain MNPs-CMC-DOX which was then used in the in vitro studies of drug release at both different pH and temperatures. Results showed a huge potential usage of this nanocomposite as a drug release agent as attested by the pH-responsive and reactive oxygen species (ROS) generating potentials [39].

Also, a pH and thermal-responsive system to deliver drug was developed through the functionalization of gel with methylcrylic anhydride (GelMA) which was subsequently co-polymerized with (2-dimethyaminoethyl) methacrylate (DMAEMA) in methacrylate-end capped magnetic NPs and triethylene glycol dimethacrylate. The developed delivery system was loaded with doxorubicin hydroxide (Dox) for chemo and hyperthermia therapy. Results showed that the delivery system exhibited good pH and thermal triggered release characteristics indicating a combined synergic effect of chemotherapy and hyperthermia [36].

A drug nanocarrier was fabricated from an iron oxide core combined with polyethyleneimine and poly(-maleic anahydride-al-1-octadecene) shell to produce Fe3O4@PIMF which was then labeled with folic acid and curcumin drug loaded (Fe_3O_4@PIMF-CUR). The theragnostic carrier was used as a drug carrier and MRI contrast. It was observed that the Fe_3O_4@PIMF-CUR has good blood compatibility, and pH-sensitivity and showed more toxicity against Hela cells compared to MCF-7 cells. The evaluation presents this nanocarrier as a promising candidate in MRI imaging and nonvehicle for CUR delivery [35].

A drug delivery nanocarrier designed for the treatment of breast cancer, solid and primary cells was [65]. The nanocarrier was developed from polyvinylpyrrolidone which was stabilized by magnetoflourescent NPs (FL-PMNPs) and loaded with the drug. Evaluation of dead cell and nanoparticle intake was done on the following cells; metastatic cancerous MCF-7, nontumorigenic MC7-10A and MDA-MB-231. Results indicated that the even at highest concentrations, FL-PMNPs did not exhibit toxicity to cells. Conversely, meaningful potency and effective killing of various breast cancer were shown in Dox-loaded FL-PMNPs. Also, subcutaneous MDA-MD-231 nude mice were used to analyze the therapeutic efficacy of N6L: MF66-N6L, DOX: MF66-DOX and MF66-N6LDOX obtained from functionalized iron oxide (superparamagnetic) NPs -MF66. Results showed cytotoxicity to breast cancer cells compared to free ligands when MF66-N6L-DOX and MF66-DOX were used together with hyperthermia. Also, an inhibition growth of the tumor (40%) was noted during in vivo studies [66].

4 Conclusion and Future Projections

Magnetic NMs have the huge potential to be used as nano-vehicles owing to their remarkable physiochemical properties. The fact that they can be employed in targeted delivery by means of stimuli-responsive processes ensures guaranteed delivery to specific cancer cells thus averting side effects experienced in an alternative form of treatment. Owing to this, careful synthesis of magnetic NMs, their surface modifications and drug loading/release should be highly considered during pharmakinetic studies. Equally, the interaction between drugs and coating/ modifications of NPs and stimuli-responsive mechanisms should be given prominence to enable the designing of efficient drug delivery nano-vehicles. This can be made possible through the optimization of synthesis methods to ensure mass production of magnetic NMs and define standardized characterization procedures which will precisely determine physiochemical properties hence providing insights into immunogenicity, clearance toxicity and safety profiles.

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Role of Magnetic Nanomaterials in Biosafety and Bioregulation Facets

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Abstract Due to their inherent magnetic properties and multifunctional design, magnetic nanoparticles (MNPs) fall within a category of highly customizable instruments that can be utilized as imaging agents, medicinal medications, biological devices, nano-electronic biosensors, or molecular nanotechnology for the delivery of drugs and genes. Human biosafety (HBS) of MNPs for clinical usage has grown to be a significant concern as the configuration, shape, chemical characteristics, and implant locations, along with their possible uses, become increasingly complex. Health hazards could also arise if MNPs build up in the cells or organs of humans or interact with their particles or chemical constituents. Consequently, this chapter reviews the special physical and chemical features, possible medical applications, as well as HBS in clinical studies of MNPs. Finally, the chapter will attempt to look at the challenges of practical translation and the prospective applications of MNPs in the biomedical fields. In conclusion, this chapter makes some recommendations for further study in nanomedicine.

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1 Introduction

Potential uses of nanoparticles (NPs) in medicine and the biological domains have received a lot of investigation in recent years due to the rapid growth of nanotechnology (NTech) [1–4]. They can be utilized as imaging agents, medicinal medications, biological devices, nano-electronic biosensors, or molecular NTech for the delivery of drugs and genes [1, 5, 6]. Human biosafety (HBS) of NPs for clinical usage has grown to be a significant concern as the configuration, shape, chemical characteristics, and implant locations, in addition to their possible uses, become increasingly complex [7]. Health hazards could also arise if NPs build up in the cells or organs of humans or interact with their molecules or chemical constituents [1, 7].

For several years now, scientists have been intrigued by NPs [1, 8, 9]. The vast increase in the number of research publications devoted to magnetic nanoparticles (MNPs) over the past two decades indicates that, among the numerous types of NPs, they have attracted a lot of interest [1, 7, 10]. At the nanoscale, magnetic materials differ from their bulk counterparts in a variety of physical ways. MNPs have unique properties, such as super-paramagnetism, due to the phenomena known as nano-magnetism [1, 7, 10, 11]. As a result of the diverse applications of MNPs in the disciplines of biotechnology, biomedicine, material science, engineering, and environmental protection, there is a great deal of interest in the synthesis of different types of MNPs [1, 7, 10, 12]. Due to their distinctive physicochemical properties, magnetic resonance imaging (MRI) contrast, facile synthesis, simple surface decorations, low toxicity, and good biodegradability, MNPs have attracted enormous attention as imaging agents, medicinal medications, biological devices, nano-electronic biosensors, or molecular NTech for the delivery of drugs and genes [1, 7, 10].

Hence, in this chapter we have given an overview of the various MNP applications, recent developments in the production of these NPs for medical applications, as well as HBS in clinical studies. The difficulties of clinical translation and the potential applications of MNPs in nanomedicine (NMed) are then highlighted. This chapter concludes with some suggestions for additional research in NMed.

2 Biomedical Applications of NPs Vis-À-Vis MNPs

There are several reported studies on the biomedical applications of NPs [13, 14], vis-à-vis MNPs [7]. Figure 1 illustratively shows some of these applications, which include NMed, (imaging diagnosis, laboratory diagnosis, genetic disease diagnosis, tumour early diagnosis), drug carriers, medical instruments (nanoprobe, nanorobot, handheld disease diagnosis instrument, nano-sensor), tissue engineering (nano-bone, nanoscale red blood cell substitutes, new tissue engineering NPs), therapeutic drugs

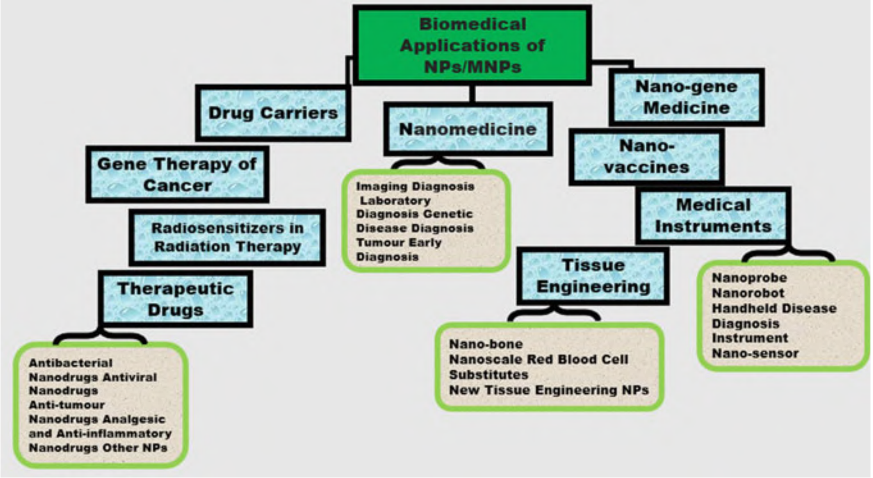

Fig. 1 Some of the biomedical applications of NPs vis-à-vis MNPs (MNPs: Magnetic nanoparticles, NPs: Nanoparticles)

(antibacterial nanodrugs, antiviral nanodrugs, anti-tumour nanodrugs, analgesic and anti-inflammatory nanodrugs, other NPs), nano-gene medicine, gene therapy (GT) of cancer, nano-vaccines, and radiosensitizers in radiation therapy (see Sects. 2.1–2.9).

2.1 Nanomedicine

According to studies, NTech has accelerated the development of diagnostic technologies in the medical disciplines, with the key categories being as follows:

- Imaging diagnosis [15–17].
- Laboratory diagnosis [18–20].
- Genetic disease diagnosis [21–24].
- Tumour early diagnosis [25–27].

2.2 Drug Carriers

Due to the common penetration of the science of NPs and contemporary technology [7], NPs are being extensively researched in the medical domains for medication delivery. Drug delivery aims to increase bioavailability both at specific locations and throughout time in the body, which may be accomplished by molecular targeting using nanoengineered carriers [28]. Medications transported by nanocarriers (NCRs) when compared to conventional drugs have the following features [7]:

- Nanodrug carriers may cross the endothelial cell gap and enter lesions in addition to passing through blood vessels and capillaries. "Pinocytosis" is the process by which cells can take up drugs that have been supplied by nanodrug carriers. The medications' bioavailability will be significantly increased in this method.
- The nanosized carriers can be utilized to embed hydrophobic pharmaceuticals due to their huge surface area, enhancing the drug's solubility and lowering the negative implications of co-solvents typically present in traditional drugs.
- Drugs can be delivered to the targeted tissue more effectively with the help of nanodrug carriers that have been altered with targeted specific tissues, such as folic acid alteration for drug-loading NPs and MNPs. This can lower the dosage required for administration and lessen side effects.
- It was shown that nanometre (nm) drug carriers can increase the time and effectiveness of the concentration of the drug in the blood, lengthen the half-life of the removal of the drug, and decrease the frequency of drug administration.
- Drugs can reach the lesions and become more effective thanks to nm drug carriers' capability to cross biological barriers in the body, including the blood–brain barrier and the blood-eye barrier.
- Drugs carried via NCRs, as opposed to a drug administration alone, can accomplish targeted medication therapy with high bioavailability and fewer side effects, resulting in reduced drug dosage, and treatment costs.

2.3 Medical Instruments

For the diagnosis or treatment of disease, nanomedical devices can be created at the micron scale, as opposed to conventional instruments at the macro scale [7]. NTech has the potential to dramatically improve tissue examination tools [7]. We may be able to see ongoing human bodily functions with the insight and incredibly fine detail of sensors that are smaller than a cell [29].

- Nanoprobe [30–33].
- Nanorobot [34–36].
- Handheld disease diagnosis instrument [37, 38].
- Nano-sensor [39–41].

2.4 Tissue Engineering

- Nano-bone [42–44].
- Nanoscale red blood cell substitutes [45].
- New tissue engineering NPs [46–51].

2.5 Therapeutic Drugs

- Antibacterial nanodrugs [52–57].
- Antiviral nanodrugs [52, 58].
- Antitumor nanodrugs [59–62].
- Analgesic and anti-inflammatory nanodrugs [63].
- Other NP drugs [64–66].

2.6 Nanogene Medicine

Nano-gene medicine is the shorthand term for GT performed using NTech. Exogenous genes are made primarily of nm-sized DNA molecules. Nano-gene medicine is the branch of science that uses NCRs to introduce these exogenic genes into receptor cells [67]. Owing to their unique characteristics, which include exceptional biocompatibility, protracted gene circulation duration, barred gene dilapidation, unreceptive targeting utilizing the improved permeability and retention consequences and potential modulation of polymer structure to achieve desired therapeutic efficacy, they are regarded as the most promising gene delivery vehicles [68]. For instance, liposome protamine/DNA lipoplex (LPD) lipid NPs are employed to deliver genes to the eyes [69]. LPD NPs have recently shown promise in treating retinal illnesses by delivering functional genes and microRNAs [70, 71]. These peptide-modified LPD NPs may have the following benefits: liposome NPs can deliver huge molecular loads; optimization of peptide-altered LPD NPs enables simultaneous co-delivery of multiple mutant genes to a single vector, and peptide-modified LPD NP formulations are further biocompatible and secure [69].

Polyak et al. [72], attempted to treat solid tumors in a mouse model of ovarian adenocarcinoma by systemically delivering siRNA via aminated poly(α) glutamate, a new nanocarrier. Following systemic administration, they discovered that it is an effective and secure anti-cancer siRNA delivery mechanism. This nanocarrier's delivery of an anticancer siRNA, siPlk1-polyplex, reduced tumor growth in mice treated with saline or siCtrl-polyplex by 73 and 87%, respectively, lengthening overall life. In conclusion, despite certain advancements, nano-gene medicine is still in its early stages of development.

2.7 GT of Cancer

As was previously said, GT has become a viable solution for the treatment of illnesses [73]. The ability to create therapeutic particles with numerous treatments and a defined structure and stoichiometry is one of the benefits of NTech [7]. Consequently, RNA NTech is a growing field [7]. Refolding after fusion makes it difficult to manage the formation of stable RNA NPs with numerous capabilities that maintain their original function. By delivering siRNA to tumour cells, researchers at "MIT and Harvard Medical School" have created a novel type of NP delivery system that can eradicate tumours by eliminating the mRNA [7].

This type of NP has a membrane layer on the outside and a siRNA and protein mixture inside. NPs by means of a protein and siRNA combination can sever the targeted mRNA after entering the tumour cells. According to Ren et al. [74], RNAi (RNA interfere) NP therapy can successfully eradicate the majority of tumours in ovarian tumour-bearing mice. By self-assembling re-engineered tiny RNA fragments, researchers at the "University of Kentucky" have created X-shaped RNA NPs that are thermodynamically stable for delivering beneficial RNA motifs. These NPs are thought to be helpful for treating cancer at the RNA and DNA levels [7].

2.8 Nanovaccines

An innovative approach to immunizations is the nano-vaccine [7]. It is made up of tiny biodegradable polymer particles that contain an antigen from a disease or a therapeutic component. Traditional vaccines are more effective than nano-vaccines because they trigger an immune response that is both humoral and cell-mediated. The majority of nano-vaccines are non-invasive and administered orally or nasally, resulting in no pain and little harm. Additionally, the related antigens can be delivered by nano-vaccines to a specific area and for an extended time [75]. The major benefit of nano-vaccines over conventional vaccinations, which often use multiple injections and dose delivery systems, maybe that they don't cause any pain during administration [7]. Nano-vaccine drawbacks may include formulation difficulties that arise during manufacturing, and potential toxicity brought on by the body's protracted clearance of the NPs. Therefore, assessing the safety of nano-vaccines should be just as important as researching their effectiveness [7]. NPs, such as bacterial spores, virus-similar constituent parts, exosomes, and phage, as well as synthetic NCRs including virosomes, proteosomes (proteosome vaccine), liposomes, super-fluids, and nano-beads, can be utilized to create nano-vaccines [76]. Potentially effective treatments for chronic diseases [7], include liposomes [77], polysaccharide [75], polyanhydride [78], polymeric [79], HIV [80], influenza [81].

2.9 Radiosensitizers in Radiation Therapy

At the moment, the potential worth of NPs as innovative radio-sensitizers in radiation treatment (therapy) has been researched, along with the rapid advancement of NTech [7]. One of the most popular non-surgical methods for tumour treatment is radiation therapy. Its effectiveness is frequently limited [82]. According to research, NPs can increase the effectiveness of radiation treatment (therapy) by serving as both a beneficial (therapeutic or healing) and a carrier for other medicines. Due to their physicochemical characteristics, NPs, in particular, big atomic number metal NPs like Au, can also make tumour cells more sensitive to ionizing radiation or enclose radiation-sensitizing compounds, shielding them from deterioration [82, 83].

Currently, Au, Ag, and Fe NPs are being extensively researched for cancer treatment (therapy) owing to the possibility of a greater beneficial (therapeutic or healing) index with radiation treatment (therapy) [7].

3 HBS of MNPs Used in Clinical Trials

As a result of the rapid growth of NTech, MNPs are being extensively produced for medical and pharmaceutical (biomedical) reasons. Despite the many alleged benefits of MNPs, growing worries regarding HBS have been voiced [84]. First, as mentioned above, due to their incredibly small size and vast surface area, NPs have different physicochemical properties from their bulk analogues, making them more reactive and catalytic. Second, by intravenous or interstitial injections, exogenous NPs may be administered to people without first going through the regular gastrointestinal absorption process in the field of NMed. Third, NPs may interrelate with the biological particles or build up in cells or organs of humans while inside the body. The key to the harmless use of NP products in medical practice is HBS evaluation. However, keep in mind that the majority of published data on NP products used in NMed are still in the in vitro or in vivo animal experimentation stages. The final and most crucial phase in the clinical translation of NP products should be human clinical trials. However, due to the lengthy, difficult, and resource-intensive nature of clinical translation in NMed, the transition likelihood may be minimal [85].

Additionally, clinical trials for NMed products create numerous ethical issues due to the ambiguity surrounding HBS [86–88]. Inhalation of NPs is typically the main method of entrance into the human body under circumstances of occupational and environmental exposures. However, the specific exposure methods in NMed include intravenous and interstitial injections of nanoparticulate carriers. In a previous publication titled “Toxicology of NPs employed in NMed” [84], they evaluated HBS evaluation information pertaining to animal studies of NPs. The body of knowledge about the genotoxicity, carcinogenicity, reproductive and developmental toxicity, acute and chronic toxicity, and genotoxicity of NPs in animal investigations is growing but is not hitherto comprehensive [7].

According to studies conducted on animals, some NPs may possibly have harmful impacts on human health. For instance, the WHO as well as the “International Agency for Research on Cancer” have characterized TiO_2 and carbon black NPs as potentially carcinogenic to humans based only on data regarding their ability to cause cancer in test animals [89]. Multiwalled carbon nanotubes (MCNTs) have a limited record of carcinogenicity in animal studies following intraperitoneal injections [90], but there is no information on lung inhalation exposure. There are few current research findings on the genotoxicity of NPs [84]. Additionally, there is no information to support the carcinogenicity of other NPs [91].

On the other hand, Sargent et al. [92], demonstrated that inhaling MCNTs can result in cancer in mice. It is also unknown the extent to which human exposure to NPs created for medicinal utilization causes cancer [84]. The outcomes of all these animal experiments do have some ramifications for the assessment of the HBS of NPs intended for NMed. However, compared to human administration methods used in clinical practice, high doses and brief exposure times are typically used in animal investigations. Additionally, findings from animal tests can hardly be immediately induced to people as a result of the significant modifications in anatomy, genetics and physiology between humans and other creatures (animals), and in the majority of cases, animals have been meagre predictors of how humans will react to medications [7].

In light of this, studies are primarily concentrated on human clinical (medical) trials, and this chapter attempt to offer a broad overview of the current situation regarding the HBS of NMed products utilized or to be employed in clinical (medical) practice. We will attempt to respond to the inquiry: Are there any toxicities or negative health implications following human exposure during clinical trials? 2013 saw the completion of a thorough literature search by Etheridge et al. [15], using the search terms “clinical trial and NMed” on some data base such as PubMed, Scopus, Google Scholar, etc. They discovered an overall of about 247 accepted or in various phases of clinical (medical) research applications and products. All of the actively targeted products are intended for the diagnosis or treatment of different types of cancer.

2015 saw the discovery of 145 clinical (medical) studies for the phrases “NPs and cancer” via the database of the “US National Institute of Health”, a significant decrease from the 45,139 clinical studies in oncology that were recorded by this website at the same time. According to more than 9000 publications in PubMed, this illustrates a significant gap between NP design and clinical translation. The fact that there are so few clinical (medical) trials for NMed products may be because many firms creating NPs post extensive clinical trial data on authorized systems or nanoparticulate (NP) systems on their websites (internet sites) rather than in open publications [93].

According to research by Thomson Reuters Life Science Consulting, 21% of phase III clinical trial failures reported between 2007 and 2010 had safety-related causes [94]. The majority of these clinical trial failures, meanwhile, are not listed in the publicly available scientific literature. Anticancer drugs are delivered using liposomes, spherical structures with sizes between 100 and 400 nm and polymer-based chemical units (below 100 nm). Also employed are certain structures like antibody–drug conjugates or NPs that are albumin-bound. After a thorough analysis of clinical trial articles on NMed published in open-access journals, it was discovered that most of them concentrated primarily on reporting the therapeutic efficiency of the medications, rather than assessing the NPs’ HBS for use in humans [7].

Although all substances allotted for clinical trials have been proven to be biocompatible by current standards, it is still unknown whether continued exposure to them in the human body may result in acute or long-term negative consequences [15]. Due to their special characteristics, NPs can be utilized as potent antitumor agents or as a supplement to conventional anticancer treatments to increase their therapeutic potency. Nevertheless, despite the large number of NTech-based formulations that have been published, only a small number of them have been used in clinical studies [7].

According to Al-Hajeili et al. [95], NP albumin-based paclitaxel (nab-paclitaxel), also recognized as Abraxane®, is a colloidal suspension of 130 nm constituent parts regulated in human blood serum albumen bonded to paclitaxel. It has been approved for the treatment of metastatic breast cancer. Patients who received nab-paclitaxel compared favourably with those who received solvent-based paclitaxel in terms of overall survival. In order to enhance nab-paclitaxel-based (Abraxane®) therapy (treatment) for metastatic and preliminary-stage breast cancer, several clinical trials have since looked at various schedules, dosages, and combinations [96]. In these clinical trials, no significant negative effects associated with human serum albumin NCRs were noted.

Yamamoto et al. [97], discovered that in a crucial relative randomized phase III investigation for the treatment (therapy) of breast cancer, the group treated with nab-paclitaxel had a greater occurrence of sensory neuropathy than the group treated with solvent-bound paclitaxel. A new kind of paclitaxel called nab-paclitaxel does not need ethanol or poly-ox ethylated castor oil as solvents. The utilization of these solvents has been linked to toxic reactions, together with extended sensory neuropathy and hypersensitive reactions, as well as a detrimental effect on the therapeutic index of paclitaxel [97]. In this clinical experiment, there was no plausible explanation for why the human serum albumin nano-carrier group demonstrated a higher occurrence of sensory neuropathy than the group receiving solvent-bound paclitaxel.

The fact that these negative side effects vanished quickly following treatment interruption and dose reduction was acknowledged by the authors. According to animal studies, changes in congealing, renal, cardiovascular, and pulmonic roles are primarily responsible for any potential negative consequences that may result from the high-dose injection of human serum albumin [98]. It is still unknown whether there is any connection between human serum albumin NCRs and a higher prevalence of sensory neuropathy. In a clinical investigation, an aqueous dispersion of iron oxide (magnetite) NPs (Nano-Cancer® therapy) was administered to 66 patients (59 of whom had recurrent glioblastoma) in a clinical investigation, and the constituent parts were then heated in an alternating magnetic field.

Fractionated stereotactic radiation was used in conjunction with the treatment. This therapy strategy had few adverse effects, and no major consequences were noticed. They came to the conclusion that MNP thermotherapy combined with low radiation doses is secure and efficient [99], another clinical trial, aminosilane-layered FeO NPs (core diameter: 15 nm) distributed in water with a Fe content of 112 mg^{-1} were injected intratumorally under the guidance of three-dimensional images into 14 patients with glioblastoma multiforme. Following the injection of 0.1–0.7 ml (median: 0.2) of magnetic fluid per ml of tumour volume and single segments (2 Gy) of a radiation series of 16–70 Gy, patients underwent 410 (median: 6) thermotherapy treatments (median: 30). They found that MNP thermotherapy was generally well tolerated by patients and had minimal to no side effects [99]. The prospective phase I clinical research involving ten patients with biopsy-confirmed locally recurrent prostate cancer examined the treatment-connected morbidity and value of life next intra-prostatic injection of an NP scattering and thermo-therapy employing super-paramagnetic NPs. The findings disclosed that NP deposits could be found in the prostate a year after heat therapy.

However, based on prior research, we can take the following findings from this clinical trial [7]: (i) a specific dose of rigid, solid Au NPs could be administered into the human body by venous injection without causing serious, immediate side effects. (ii) the human body can handle formulations of 200–400 nm-sized Au NPs. (iii) not only normal tissues or organs but also malignant tissue will receive Au NPs. Therefore, even if this treatment formulation is given clinical approval, further research into the possible long-term harmful effects is necessary.

4 MNPs' HBS and Hazard Issues

A thorough HBS evaluation is necessary if MNPs are to become promising NPs for the diagnosis and treatment of disorders in clinical settings. Studies on safety evaluations include [7]:

- Cell models are used to investigate how MNPs impact cell proliferation or differentiation, cell models are used.
- Examine the distribution, accumulation, and toxicity of any potential organ harm brought on by MNPs once they have entered the body using animal models.
- Clinical applications; observing and describing any potential side effects of MNPs.

NPs such as MNPs have a variety of fascinating uses, but they also pose safety risks such as negative effects on the consumer, environment, and worker health [1, 7, 10, 100, 101].

The following evaluations should be taken into consideration in order to properly identify and manage the risks related to NTech [102]:

- By being aware of the ways that manufactured MNPs can be exposed to the body,
- examining the possibility of translocation, or the transfer of changed MNPs from their site of entrance to other regions of the body.
- Identifying possible biological effects of exposure to altered MNPs is known as toxicity (toxicity).
- Exposure and dose metrics; recognizing which metrics for exposure and dose most closely resemble toxicity.
- Understanding the most effective technique to monitor exposed populations for potential health effects is essential to health monitoring.

5 Conclusions and Suggestions for Research Strategies

In conclusion, this chapter reviews the exceptional chemical and physical features, possible applications, and HBS in NP clinical (medical) trials. Minute size, surface area, quantum magnitude, chemical reaction characteristics, catalytic characteristics, optical characteristics, and other characteristics are some of the distinctive chemical and physical features of NPs. Medical analysis (diagnosis), drug carriers, medical tools, tissue engineering, therapeutic medicines, nano-gene medicine, cancer GT, nano-vaccines, and radiosensitizers are the main possible applications of NPs in the biomedical domains.

A speedier, more precise, and more reliable diagnosis is now possible thanks to NTech. Medication carrier NPs are easily administered and absorbed, lengthening the half-life of the drug and lowering the dosage requirements. More precise targeting in GT for cancer can prevent medications from harming normal tissue or cells too severely. NTech may potentially be crucial in tissue engineering. Currently, NPs are most frequently used in formulations that are liposomal and polymer-conjugated for NMed products. Clinical trials with open publications only provide a small amount of data on HBS. The majority of clinical trial reports for NMed products place too much emphasis on the therapeutic efficacy of medications and not enough on HBS or side effects.

We outlined the following tactics as recommendations for upcoming research in NMed to aid in the development of NMed:

- The special chemical and physical characteristics of NPs have advantages and disadvantages. It is important to first ascertain whether these distinctive features could have either short-term or long-term negative impacts on people before creating NPs for medicinal application. NPs could be hazardous to the immune system, heart (central circulatory system), vascular system, liver, kidneys, lungs, and kidneys. Except for non-invasive medical devices or medications for exterior applications alone, several NPs might not be appropriate for human usage, predominantly via venous or interstitial injections. Therefore, any NMed products intended for invasive delivery should offer thorough safety data prior to any clinical application.
- One can access thousands of different studies released every year to research the possible medical applications of various NPs by searching through some prominent data base. However, the majority of these investigations use in vivo animal experimentation or in vitro cell culture. There is still a long way to go before medical technology can be used from the bedside. Additionally, we discovered that a large portion of scientists and researchers working in the field of NMed have no medical training. There will always be a chasm between the use of NPs in laboratories and in clinical settings. The ideal technique to develop NMed goods should be through a research group made up of multidisciplinary (diverse) sciences such as applied, toxicological, chemical, material, biological, basic, and clinical medical (biomedical) sciences. Therefore, when requesting financing for

the use of NPs in clinical settings, research teams made up of multidisciplinary scientists, notably medical doctors, are essential and should be given preference.

- After reviewing, we identified two significant barriers to the advancement of NMed. First, there is a significant gap between clinical transformation and research. The ultimate goal of clinical medicine is to go from bench to bedside use. As previously mentioned, collaboration among diverse scientists should be used to build a bridge between the lab and the bedside. Second, the quick and healthy development of new NMed products depends greatly on the evaluation of clinical trials' HBS. Therefore, it is advisable to encourage the publication of both successful and unsuccessful clinical trial findings on NMed products in open publications. In this approach, failing clinical trials brought on by unfavourable effects on humans may aid researchers in avoiding similar errors while creating new NMed products.
- The majority of clinical trials for medications carried by NMed products concentrated on the therapeutic efficacy of drugs rather than the NPs HBS. It will be best to identify whether side implications and/or bad consequences are brought on by the medications or by the NPs when they are utilized as drug carriers in upcoming clinical trials. Furthermore, following clinical usage, chronic adversative implications of NMed products, mostly those utilized for bellicose delivery, must be further assessed as a result of the length of duration it takes for clearance or build-up in tissue or organs. Evaluation of HBS after several years of deployment in clinical (medical) practice also requires epidemiological research.
- HBS testing for NMed products is still in its early stages at the moment. It is challenging to compare published findings for preclinical and clinical testing from various laboratories or hospitals because there are hardly any defined evaluation techniques. For the purpose of evaluating the HBS of NMed products in clinical (medical) trials, a unified, standardized test battery that may encompass all blood chemistry indicators, immunological, neurological, reproductive, evolving, carcinogenic, teratogenic, and mutagenic noxiousness should be developed.
- We must be ready for unintentional overdose, abuse, or accretion of NPs in human tissue and organs as we investigate NMed products for use in humans. This means that it is also important to look at ways to encourage superfluous NP excretions from the body as well as ways to deactivate or treat the harmfulness of overdose. Before allowing any NMed product for clinical application, emergency medicine and emergency clinical (medical) procedures should also be investigated.
- Even though soft NPs are typically thought to be less harmful than rigid solid NPs, it is important to take into account the possibility of detrimental effects during long-term accretion in the cells or organs of humans. In addition, the human body may digest or metabolize certain soft NPs, including liposomes themselves. Therefore, while assessing the clinical (medical) usage of medicinal NP products in clinical (medical) trials, a number of crucial questions should be addressed. Some of these queries are bio-distribution, dynamic changes in particle dimensions, eradication half-life, and accretion in the cells or organs of humans, mostly in non-targeted cells or organs of humans.

- The most recent clinical trials have not sufficiently proved how to avoid bacterial or other microbe contamination in NMed products, particularly those supplied intravenously. We are aware that traditional disinfection techniques might not be appropriate for NP decontamination. Therefore, it is important to continue researching standardized disinfection techniques for various types of NMed products.
- The prevention of NMed product contamination during clinical (medical) trials or clinical (medical) applications should also be taken into consideration, though it is not necessarily the least significant factor. Prior studies on the health concerns associated with occupational exposures of scientists, laboratory employees, healthcare professionals, and family members during medical (clinical) usage of NMed products are lacking. Additionally, environmental dangers have not been looked into. It would seem prudent to take a more cautious approach when monitoring such exposures or pollution.

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Potentialities of Magnetic Nanomaterials in Tissue Engineering Applications

Benedict Okundaye, Uyiosa Osagie Aigbe, and Kingsley Eghonghon Ukhurebor

Abstract In the human body's ecosystem tissue engineering's prior procedures for building, inspecting, and repairing or reconstructing damaged tissues or organs have profited considerably from advances in magnetic- nano-sized-particles/ nanomaterials technological uses. Safe physiological/economic/environmental enhancements and applications are required to comply with future global demands on beneficial magnetic-induced nanoparticle engineering to sustain man's health and well-being. The review introduces the fundamental attributes, and methods for preparing, characterising, and functionalised nanomaterials. It also catalogues the uses and advancements of magnetic-induced nano-sized-particles in tissue engineering and drug delivery.

Keywords Discharge processing · Magnetic-induced nano-sized-particles · Magnetic liquids · Densimetric partition · Medical applications · Metal ion elimination · Superparamagnetic

1 Introduction

Magnet-inducible nanotechnologies that are logically constructed along the line of the pillars of tissue engineering are required to address the majority of issues of the human body that are now plagued with ailments and addressed in nano tissue engineering. Hence, a brief overview of the potentialities of magnet-inducible nanomaterials is embarked on in this chapter.

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The body is made up of various ecosystems ranging from highly damaged, extremely dry habitats on the skin's surface such as elbows— or continuously damp, super nutrient-rich membrane-forming planes such as the mucous membrane that covers the front of the eyes (conjūnctīva). From pockets with minimal concentrated mass and a hydrogen concentration of 3 (the abdomen) to the guts habitats with a hydrogen ion concentration ten-one hundred thousand times lower and 1011 cells/ gram concentrated mass. After that, there are extensive regions of the same body that, in a healthy condition, the blood remains sterile.

Sporadically, conditions that support microbial colonisation are created by pre-existing pathologies such as cystic fibrosis even diabetes, anatomical abnormality, injury, or the implantation of a foreign object. The conditions containing biological film a thin, slimy film of bacteria that adheres to a surface population may cause pathology, and because they are antimicrobial resistant, these "misplaced" biofilms are frequently unmanageable and may have serious and fatal, repercussions for the host as well as incur enormous additional medical expenses.

There are many potential uses for magnetic-induced nano-sized-particles and numerous kinds in enhancing human health sustainably [1]. Therefore, it is important to emphasise feasible magnetic nanomaterials (MNM) for various tissue engineering applications. According to the patterns of interest in current nanotechnology, increasingly, research focuses on creating new methods of magnetic functionalisation of biomaterials as found in nature— by combining various magnetic nano-sized-particles to achieve the desired goal as sustainably, cheaply, and safely as possible. Magnetic-induced nano-sized-particles explored cell mechanotransduction (the mechanism through which cells transform mechanical stimulation into electrochemical activity), production of compound three-dimensional tissues, regulating cell designing, and gene distribution. Nanomedicine advancements involved with MNM can be used for targeted medication delivery [1], nanotechnology-based chemotherapy in treating chronic diseases such as cancer and heart diseases, or microorganism detection in the body system. In order to use nano-sized-particles for their intended purposes, scientists must model, measure, construct the image, and manipulate them.

Tissue engineering in medicine is used in regenerative medical practice to repair or replace bodily systems, -parts of or entire tissues such as bones, blood vessels, bladders, skin, or muscle. Affected tissues or organs require biomechanical or metabolic functions to be performed by cells inside a synthetically produced support system, such as in a bioartificial liver— or a delivery mechanism containing particles of functionalised superparamagnetic magnetite. Body structure, organs, and systems are examples where magnetic nano-sized-particles have been applied. These charged particles actuate according to their programming and perform specific functions [2]. However, the potential sensitivity of these implanted foreign body materials and the impact on reproduction, and even the impact on foetal development all need to be carefully considered when these magnet-inducible nanomaterials are used in tissue engineering to replace damaged organs [2].

1.1 Some Terminology Frequently Adopted in MNM Studies

Some terminologies are specific to MNMs' research and studies, the list below is not exhaustive but indicates commonly used phrases in the field.

1.1.1 Susceptibility

The degree to which a substance becomes magnetised when exposed to an external magnetic field is known as susceptibility.

1.1.2 Superparamagnetism

Contrary to larger single-domain magnetic particles, these particles are particularly intriguing for medical or (bio)technological diagnostic and therapeutic applications [3]. A single-domain magnetic particle generated when a ferromagnetic, multidomain sample of Iron-Oxide-Black (Fe3O4) is reduced in size below 40 nm is of potential benefit in bio-tissue development. When this newly formed single-domain magnate is exposed to an external magnetic field, it generates a significant internal magnetisation as a result of electron exchange coupling inside the domain and so becomes superparamagnetic. Particles with unique characteristics that adapt remarkably well to functionalities of interest in biomedical applications [3] are those that are 20 nm or smaller [4].

1.1.3 Ferromagnetism

Ferromagnetism is the feature of some substances, such as iron, that causes them to exhibit high magnetic-charged permeability and, frequently, high magnetic-charged coercivity, enabling the substance to create a perpetual magnet (see Fig. 1).

1.1.4 Transition Metals

Metal with a partly filled d subshell or the capacity to form cations even with an empty d subshell. Included in this group of metals are Cadmium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Meitnerium, Darmstadtium, Roentgenium, Copernicium, Yttrium, Zirconium, Niobium, Molybdenum, Technetium, Ruthenium, Rhodium, Palladium, Silver, Scandium, Lutetium, Hafnium.

Gold MNMs have broad applicability in tissue engineering for in vitro and in vivo sensing and much as isolators because they can detect specific bladder cancer biomarkers at low levels and in the presence of other proteins [5]. While

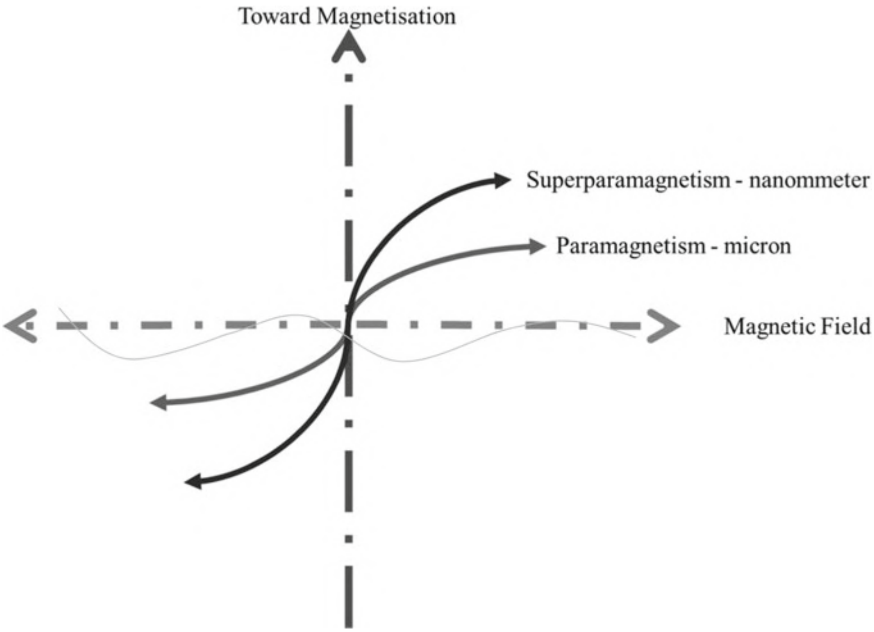

Fig. 1 An example of a particle magnetic state about an induced magnetic force. [From authors' rendition]

silver and gold metals provide good biosensing platforms because of their plasmonic features and are now often used in many optical platforms, silver nanoparticulate has outstanding antibacterial properties that can be used in the creation of biomaterials [6]. Gold nanoparticles bind to serum proteins with positive charges in addition to aggregating when injected intravenously [7]. The protein cytochrome C oxidase, which is necessary for aerobic respiration, reduces oxygen through the actions of copper and iron. In an electron transfer chain, some blue Copper proteins assist in relaying electrons for the synthesis of ATP [8] as the cell's primary source of energy.

1.1.5 Post-transition Metal

On the periodic table, they are a group of elements that fall between transition metals and metalloids. Gallium (Ga), Indium (In), Tin (Sn), Thallium (Tl), Lead (Pb), and Bismuth are some examples of metals (Bi) [8].

1.1.6 Metalloids

They serve as catalysts enabling desired outcomes in many MNM applications (which have some basic application setup principles), raising the rate of a chemical process or lowering the temperature or pressure required to initiate one without being destroyed themselves**.** Although metalloids make excellent semiconductors and amphoteric oxides, they are neither good thermal nor electrical conductors and make good biological agents. Compared to metal elements, these elements conduct less heat or electricity and are made up of Tennessine, Arsenic, Silicon, Polonium, Tellurium, Germanium, Antimony, and Boron.

2 Pillars of Tissue Engineering

For the repair or regeneration of damaged tissue, the discovery of magnetic nano-sized-particles and their use in tissue engineering are crucial. According to Singla et al. (2019) the three fundamental pillars of tissue engineering are:

1. Material scaffolds: hollow frames of three-dimensionalities biomaterials that are permeable, stringy, or absorbent allowing cells to grow, multiply and differentiate into different types of cells [9] and designed to move bodily fluids and vapours, stimulate cell contact, practicality, and extra-cellular material accretion with little swelling and poisonousness, and biologically-decay at a regulated pace.
2. Cells: the biochemical, structural, and functional building blocks of all living things capable of autonomous replication are called cells. They consist of cytoplasm, a liquid found inside of cells and surrounded by a membrane. Numerous biomolecules, including proteins, nucleic acids, and lipids, are also present. Cells, the fundamental units of life, are classified into two categories. Firstly, prokaryotes, such as bacteria, lack a well-defined nucleus and have a relatively basic structure. Secondly, eukaryotes have a well-defined nucleus and are more complicated in structure and function— organisms such as animals and plants are made up of eukaryotic cells.
3. Bioactive chemicals: a physiologically active material/substance/compound that, depending on its availability or measure to the organism, can have an immediate—favourable or unfavourable impact on a living thing.

3 Nanomaterials

Liposomes: A liposome is a nanoscale synthetic vesicle used in tissue engineering applications with at least one lipid bilayer and a spherical form [10]. To administer therapeutic medications and nutrients to tissues and organs, liposomes can be employed as drug delivery vehicles due to their hydrophobicity [11] or hydrophilicity [12], biocompatibility [13], particle size and many other features. Micelles: Micelles are vesicles made of copolymers that are amphiphilic [14]. Polymer-conjugates: Due to their special characteristics, conjugated polymers are appealing for a variety of applications. They are excellent for a vast range of specialised applications as their molecular structure can be easily chemically modified [15]. However, with complex chemical structures resembling biomacromolecules, multi-bonded polymers can achieve electric resources that are akin to non-crystalline mineral partial conductors [16]. Polymersomes: Polymerosomes are a type of artificial vesicle, which are tiny hollow spheres that contain a solution in biotechnology. dendrimers, aptamers, and carbon nanotubes are all examples of nanomaterials.

3.1 Hydrogels

A hydrogel is a covalently bonded hydrophilic polymer that is impermeable to water. They keep their distinct contours while being super absorbent. A crosslinked hydrophilic polymer that does not dissolve in water is known as a hydrogel. They are extremely absorbent while still retaining well-defined shapes. Crosslinks that connect the polymers in a hydrogel are classified into two types: physical and chemical. Numerous applications, notably in the biological realm, are based on these properties. Numerous hydrogels are artificially manufactured, and some are found naturally. In 1894, the word hydrogel was invented and used to define a colloidal salt that is an inorganic gel [17]. In 1960, hydrogel research for biomedical applications was used in contact. In 1894, the word "hydrogel" was invented for lens production but was later used for drug administration. Due to its great accuracy and efficiency, tri (3-D) printing, a kind of additive fabrication, has found several uses in the field of medicinal engineering [18].

3.2 Nanospheres (NS)

NS are nanohaulers that range in bulk between 10 and 200 nm and are mostly used to carry medications and genes. They can shield the medications from enzymatic and chemical corrosion and can be crystalline or amorphous in form. dextran-NS, Albumin-NS, gelatin-NS, and polylactic acid-NS are a few examples of biologically degradable-NS [7].

3.3 Metals Polymer

Metal polymers are solid materials that include metallic ions or metals such as gold or copper; a polymer is made up of tiny molecules that reoccur resembling links in a chain. Preclinical investigations for numerous applications are currently being conducted on gold nano-sized-particles as the topic of an extensive international research effort [19]. Gold is one of the fewest reactive chemical components and under normal conditions solidifies. In rocks, veins, and alluvial deposits, when functionalised, gold can occasionally be found in elementally loose native form as nuggets and granules. A few nanometre-sized gold nano-sized-particles were discovered to possess paramagnetic characteristics, which means they may attract other magnetic materials like tiny bar magnets.

3.4 Ceramics and Glass–Ceramics Polymer

Glass is a solid that is noted for not being crystalline and for having no long-range order in the arrangement of its molecules. Hench (2006) indicated that in 1969 some silicate-based non-crystalline compositions were bioactive, and chemically connected with bone material [20]. The use of a silicate base prevents the oxidation of magnetic nano-sized-particles and enables a variety of functionalities to be applied to the surface of the particles [21].

3.5 Natural and Synthetic Polymers

Polymers come in two different varieties: artificial and natural. Natural polymers can be derived from the environment. Natural polymers include silk, deoxyribonucleic acid, cellulose, and proteins. Pectin is an illustration of a natural polymer, whereas vulcanised rubber is a manufactured (imitation) polymer.

Widespread utilisation of artificial biologically degradable polymers in tissue engineering, including.

- Polyesters: Beta-Hydroxy-butyrate Polymer is an aliphatic polyester that is a short-chain poly-hydroxy-alkanoate (PHA).
- Polyanhydrides: biocompatible and breakdown in vivo into non-toxic diacid equivalents that are removed as metabolites from the body.
- Polystyrene: due to their capacity to manufacture porous polymer beads as matrices for the creation of magnetic particles, they were chosen as the first optimal polymer for creating magnetisable polymer pellets used for constructing carbon-based magnetising systems [22].
- Polyphosphazenes; consist of a variety of mixed-fusion inorganic–organic polymers with a variety of bone structures, including the spine P-N-P-N-P-N-
- polyurethane: a thermosetting organic polymer that features many organic units linked via urethane and those with thermoplastic properties can incorporate MNM.
- Poly glycerol sebacate.

4 Types of MNM for Tissue Engineering

Most research falls into the category of particles and a lot of research over the last twenty years has focused on creating novel magnetic nano-sized-particles that might help with illness detection and therapy [23]. MNMs are classified into two types: natural and man-made. Both types comprise particles that react to the passage of a magnetic field at the molecular level. These nano-sized-particles can be functionalized to carry payloads that impact or change the state of matter to assist a system. Magnetic fields of appropriate intensity and direction are carefully monitored. Particles are made from a wide variety of magnetic materials [24]. MNMs contain magnetic element particles such as iron oxides, magnetite, ferromagnets (nickel), or cobalt. Magnetic nano-sized-particles' chemical and physical characteristics are determined by their chemical structure and technique of manufacture. Superparamagnetism refers to the behaviour of nanoscale magnetite particles in the presence of a lower transition temperature function in a state that is lower than the transition temperature of the bulk material. Obtaining stability at the ideal temperature without undesirable consequences is a typical challenge in many applications of nanomagnetic particles are sources for progression in the field. For instance, pure $CoFe_2O_4$ as a stable high-rate conversion anode [25], or as molecules switches at a lower temperature [26].

4.1 Bond Structure of MNM

Metallic bonds can be exceedingly strong or very weak. Its potency largely depends on how well valence electrons are protected from nuclear attraction by electron shells. Mercury and lanthanides have weaker metallic bonding than lighter transition metals in part because of relativistic effects in big atoms. When two atoms have equal electronegativity values, metallic bonds are formed. Metals and some metalloids are composed of atoms that form metallic bonds. Silver, gold, brass, and bronze, for instance, all include metallic connections. Additionally, compressed hydrogen and carbon allotrope graphene use this type of bonding. Some of the qualities possessed by magnetic nanomaterials include:

- Malleability and ductility are two mechanical properties of metals that are explained by a metallic bonding. Metals' malleability, may be shaped without losing their structure and drawn electrons can flow past one another known as ductility.
- Varied electrical and thermal conductivity: In terms of electrical conductivity, free electrons carry charges, while in terms of thermal conductivity, they carry thermal energy that may be directable.
- Nanometals with high melting and boiling temperatures have strong attractive interactions between their atomic nuclei and delocalised electrons.

Ionic bonds are created by metal atoms and nonmetals. They join themselves or other metals through covalent or metallic bonding. Particularly, covalent, and metallic connections are formed between hydrogen and alkali metals. Lithium and metallic hydrogen therefore exist. Gas molecules H_2 and Li_2 also accomplish this.

5 Methods of MNM Synthesis

There are numerous ways to produce MNM or composites such as hydroxyapatite-based nanocomposites. Wet methods [27], dry methods [28, 29], high-temperature methods, and combination methods are the four main categories that can be recognised [30]. Scaffold design and fabrication take many forms such as— a two-step synthesis technique for producing a multi-porous structure of glycerol sebacate urethane composed of nano-clay and polyacrylic acid. The permeable framework was created by adding spun sugar and curing it for 3-days at room temperature within a Teflon mould [12]. Different amounts of nano clay were ultrasonicated for 2 X five-minutes in 1, 4-dioxane— a predetermined amount of (II)-2-ethyl-hexanoate, and HDI, pre-PGS, tin was added to the solution [12]. By copolymerizing cyclic phosphate monomers with various pendant groups through ring-opening, biodegradable and biocompatible polyphosphoesters such as butenyl, methyl, or butyl) were created [31]. After UV exposure, a stable and well-defined cross-linked material is produced, and the mechanical properties of the related polymer films are determined by the initial PPE copolymer's chemical makeup [31].

6 Methods of MNM Characterisation

Due to their ability to generate vital physiological traits that improve their performance and make them useful for a variety of applications, nano-sized-particles are distinguished by their nanoscale dimensions [9]. A method for probing and measuring a material's structure and properties. For example, magnet-inducible gold nano-sized-particles' surface conjugation and silver's conductivity, as well as the antibacterial properties of other metallic nano-sized-particles and metal oxides, and the distinctive electromechanical qualities of carbon nanotubes are particularly helpful in a variety of tissue engineering applications.

Nano-sized-particles have an advantage over peptides and small proteins in TE because of their tiny size and the high surface-to-volume ratio that goes along with it. They are simple to diffuse through membranes, which aids cell uptake.

Nano-sized-particles can also be created in customisable sizes and surface properties to fit any need; thus, one is not constrained by a predetermined size. Additionally, nano-sized-particles imitate the extracellular matrix (ECM) elements of tissues' at their inherent nanometre size scale. In a certain sense, nanoscale structures can be seen as an important part of our body, as cells and the ECM that make up organs and tissues are composed of a variety of atoms, molecules, nanostructures, microstructures, and macroscale structures.

7 Application in Body Tissue Systems

Standard fluorescent magnetic materials are built on one of the magnetic iron oxides, however, a lot of contemporary materials employ extremely minute iron particles, either alone or in conjunction with iron oxide. In the field of biomedical engineering known as tissue engineering, many biological tissues can be repaired, improved, or replaced by using a mix of cells, engineering, materials techniques, and the right biochemical and physicochemical parameters. Although not exclusively used in cell-and-tissue scaffold applications, tissue engineering frequently entails the utilisation of cells positioned on tissue scaffolds to create new, live tissue for medical purposes. Once considered a sub-field of biomaterials research and study, due to its increased significance and breadth of magnetic applications in the field, the tissue nanomagnetic particles engineering field is well established and highly exemplified in the fundamental pillars of tissue engineering.

8 Hydrogels in Tissue Engineering

Reviews of the use of magnetically sensitive nanocomposite hydrogel materials. In tissue engineering, artificial or substitute tissues or organs are implanted to replicate the functions of wounded or diseased tissues. Modern techniques place more emphasis on regulating cell behaviour and tissue creation through nanoscale topography. Magnetic nano-sized-particles may be used as mechanical remote actuators to regulate the behaviour of cells embedded in hydrogels, when external magnetic fields are applied. Uses include metal ion removal from effluent, densimetric split in magnet-induced liquids, restorative and analytic testing, and waste refining.

When combined with functional materials like magnetic nano-sized-particles, hydrogels, which are a type of bio-ink, can be used for innovative construction techniques [32] for 3-Dimension biologic printing with the ability to replicate cells possessing high mechanical characteristics skilled with supporting 3-Dimension forms [33]. Likewise, when combined with 3-Dimension biologic printing, hydrogels enable researchers to create a variety of scaffolds that may be employed to construct fresh tissues or bio-organs. Many obstacles remain, such as attaching vascular to 3-Dimension printed tissues. In the interim, 3-Dimension printing of bio-tissues will undoubtedly increase scientific understanding of human biology, therefore speeding up both scientific and clinical research.

While hyaluronic acid, a naturally occurring molecular present in several bio-tissues all in the body mass, possesses many qualities that are perfect for building specialised scaffolds, it lacks the necessary stability. Thus, the potential for tissue regeneration is being studied in hydrogel systems based on polyethylene glycol diacrylate and magnetic particles such as hyaluronic acid treated with thiols [34].

9 Applications of MNM in Tissue Engineering

For the Tissue Engineering of various organs and/or tissues, such as skin, bone, cartilage, heart, liver, corneal, neural, pancreatic, and others, a variety of nanomaterials have been employed as scaffolds. Mechanical strength, high conductivity, and nanoencapsulation of significant growth agents are only a few of the qualities of nanomaterials that are taken into consideration for tissue engineering [35].

Metals, ceramics and glass–ceramics, natural and synthetic polymers and composites are four categories under which biomaterials used for 3D scaffolds are classified [36]. The magnetic polymer exhibits functionalised features such as paramagnetic, ferromagnetic, and ferrimagnetic [37]. In the process of polymerisation, monomer molecules are chemically combined to create a network of three-dimensional polymetric chains. At various temperatures, these polymers exhibit paramagnetic characteristics, and as the degree of polymerisation increased, so did their magnetic susceptibility. The polymerisation can also result in one-dimensional or two-dimensional polymer chain viable systems [38].

Molecularly imprinted polymer (MIP) composites, on the other hand, are materials made of at least two substances: MIP and the other one is chosen based on the additional qualities required for the finished composites [21].

9.1 Applications of MNM in Lung Engineering

For the creation of nanotherapeutics, inorganic materials including metal and metal oxide nano-sized-particles like gold, silver, silica cerium oxide, and iron oxide are frequently employed [7]. A clinical diagnosis and identification of individuals at substantial risk of acute traumatic lung injury could not be made as a result, and no trustworthy surveillance or predictive biomarkers could be developed [39]. But many encouraging signs require more clarification [39] Lungs have an exceptionally low biologically controlled microbial population. The most common obstructive lung disease in the world, chronic obstructive pulmonary disease (COPD), is defined by a loss in lung function [7]. For the creation of nanocarriers for chronic lung disorders, a variety of materials, including organic and inorganic ones made of proteins, synthetic and natural polymers, lipids, and metals, can be employed [7].

9.2 Applications of MNM in Skin Engineering

Bacterial cellulose has the potential to be integrated as a substrate for cartilage tissue engineering because of its high wet strength, in-situ moldability, biocompatibility, and quite easy, affordable manufacture [40]. Due to its many uses, Poly-beta-hydroxybutyrate is a substance that attracts interest in a variety of fields [41], including medicine, it is used as a therapeutic agent in the treatment of diseases affecting the nervous and circulatory systems as well as cancerous cells or tissues.

9.3 Applications of MNM in Bone Engineering

Significant research efforts are being made in the fields of allografts, xenografts, and other artificial implants on a global scale on both livestock and man, such as [42–46]. A wide range of possible materials that can be employed as bone graft substitutes has been generated thanks to advancements in surgical management and medical research. Characteristic capabilities, availability, patient morbidity, immunogenicity, potential disease transmission, and cost variations are factors to be considered when choosing bone grafts and substitutes [42]. The articular cartilage serves as a protective layer over the ends of bones in joints, allowing for smooth movement and distributing loads [40]. Certain MNMs can help regenerate bones by increasing bone density and their mineral and mass content. Both injectable composites containing ceramic particles and implantable gas-blown porous scaffolds are possible forms of polyurethane bone transplants.

A promising method in the field of bone tissue engineering has been the use of regeneration scaffolds to mend or reconstruct bone damage. Poly-beta-hydroxybutyrate (ketones) stands out among the materials available for this use for its adequate biocompatibility and ability to induce bone formation [13]. Inhibiting the activity of histone deacetylases and the subsequent epigenetic control of many genes is one of the ketones' most significant regulatory actions [47]. Increasing bioactivity and cell proliferation are hydroxyapatite's primary properties [30, 48]. These water-insoluble-thermoplastics, enantiomerically pure, non-toxic, biocompatible, and notably biodegradable materials are of tremendous interest in tissue engineering fields [41].

The retrieval of in vivo investigations on sheep metatarsus defects by [46]. The area that was most frequently used to execute serious size deficiencies was the mid-diaphysis of the metatarsal according to the authors. In addition to bone marrow mesenchymal stem cells and osteogenic protein 1 and plasma with platelet abundance, also natural, synthetic, and hybrid scaffolds were implanted in the experiment. Some methods of observation included radiography, histology, histomorphometry, computed tomography (CT), and biomechanics to assess the healing status with 4- and 6-months follow-ups. The metatarsal deformity in sheep appears to be an ideal habitat for combining biological and biomechanical characteristics. Natural scaffolds (homologous grafts or allografts) are used to treat defects larger than 3 cm, and natural, synthetic, or composite scaffolds are used to treat defects smaller than 2.5 cm. Regardless of the defect magnitude, no differences in the outcomes were discovered [46].

The majority of bones are made of collagen protein, but they also contain calcium, phosphorus, salt, and other elements. Collagen is a living, evolving substance that gives bones a flexible basis that enables them to withstand the strain. Numerous medical problems like osteoporosis have shown promising results when treated with MNM technology. Metallic fillers are beneficial for the polymer matrix due to their strengthening effect and amazing impact on the biological characteristics of the polymer-based 3D porous scaffolds [49].

A family of metal ions known as therapeutic metal ions has unique biological characteristics that could be used in bone tissue engineering. According to [50] utilizing the osteoblast cell line, basic biological characterization was conducted using MNMs— showing that the use of strontium, chitosan, and hydroxyapatite in combination offers a lot of potential for creating novel scaffolds. Chitosan/HA composites may be the perfect technique for creating tissue engineering scaffolds that supply a complex array of therapeutic ions in both components of the composite, resulting in specific biological effects such as osteogenesis and angiogenesis as well as antibacterial activity [50].

Magnetoliposomes are effective multimodal contrast agents when used as a delivery mechanism for CT or MRI studies [51], as a non-evasive technique [52]. Additionally, they can add targeting ligands and polyethylene glycol chains to increase the aggregation of nano-sized-particles at the region of interest and the bioavailability, respectively [53]. They can withstand both sorts of contrast simultaneously, whether it comes from transition and lanthanide metals, iron oxide nano-sized-particles, or ferrite nano-sized-particles [53]. Estelrich et al., (2015) claim that when a sample was exposed to a high magnetic field, the alignment of the protons' magnetic moments led to an equilibrium magnetization along the sample's longitudinal axis (in clinical diagnosis, magnetic fields of 1.5 or 3 T are typically used). Hence, protons' magnetic moments can then be rotated away from the longitudinal axis, in phase, to an angle known as the flip angle, using an RF pulse at a resonant frequency (5–100 MHz) capable of transmitting energy to them [53].

9.4 Applications of MNM in Liver Engineering

Next to the skin, the liver is the biggest internal organ in humans, conducting digestive processes. The liver's primary duties consist of processing nutrients from dietary intake and eliminating body pollutants. The numerous functions of the liver can be adversely affected by inflammatory diseases such as fatty liver disease or hepatitis, which eventually result in poor health. The liver generates proteins and distributes them throughout the body for skin, muscle, and bone formation. Hepatocytes, which are liver cells, are responsible for producing most bodily plasma proteins, including albumin, the primary plasma protein. Albumin, like many non-essential amino acids, is virtually entirely produced by the liver. Copper participates in cell signalling and cell growth [50, 54] but it can be toxic [55], although mutation in the ATP7B gene, which controls the excretion of extra Copper by the bile, results in Wilson's disease [8]. Cirrhosis and haemolysis are brought on by the accumulation of too much copper in the liver due to a mutation in this gene.

Hepatocyte transplantation is expected to be a successful approach to replacing liver functions. Understanding the intricate architecture of the liver provides a potential for hepatic Tissue Engineering to create solutions such as scaffolds, micro/nanotechnology, in situ regeneration, and cell patterning.

9.5 Applications of MNM in Pain Management

Acute tissue pain affects around 1.5 billion individuals globally, with lower back pain especially affecting 23–26% of the population [56]. Opioid therapy is the most advanced therapy for treating chronic pain because it provides long-term pain relief [57] but opioids are addictive and subject to abuse. Alternatively, nanomedicine has the potential to improve medicines and diagnostic methods [56]. Nanotechnology focuses on the formulation of therapeutic drugs enclosed in biocompatible nanomagnetic carriers between10 and 200 nm [58, 59].

10 Perimeters of Applications

10.1 Magnetisation Changes Within Particles

The interaction field factor, anhysteretic and thermoremanence curves, thermal relaxation processes, superparamagnetism, saturation and magnetic moment, and coercive forces are some states of nanoparticle magnetisation investigated in medical engineering.

10.2 Inspection of Tissue or Organs Using MNM Technology

Application of a wet or dry approach in a non-destructive test is required for the inspection of tissue employing magnetic-inducible nano-sized-particles.

10.3 Conclusion

Tissue engineering has a great chance to meet patient expectations and clinical requirements through the use of novel magnet-inducible nanomaterials. Despite the undeniable hazards associated with their use, the advantages that magnet-inducible nano-sized-particles have for medicine are significant. There are numerous types of nano-sized-particles having biomedical applications, including metal nano-sized-particles and polymeric nano-sized-particles [1]. When creating, evaluating, and applying these materials the risk of rejection, failure, or infection are high, these risks must be kept to a minimum following the precautionary principles set in place by maximising the potentiality of the materials over risk. The biosafety, use, and stability of magnet-inducible nano-sized-particles still need to advance significantly to meet with increasing expectations in sustaining life and healthy bodily functions.

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Utilization of Magnetic Nanomaterials for Combating Pathogens

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Abstract The incidence of infectious sicknesses like HIV, AIDs, gonorrhoea, malaria, typhoid, Hypes, smallpox, chicken pox, COVID-19, and measles from microorganisms have been spotted as one of the principal indicators of mortality. Several strains of drugs have been used to treat these diseases in recent years but have been proven ineffective and low potent in their mode of reaction because of the resistance potential of the microbes to the drugs. This reason had led healthcare givers and medical practitioners to increase the dosage range for therapeutic management of any disease. However, this has been reported by many studies to portend possible health hazards that ingesting them. So, there is a necessity to explore an alternative means for the sustainable production of antibiotics that is safe, health-friendly, and effective to combat microorganisms that have high resistance to multi-antibiotic drugs. To this end, this chapter reviews the utilization of magnetic nanomaterials as more effective potent tools for combating pathogens. Literature on the mechanisms

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of magnetic nanomaterials on pathogens, therapeutic potentials of magnetic nanomaterials against yeast, bacteria, fungi, and bacteria, and the health and environmental impacts of magnetic nanomaterials will be highlighted and discussed.

Keywords Nanomaterial · Health-friendly · Pathogens · Risks · Diseases · Antibiotics

1 Introduction

Recently, the incidence of disease-causing agents (pathogens) carrying destructive and deadly microbes, has been recounted to result in millions of deaths globally and yearly [1–3]. Pathogens like *Klebsiella pneumonia*, *Staphylococcus aureus*, *Escherichia* coli, *Pseudomonas aeruginosa*, *Acinetobacter baumannii*, *C. stellatoidea*, *C. guilliermondii*, *C. Kefir*, *C. dubliniensis*, *C. lusitaniae*, *C. parapsilosis*, *C. tropicalis*, *C. glabrata*, *C. krusei*, and *C. Albicans* have known to cause severe damage to the organs of humans and likely death in some cases [2].

Despite the enormous efforts put into the treatment of infectious illness, the potential health risks to public individuals have remarkably increased globally based on facilitated traveling by infected individuals and contacts. WHO (World Health Organization) in a report in 2018 stated that bacterial infection is the deadliest microorganism next to the infections from the virus which have resulted in over 10,000,000 deaths globally [4].

However, the use of antibiotics to manage or treat pathogenic infections has been long used for hundreds of years, nonetheless, there has been a series of reports of resistance to complex drugs utilized for the management of diseases caused by microbes based on their mode of action(s) [5]. This has added to increasing uncontrollable management of microbial resistance and propelled better efficient ways or alternatives for therapeutic control.

In recent times, use medicinal plants by Hossan et al. [6], and Adetunji et al. [7–9], and nanomaterials by Slavin et al. [10], have been utilized for the management of pathogenic illnesses because of their antimicrobial and effective properties. The optimization of nanomaterials with some magnetic particles like Ag, Au, and Fe_3O_4 (dendritic forms) has sparked great interest in the field of nanotechnology in different biological and industrial sectors. In the medical and pharmaceutical sectors, nanomaterials have been employed in the therapeutic management of various diseases caused by microorganisms. Amongst the nanomaterials, magnetic nanoparticles (MNPs) have sparked interest in this field because of their wide applications in the diagnostic and therapeutic management of strains of diseases in the biomedical sector [11, 12].

Therefore, MNPs behave as adjuvants which act as a drug messenger when combined with antibiotics for the effective combat of resistance spores of microorganisms during actions in humans. This composite possesses distinct benefits like little or no side effects and more resistance vigor when compared with traditional antibiotics [1]. More so, MNPs can avert microbial infection and adhesion. So, we provide here a chapter review of the utilization of magnetic nanomaterials for combating pathogens. Literature on the mechanisms of magnetic nanomaterials on pathogens, therapeutic potentials of magnetic nanomaterials against yeast, bacteria, fungi, and bacteria, and the health and environmental impacts of magnetic nanomaterials will be highlighted and discussed.

2 Mechanisms of Magnetic Nanomaterials (NMPs) on Pathogens

The mode of action of MNPs on pathogens is similar to various strains of nanoparticles or nano-composites when used in drug delivery processes. However, this is different from the mechanisms in which antibiotics act on a dreaded resistant microorganism (RMs). Under this context, the mode of action is basically through the deactivation of protein, the inhibition of enzymes, ROS (reactive oxygen species) formation, non-oxidative mode of action, the release of metal, and other relative OS (oxidative stress) patterns Fig. 1 [10, 13, 14]. In addition, complex mechanisms also occur to significantly diminish the effectiveness of the microorganisms possessing resistance [14–17].

The production of free oxygen radicals or ROS like O_2^- or H_2O_2 (superoxide anions or hydrogen peroxide) is circuitously induced by the MNPs themselves. When it is excessive, it leads to protein and DNA alterations, lipid-membrane distortion, severe OS, and distressed homeostatic processes [14, 18]. Furthermore, MNPs gradually discharge ions of metals that can penetrate the internal cellular components of the RMs and react with the -COOH, -SH, and -NH (carboxyl, mercapto, and amino) functional assemblies of nucleic and protein acids respectively [14, 19]. Based on this, numerous noxious effects are generated like blockage of the activities of enzymes, deregulation of the RMs metabolic pathways, alteration of electron transfer in the protein molecules, and coagulation of the internal protein molecules [20].

Hence, the production of ROS is broken down by the ions from the MNPs causing DNA and lipids damages in the cells of the RMs. This leads to a non-oxidative mode of action with the microorganism's membrane and cell walls which the organisms use as a shield against antimicrobial drugs such as antibiotics- a defence against internal and external aggressions. Therefore, the RMs membrane and cell walls are disrupted by the actions of the MNPs thus compromising the internal cellular homeostatic processes and leading to the eventual death of the organisms [13, 14].

However, in the case of Gram (+) microorganisms- bacteria, the cell wall is usually rigid and is composed of a thin film of peptidoglycans made of cellulose or carbohydrates chains of polymers linked via residues of peptides. On the other hand, in the Gram (−) microorganisms- bacteria the cell wall is more rigid which is composed of a thinner film of peptidoglycans with more polymers links around the cell wall surrounded by a lipopolysaccharide forming a blockage at the superficial region of the cell wall [21, 22]. These features enable the bacteria to possess a different pathway

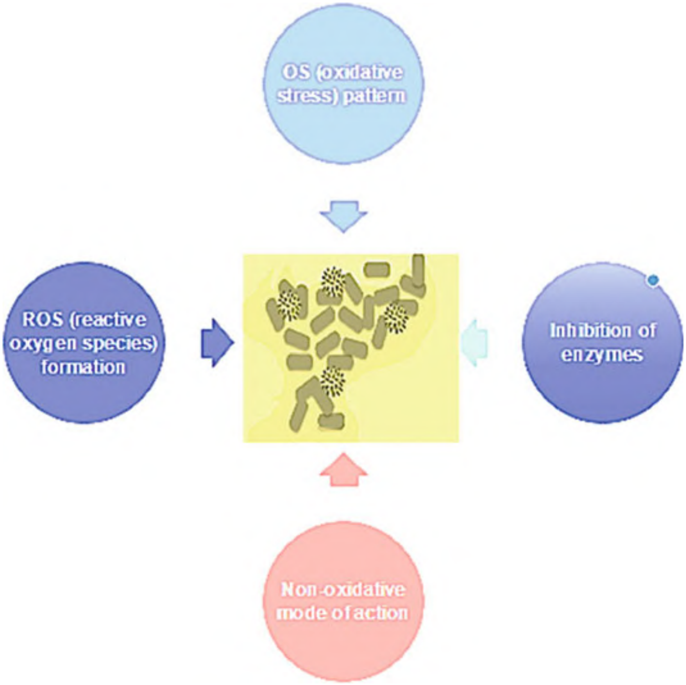

Fig. 1 The mechanism of action of magnetic nanoparticles on microorganisms

for the adsorption of the nanocomposites thus creating a—charge on the superficial region on the cell wall of the bacteria and a + electrostatic contact for the accumulation of the nanoparticles (Au and Ag). This could disrupt the metabolic activities of the organisms and thus cause leakage of the cell protoplasm via perforation of the cell walls [23].

3 Therapeutic Potentials of Magnetic Nanomaterials Against Yeast, Bacteria, Fungi, and Bacteria

Allafchian and Hosseini [5] in a review evaluated the therapeutic properties of MNPs as antibacterial messengers. Microorganisms exist in different sizes ranging from nano-micrometres. The potential of MNPs that is engineered to cure or manage many RMs had been improved in recent times [5]. Studies have shown that there are different biocompatibility of MNPs that have evolved which have remarkable effects on numerous strains of microbes. Allafchian and Hosseini, [5] reported that traditional synthesis techniques like hydrothermal/coprecipitation have been used widely to manufacture MNPs. In the application for the treatment of microbial infections, MNPs need biocompatible, recyclable, and superparamagnetic media to implement their mechanism of action effectively. Apart from providing these features, MNPs possess a superficial coating technique that aids its optimization and impacts against the RMs. The biocompatibility of MNPs with polymers has been reported to act in an excellent way to reduce the aggregation of MNPs and provide a pathway for nanomaterials with other structural composites. Allafchian and Hosseini, [5] stated that there have been promising in vitro breakthroughs in the utilization of MNPs, however, the application of the in vivo methods will expand more outlooks because of the physiochemical and biological properties of magnetic nanoparticles.

As the problems of diseases continue to pervade the world, several alternative therapeutic and preventive measures are put in place to combat such menace. Liakos et al. [24] examined in a review the therapeutic strategies used in the management of infections by using MNPs. The authors stated that their many 2 ways to develop effective MNPs to combat diseases. One of the ways is the inhibition of biofilms and microbial accessories developed on coated surfaces and the second is the improvement of the delivery processes of nano compounds to inhibit or reduce the drastic effects of antimicrobial compounds concentrated on used drugs. These combinations have been proven to be effective against serious resistant spores of microbes in humans. The minute sizes of MNPs make them good biochemical and biocompatible materials or nano-bioactive ingredients for the management of microbial infections. Liakos et al. al. [24] reported that these properties make it to be utilized in the medical sector as prosthetic tools for the delivery of special drugs to target organs, tissues, and the reduction of toxicity impacts with added antibiotics. The recent application of drugs derived from plant materials like oil has served as a potential and promising candidate in the management of infectious illnesses ranging from mild to complex forms. The use of antimicrobial-based creams like nano aerosols in the therapeutic management of respiratory-related drugs has been in the limelight in nanotechnology recent. Liakos et al. al. [24] recounted that this technology has proven to be more efficient in the stabilization of the delivery of drugs to target areas in the human body against several microbial infections fungi, bacteria, and yeast. Thus, the authors recommend MNPs as a first-class tool for the effective management of infectious diseases.

Wang et al. [25] assessed the mechanism of nanomaterials and their future utilization in the management of microbial infections. The increasing utilization of nanomaterials in the therapeutics of microbial diseases of recent had gained a great advantage over the traditional methods of treatments. Nanomaterials can be used to manage infections from bacteria, as an antibiotic delivery tool in disease management, and improve the healing, and prevention of wounds when used as a medicinal or implantable coating device. However, Wang et al. [25] reported that their antibacterial mode of action is not well understood but recently, some of the mechanisms include non-oxidative stress, the release of ionic metals, and oxidation stress. In conclusion, the authors recommend nanomaterials as a plausible substitute for antibiotics because of the great potential to solve serious health issues related RMs. A clearer picture of the mode of action of nanomaterials will pave a better way to develop modern engineered materials that could be used to prevent cytotoxicity of nanoparticles when utilized as an antibacterial tool (s).

Globally, the issues of resistance to antibiotics by some strains of microorganisms have been discussed in the health sector recently. This has posed serious public concern as reported by the World Health Organization. However, Mba and Nweze, [26] did a review of the therapeutic properties of nanoparticles in resolving the issues of complex drug-resistant by some microorganisms. The sharp increase in the mortality and morbidity rate globally has been linked to the incidence of the advent of complex drug-resistant by some microorganisms.

The absence of an effect antibiotics in the management of recalcitrant microbes have been one of the problems faced in the health sector [26]. Nonetheless, this had led to a more novel, sustainable, and effective way in the management of RMs. The utilization of nanomaterials in the therapeutic management of the disease has been at the forefront in the treatment of RMs in recent times. In conclusion, the authors recommend that a full understanding of the mode of adaptation of the RMs should be understudied properly so that better and innovative ways of using nanomaterials to combat them will be enhanced for full stability and bioavailability to reduce possible noxious impacts on humans.

The prevalence of the inefficiency of some antibiotics in the treatment of infections caused by some strains of microorganisms has led to the production of a more efficient and health-friendly drug. In this context, Vallet-Regí et al. [14] investigated the promising utilization of nanomaterials as a substitute for traditional drugs used in the management of infections caused by microbes. For some decades nanotechnology has paved a breaking ground for novel findings in addressing the need for a healthy society. The need to produce an effective antimicrobial drug from nanomaterials has been heralded by many scientists globally [14]. So, nanomaterials act as a vehicle that aids in breaking down the spores of microorganisms and their biofilms by preventing their adhesion to human cells with specific properties of targeting the sites of infections using a nanocarrier system via several modes of action. The authors recommend nano-structures coatings and zwitterionization as powerful instruments to prevent the formation of biofilms and adhesion caused by the microbes in the human cells after the invasion. Vallet-Regí et al. [14] reported that the surface of the nanomaterials shows a level of good biocompatibility with magnetic metals/nanomaterials showing effective mechanisms, evasion, and rapid killing of microbes when utilized for therapeutic management of diseases like bacterial infections. In addition, the use of nano-based particles mesoporous silica aid as a superficial targeting messenger in improving treatments in which the traditional methods could not. However, the safety of the use of the materials should be put into cognizance because of the issue of cytotoxicity it portends.

Vishwakarma et al. [27] evaluated in a review the mechanisms of nanomaterials in disease management. Apart from the use of nanomaterials in cosmetics, agriculture, and agriculture, the utilization of nanomaterials in disease management has gone wide in the health and medical sectors of the world. It has been used in the detection and identification of fungal and bacterial toxins in food materials with a high level of sensitivity and specificity. The inhibitory mode of actions of nanomaterials against various fungi and bacteria include inhibition of cell development, arrest of the cycle of cell growth, damage of the DNA and cell wall structures, pore formation of the membrane of the cells, and generation of ROS. The authors recommend the use or application of nanomaterials in the management of plants related diseases to ensure food security and safety.

Abbas and Krishnan, [2] investigated MNPs in the therapeutic management of infectious fungi. The misuse of antibiotics is one of the reasons for the complex resistance of drugs by microorganisms. Recent nanomaterials have been deployed as an alternative to traditional drugs (antibiotics) in the management of microbes like fungi because of their efficiency to act as a swift vehicle to target diseased organs and tissues. Many studies have focused on the use of oxides of metals and metals of nanoparticles in this effective delivery process which has been termed cheap and eco-friendly [2]. In addition, the utilization of biological subjects like plant-based materials and nanomaterials has also attracted some level of environmental stabilization and compatibility for the combat of pathogens. The author opined that superficial coatings of nanoparticles with Fe oxide will not only reduce the cytotoxicity effects of fungi infections but the efficiency and stability of the organisms. Hence it is a potential therapeutic tool for anticancer and antifungal management.

Makabenta et al. [28] evaluated the potential of nanomaterials as an antibiotic tool for the treatment of infections from bacteria. The authors stated that the formation of biofilms from RMs resulted in scientists in the nanotechnological fields thinking outside the box in finding out ways to solve infections from resistant bacterial attacks in humans. This has become a promising instrument in combating the invasion of microbial attacks. This is because of their exclusive properties both chemical and physical they have the potential to reduce toxicity and treat biofilms and planktonic forms of microbes in a wide range of modes of action. In conclusion, Makabenta et al. [28] recommended that for effective management of infectious disease, an interdisciplinary approach amongst engineers, microbiologists, biomedicals, chemists, and pharmacists should work together to address the rapid incidence of RMs by providing a sustainable and more effective anti-MNPs complex that is more effective, eco-friendly, and cheap in alleviating the menace caused by RMs.

Zhua et al. [29] in a review evaluated the potential of nanomaterials as a curative tool in medicine for the management of infections from microorganisms. It has been estimated that microbial infections existed over two billion years ago and have also caused several health-related diseases to humans, animals, and plants. However, for over 100 years, there has been a need to combat the disease caused by microorganisms using vaccines and antibiotics. Nonetheless, there have been several reported cases of RMs to strains of antibiotics used in the management of infectious microbes. In addition, the emergence of new strains of microorganisms that are bio-engineered and virulent has paved the way for the production of more efficient drugs that cannot be resisted by the RMs when utilize as vaccines or antibiotics Table 1. To this end, a new technology using nanomaterials has evolved to remedy such impacts on humans [29]. Nanomaterials can be used in medicine as a drug vehicle to deliver drugs to infectious sites in humans. This technology has been proven to be more effective and health-friendly. In the biotechnology and pharmaceutical industries nanomedicines have been fully accepted as a therapeutic tool for disease management (vaccines, medical tools, drug transport, antimicrobial treatment, and diagnosis) which are the

Table 1 Magnetic nanoparticles and their therapeutic actions/mechanisms on pathogens

S/N	Sites of actions	Species of microbes	Magnetic nanomaterials	References
1	Cell membrane and cytoplasmic membrane	*Saccharomyces cerevisiae*, *Candida albicans*, *Aspergillus niger*, *Candida parapsilosis*	Ag (Silver)	Nasrollahi et al. [30], Devi and Bhimba [31] and Mallmann et al. [32]
2	Cell membrane	*Penicillium expansum* and *Botrytis cinerea*	ZnO	Lili et al. [33]
3	Cell membrane	*Candida parapsilosis*, *Candida tropicalis*, and *Candida albicans* (1 and 2)	γ-Fe_2O_3 Fe_3O_4	Prucek et al. [34]
4	Cell membrane	*Escherichia coli*	Cu/chitosan ions	Du et al. [35]
5	Interface with proteins	*Enterobacter cloacae*, *Escherichia coli*, and *Staphylococcus aureus*	Cu-silica	Kim et al. [36]
6	Cell membrane	*Escherichia coli* and *Bacillus subtilis*	Cu and Zn	Yoon et al. [37]
7	Cell membrane	*Bacillus megaterium* and *Escherichia coli*	MgO	Stoimenov et al. [38]
8	Cell membrane	*Streptococcus mutans*, *Prevotella intermedia*, *Porphyromonas gingivalis*, *Staphylococcus aureus* and *Escherichia coli*	TiO_2/ Silver-nHA	Liao and Li [39]
9	Cell membrane	*Staphylococcus aureus* and *Escherichia coli*	Ag/Styrene–acrylic acid	Paula et al. [40]
10	Cell membrane	*Bacillus subtilis*, *Staphylococcus epidermidis*, and *Escherichia coli*	Fe_3O_4-Ag	Gong et al. [41]

next generational immune scrutiny, bio-distribution, and pharmacokinetics health management tool.

4 Health and Environmental Impacts of Magnetic Nanomaterials

Gwinn and Vallyathan, [42] investigated the potential cons and pros of the health hazards of nanoparticles. Nanomaterials of size < 100 nm have been reported to be used for gene rehabilitation, cancer management, drug distribution, disease detection, medical tomography, and industrial utilization. Gwinn and Vallyathan, [42] reported that nanomaterials may have noxious health and biological effects because of their fine particle sizes that have been known as ‘irritation specks of dust which is a potential for respiratory or cardiopulmonary diseases. The authors recommend toxicological evaluation of environmental and occupation exposures of patients or works to elucidate the risks nanomaterials portends. In addition, the government should develop environmental guidelines that will be used to monitor the exposure of workers to nanomaterials. Ray et al. [43] investigated the environmental and toxicity hazards of nanomaterials. The application of nanomaterials in different industrial sectors like the public, medical, and agriculture, the world has raised serious concern because of evidence of toxicity to human health but no clear evidence has been shown in their interaction with the environment. Nonetheless, it is very difficult to ascertain if the noxiousness is physiological. However, a full understanding of the mechanism of actions and behavior of nanomaterials is highly recommended to ascertain the health risks it portends.

Martínez et al. [44] and Smita et al. [45] evaluated the environmental effects of nanoparticles. The authors reported that several studies have evaluated the potential ecotoxicological impacts of nanomaterials using biological models like bacteria, invertebrates, and vertebrates. Possible impact on the organism includes cell deformation, formation of ROS, and OS mechanisms. The pattern of response by these organisms depends on the exposure and dosage in concentration absorbed by them [44]. In conclusion, the authors recommend the establishment of laws that will aid in the regulations of the use of nanomaterials and their related composite for the safety of humans and the environment.

Borm et al. [46] in a review assessed the possible health hazards of nanomaterials. In the last two decades, the issues of toxicity of nanoparticles have been heralded by several scientists even the US and EU toxicity evaluation bodies. These were mainly the engineered forms of nanoparticles (iron oxides, titanium dioxide, carbon black). Possible exposures are mainly via the oral, dermal, and inhalation pathways. The target areas are mainly the epithelium region of the olfactory and brain when inhaled leading to OS and the release of ROS. Studies on rats showed tumor linked, OS, and inflammation of internal organs have been reported. While physiological via systemic exposure impacts have been reported when it comes to the skin [46]. However, more engineered nanomaterials have been produced recently and their potential toxicology has not yet been ascertained. Hence, the authors recommend an ecotoxicological evaluation of the recent data published with some dosage range to establish a systemic drug-drug interaction on nanomaterials and their related composites. Kabira et al. [47] investigated the ecosystem impacts of nanoparticles. Currently, nanotechnology has been one of the front-line technologies in recent times around the top world powers. This has impacted the environment as well as the economy respectively. This involves the production of materials that are very important in the agriculture, industrial, health care, and chemical industry sectors. However, based on the irregularities and uncertainties that paved their chemical constitute, size, and shape, they stand as one of the emerging chemical threats to human and environmental health. However, based on improper guidelines in their disposal, background studies have shown pathways (soil, water, and air) by which the particle goes through and long- and short-term impacts. Kabira et al. [47] reported that few studies on the impacts of nanomaterials on humans and animals have recounted adverse effects on their cells. The regulations and guidelines on the disposal and utilization of nanomaterials were recommended by the authors to prevent future problems. More so, non-governmental and governmental bodies, engineers, and environmental scientists should work in synergy to develop an LCE and REA (life cycle evaluation and risk evaluation analyses) on nanomaterials especially the engineered forms before wide use to prevent any future complications.

5 Conclusion and Recommendations

This chapter reviews the utilization of magnetic nanomaterials as more effective potent tools for combating pathogens. Several strains of drugs have been used to treat these diseases in recent years but have been proven ineffective and low potent in their mode of reaction because of the resistance potential of the microbes to the drugs. Despite the enormous efforts put into the treatment of infectious illness, the potential health risks to public individuals have remarkably increased globally based on facilitated traveling by infected individuals and contacts. This has added to increasing uncontrollable management of microbial resistance and propelled better efficient ways or alternatives for therapeutic control. the mode of action is basically through the deactivation of protein, the inhibition of enzymes, ROS (reactive oxygen species) formation, non-oxidative mode of action, the release of metal, and other relative OS (oxidative stress) patterns. In addition, the inhibitory mode of actions of nanomaterials against various fungi and bacteria include inhibition of cell development, arrest of the cycle of cell growth, damage of the DNA and cell wall structures, and pore formation of the membrane of the cells.

The therapeutic properties of MNPs as the antibacterial messenger have shown that in the treatment of microbial infections, MNPs need biocompatible, recyclable, and superparamagnetic media to implement their mechanism of action effectively. These properties make it to be utilized in the medical sector as prosthetic tools for the delivery of special drugs to target organs, tissues, and the reduction of toxicity impacts with added antibiotics.

The health hazards and environmental risks of nanoparticles were evaluated to have ecotoxicological impacts using biological models like bacteria, invertebrates, and vertebrates. Possible impact on the organism includes cell deformation, formation of ROS, and OS mechanisms. The pattern of response by these organisms depends on the exposure and dosage in concentration absorbed by them. It was established that mainly in the engineered forms of nanoparticles (iron oxides, titanium dioxide, carbon black) the possible exposures are mainly via the oral, dermal, and inhalation pathways. The target areas are mainly the epithelium region of the olfactory and brain when inhaled leading to OS and the release of ROS. Studies on rats showed tumor linked, OS, and inflammation of internal organs have been reported. While physiological via systemic exposure impacts have been reported when it comes to the skin.

A clearer picture of the mode of action of nanomaterials will pave a better way to develop modern engineered materials that could be used to prevent cytotoxicity of nanoparticles when utilized as an antibacterial tool (s). A full understanding of the mode of adaptation of the RMs should be understudied properly so that better and innovative ways of using nanomaterials to combat them will be enhanced for full stability and bioavailability to reduce possible noxious impacts on humans. This technology has been proven to be more effective and health-friendly. In the biotechnology and pharmaceutical industries nanomedicines have been fully accepted as a therapeutic tool for disease management (vaccines, medical tools, drug transport, antimicrobial treatment, and diagnosis) which are the next generational immune scrutiny, bio-distribution, and pharmacokinetics health management tool. In conclusion, the authors recommend the establishment of laws that will aid in the regulations of the use of nanomaterials and their related composite for the safety of humans and the environment.

More so, non-governmental and governmental bodies, engineers, and environmental scientists should work in synergy to develop an LCE and REA (life cycle evaluation and risk evaluation analyses) on nanomaterials especially the engineered forms before wide use to prevent any future complications.

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