

Chapter 8

Role of Magnetic Nanoparticles in Providing Safe and Clean Water to Each Individual

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8.1 Introduction

Environmental pollution is one of the greatest problems facing the world today. It is increasing with every passing year and causing grave and irreparable damage to the earth. Environmental pollution consists of five basic types of pollution, most commonly air, water, soil, noise, and light. Because of these kinds of pollution, the temperature of the environment increases daily, which is causing unusually warm weather, ocean warming, a rise in sea levels, coastal flooding, warming of Arctic and Antarctic zones, changes in air patterns, and others. These consequences of pollution have created serious health hazards.

Among all basic needs, water is one of the basic requirements for sustaining life, the main essential fluid on which all life depends but now a days due to our activity it has changed to global garbage cans, i.e., water pollution.

With the evolution of human civilization, the purity of pure drinking water has undergone dramatic changes. Water is recognized as a symbol for the origin of life and for its medicinal value; originally, it was not designated as a carrier of diseases. In the seventeenth century, Anton van Leeuwenhoek's discovery of the microscope opened a new door in the field of purity: humans were empowered to see beyond suspended particles, for example, tiny material particles, to microorganisms. The discoveries of Louis Pasteur in the study of microorganism-based diseases and

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those of John Snow in identifying the cause of the spread of cholera in London revealed that the quality of drinking water was changing [1]. Thus, the era of water purification had begun.

Along with industrialization and urbanization came water pollution, and according to the World Health Organization (WHO), around 1.8 million people die every year due to diseases caused by water pollution, for example, typhoid, diarrhea, and hepatitis. Water pollution is a primary cause of death mostly in developing countries as a result of unsafe water supplies, inadequate sanitation, and deficient hygiene. The WHO also reports that 1.1 billion people living in rural areas are not able to access sufficiently clean water [2]. Modern society is growing very fast but because of these developments, we have contaminated not only the surface water but groundwater as well. As a result, both water used for daily nondrinking needs and drinking water sources are becoming highly contaminated.

8.1.1 Causes of Water Pollution

In ancient times, water resources contained natural contaminants, particularly inorganic contaminants that arise from natural phenomena like water flows, volcanoes, and anthropogenic pollution [3]. In general, groundwater is comparatively more protected from pollution than surface waters. Groundwater becomes contaminated mainly as a result of human activities like discharges from industrial premises and sewage or runoff from agricultural land and hard surfaces such as roads [3]. There is also the possibility of leakage of chemicals from industry and slurries from intensive farm units that can contain pathogens. In some countries, poorly sited latrines and septic tanks are a significant source of contamination, especially of wells.

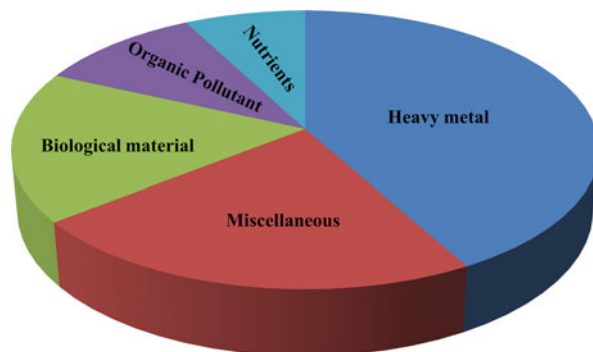
In short, there are so many ways to contaminate drinking water and groundwater that we do not even notice them, and contaminated water is not only toxic but sometimes lethal for humans and all living beings. Normal human activities are worse for nature than the greatest nuclear accidents in history.

Many regulatory bodies, such as the U.S. Environmental Protection Agency (USEPA), WHO, and the European Union (EU), have played a key role in developing regulations for many toxic species found in drinking water. The most common and chemical species responsible for water pollution are as follows (Fig. 8.1):

- Metal ions: cadmium, copper, lead, mercury, nickel, zinc, arsenic
- Nutrients: phosphate, ammonia, nitrate, nitrite
- Dyes used in industry: methylene blue (MB), rhodamine
- Biological materials: algae, viruses, bacteria, parasites
- Miscellaneous: cyanide, phenols and organic compounds, antibiotics

Therefore, it is essential to control the harmful effects of contaminants and improve the quality and quantity of fresh, clean water. In this regard, the purification of drinking water, treatment of sewage water, and protection of natural resources are among the urgent and challenging issues for government and researchers.

Fig. 8.1 Pie chart showing distribution of various water contaminants



8.1.2 Water Purification and Nanomaterials

Water contaminants exist either in dissolved forms or industrial effluents or in suspended forms as in sediments and surface and ground waters. Traditionally, dissolved contaminants have been removed from water sources by adsorption on activated carbon [4], ion exchange [5], and solvent extraction [6]. Common techniques used to remove suspended contaminants include pumping and treating, in situ adsorption on activated carbon, bioremediation, and stabilization and solidification [7]. In recent years, several methods have been proposed or used to make water clean and hygienic, for example, like adsorption, separation processing, photocatalytic oxidation, and bioremediation [7]. However, they have not been fully functional or adopted because of several restrictions, specifically restrictions related to efficiency, mode of operation, energy requirements, and, lastly, the methods' economic importance. The most popular of these techniques is the adsorption of contaminants on activated carbon, but this process suffers from mass transfer limitations, issues of bacterial growth, channeling, and difficulty in regeneration. In the case of sediment structures, carbon is often left behind in matrices being treated, which risks rerelease of adsorbed contaminants and the migration of contaminant-laden carbon to new areas. Given that carbon is concentrated in contaminants, the risk of rerelease is much greater than the risk posed by the initial contamination.

Nowadays, from the standpoint of resource preservation and environmental remediation, nanomaterials have been proposed as a very efficient, low cost, non-hazardous, and environmentally friendly alternative treatment. The highly efficient, modular, and multifunctional processes facilitated by nanomaterials could be used to provide pure drinking water treatment solutions [8]. Nanosized materials, especially nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, carbon-based material, magnesium oxides, and cerium oxides, are considered promising materials for use in the treatment and purification of water [9]. Nanomaterials possess a large surface-area-to-volume ratio caused by the size quantization effect, resulting in extraordinary optical, magnetic, and electrical properties [9]. Recent studies suggest that nanomaterials exhibit very favorable sorption properties

with respect to toxic materials present in water in terms of a high adsorption capacity and selectivity, which would result in effective and efficient removal of toxic materials. The application of nanomaterials for environmental remediation, though in its infancy, has great potential for remediating sites and effluents in a cost-effective manner.

As an alternative to existing remediation techniques, magnetic nanoparticles (MNPs) have attracted the attention of researchers and industrialists in connection with their role in water purification and treatment. Their superiority to activated carbon lies in the fact that they offer a high surface-area-to-volume ratio because of their nanosize [10]. In addition, they do not suffer from the limitations common to porous structures because the entire surface area lies outside the particles [10]. Furthermore, under external magnetic field gradients, the complete removal of particles from their medium of application is possible. Unlike activated carbon, which is left behind in the environment, it is now possible to isolate contaminant-rich adsorbents. These versatile MNPs can be applied to both treat effluents and remediate sediment matrices.

The greatest advantage of this process is that the net volume of disposal waste is reduced by concentrating contaminants from a large dilute volume to a small concentrated volume.

The advantages of using this alternative nanotechnology compared to existing methods are that it involves low-cost chemicals and magnets, can be implemented in a continuous manner for treating waste streams or as an in situ technique for remediating sediments, provides for the almost complete recovery of adsorbents owing to its magnetic properties, and it can be target specific. Additionally, MNPs can be reused after the contaminant has been stripped off. Though the proposed magnetic nanotechnology is applicable to both sediments and waste streams, the focus of this chapter is largely on the purification of drinking water. The general protocol used for the purification or treatment of water using MNPs is shown in Fig. 8.2.

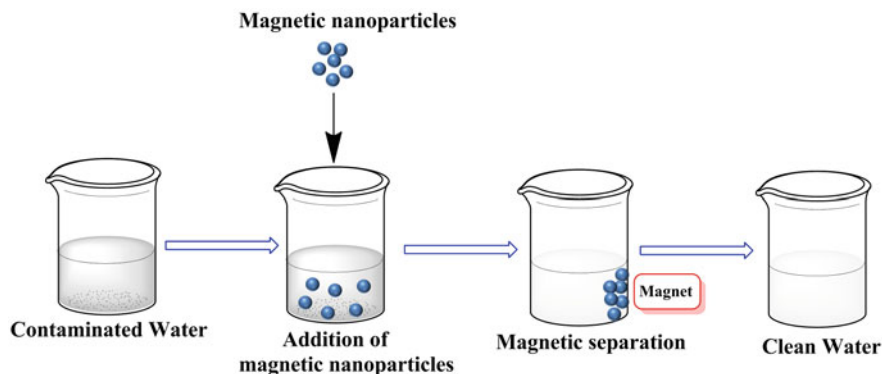


Fig. 8.2 General protocol for water purification using magnetic nanoparticles

Based on the applicability and worldwide application of MNPs in the field of water purification and treatment, several review articles have been published to compile the large world of MNPs in a small space. In 2010, Ambashta and Sillanpaa published a good review of water purification using magnetic materials [11]. In the same year, Xu et al. and Crane et al. published two reviews on the use of iron oxide nanomaterials in wastewater treatment [10] and water treatment technology based on nano zero-valent iron (nZVI) particles [12]. Recently, Fu et al. published a review on groundwater remediation and wastewater treatment using an nZVI particle [8]. Recent years have witnessed a surge of interest in the synthesis and use of MNPs due to their size in the nano range, high surface-area-to-volume ratios, large removal capacity, fast kinetics, and superparamagnetism. In addition to these properties, MNPs have a low toxicity, chemical inertness, and biocompatibility, which hold tremendous potential in combination with biotechnology. Magnetism is a unique physical property that independently helps in water purification by influencing the physical properties of contaminants in water. In addition, its combination with other processes enables an improvised efficient purification technology. MNPs, such as Fe_3O_4 , and modified MNPs are good candidates as absorption materials in light of their main advantages [13]:

- The particles can be produced in large quantities using a simple method;
- They generally have a high adsorption capacity because of their large surface area;
- They have strong magnetic properties and low toxicity;
- Particles are superparamagnetic, which means a metal-laden sorbent can be easily separated from treated water via an external magnetic field.

Since most water pollutants are nonmagnetic, it is favorable that MNPs can be combined with pollutants efficiently and be collected rapidly and thoroughly following agglomeration with pollutants owing to their high ferromagnetism.

8.2 Magnetic Nanoparticles

In general, ferrite colloids, magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are the most common and popular MNPs, which have so far received considerable attention in the fields of water purification and wastewater treatment [10]. Ferrite colloids are characterized by a spinel crystalline structure with oxygen ions forming a close-packed cubic lattice and iron ions located at the interstices. The magnetization of Fe_3O_4 arises from antiferromagnetic coupling (superexchange through oxygen) between Fe^{3+} ions in octahedral and tetrahedral interstices, making the magnetic moments of Fe^{2+} ions (in octahedral positions) responsible for the magnetization of the unit cell [10]. MNPs can be synthesized by physical, chemical, and biological methods. The physical methods [14, 15] include gas-phase deposition and electron beam lithography; the chemical methods include wet chemical preparation methods, such as sol-gel synthesis [16], oxidation method

[17], chemical coprecipitation [18], hydrothermal reactions [19], flow injection synthesis [20], electrochemical method [21], aerosol/vapor-phase method [22], sonochemical decomposition reactions [23], supercritical fluid method [24], and synthesis using nanoreactors [25]; and the biological methods comprise microbial methods [26]. Although the resulting MNPs are stable enough in their solid state and have various applications in such fields as catalysis and sensing, the major problem associated with MNPs is their poor stability in aqueous medium and high tendency toward aggregation. Naked MNPs are generally unstable in strong acidic solutions and undergo leaching, which strongly limits their reusability and reduces the lifetime of such materials. The large ratio of surface area to volume leads to another limitation, the aggregation of particles, and thus a minimization of their surface energy occurs owing to the strong magnetic attractions between particles, which limits their dispersion in aqueous solutions and matrices. The exposure of proteins/enzymes to such interfaces would result in a decrease or loss of activity. To enhance the stability of MNPs, several modifications to them have been reported using the following materials (Fig. 8.3):

- Surfactants, such as oleic acid, lauric acid, alkyl sulphonic acids, and alkyl phosphonic acids;

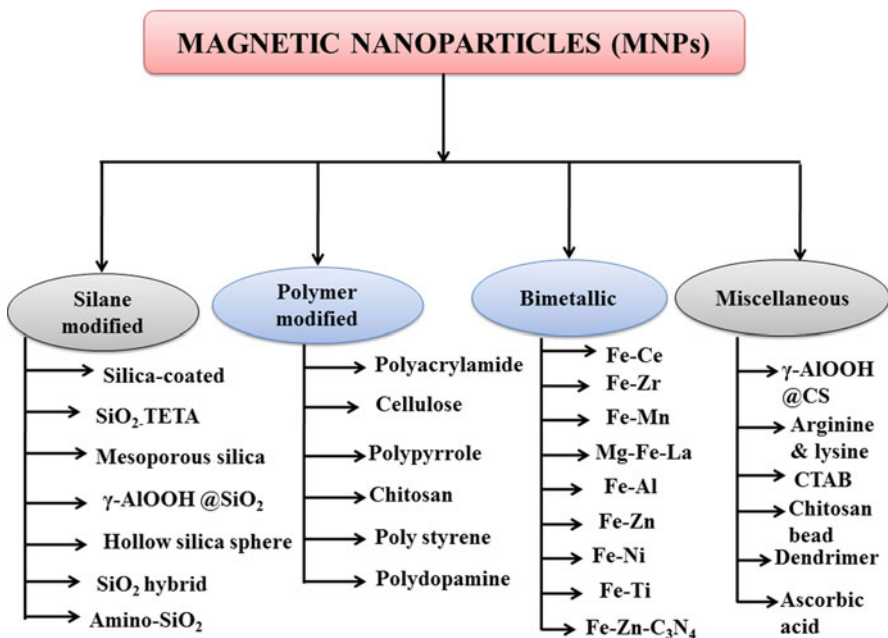


Fig. 8.3 Flowchart for different modifications of magnetic nanoparticles used for water purification

- Various polymers, such as polyethylene glycol, polyvinyl pyrrolidone, poly(ethylene-co-vinyl acetate), poly(lactic-co-glycolic acid), and polyvinyl alcohol (PVA), which have been used as coating materials in aqueous suspension;
- Natural dispersants, including gelatin, dextran, polylactic acids, starch, albumin, liposomes, chitosan, and ethyl cellulose;
- Silane compounds;
- Carbonaceous materials.

These techniques not only optimize the surface properties, such as biocompatibility, dispersibility, and biodegradability, of MNPs, they also provide an environment for the transferal of hydrophobic iron oxide nanoparticles to a hydrophilic system [27]. In this chapter we aim to assemble all aspects and roles of differentially modified MNPs in water purification and wastewater treatment. The chapter concludes with recent investigations on the issue of nanotoxicity and its implications for the future.

8.2.1 Removal of Heavy-Metal Ions

Metals are introduced mainly in aquatic systems as a result of the weathering of soils and rocks, from volcanic eruptions, and from a variety of human activities involving the mining, processing, or use of metals or substances that contain metal pollutants. The most common heavy-metal pollutants include zinc, arsenic, mercury, lead, and chromium. In this section we will discuss various modified MNPs and their role in the removal of heavy-metal ions. The role of MNPs in the removal of heavy-metal ions is summarized in the Table 8.1.

8.2.1.1 Silane-Modified MNPs

Surface silanization is undoubtedly the most widely used technique to introduce surface functional groups on bare MNPs owing to its characteristics such as satisfying responsivity, low cytotoxicity, high stability under acidic conditions, inertness to redox reactions, and ease of carrying out surface chemical modification [28]. The reaction can be carried out in either aqueous media or organic solvents at moderate temperatures, and no particular conditions or expensive equipment are required; therefore, it is considered an ideal method for the protection of the inner magnetic core. Silane molecules are first activated (hydrolyzed), followed by condensation reactions occurring between the Si–OH groups of silanol and OH groups of the surface (Fig. 8.4). This leads to the formation of a stable bond on the surface [29, 30]. According to the literature, silane-modified MNPs are the most popular nanoparticles used in the removal of heavy-metal ions from water systems [28]. Herein, we list the recent silane-modified MNPs used in the removal of uranyl, arsenic, chromium ions, and others.

Table 8.1 Magnetic nanoparticles used as adsorbent for removal of heavy metal ion from water samples

Serial number	Modification	Metal ion	Adsorption capacity	Reference
1.	3-Aminopropyl triethoxysiliane@Fe ₃ O ₄	U ⁶⁺	12.33 mg g ⁻¹	Sadeghi et al. [27]
2.	Fe ₃ O ₄ @SiO ₂	U ⁶⁺	52.0 mg g ⁻¹	Fan et al. [134]
3.	Polyacrylamide coated-Fe ₃ O ₄	U ⁶⁺	220.9 mg g ⁻¹	Song et al. [42]
4.	Poly(ethylene glycol)diacrylate modified α -Fe ₂ O ₃	As ³⁺	3.0 mg g ⁻¹	Savina et al. [43]
5.	PS-Fe ₃ O ₄	As ³⁺	139.3 mg g ⁻¹	Wei et al. [44]
6.	Fe ₃ O ₄ -PDA	Cu ²⁺ , Ag ⁺ , Hg ²⁺	112.9, 259.1, 467.3 mg g ⁻¹	Zhang et al. [45]
7.	Mesoporous iron manganese bimetal oxides	As ³⁺ , As ⁵⁺	67.8 and 93.5 mg g ⁻¹	Wen et al. [47]
8.	Fe-Mn binary oxide nanowires	As ³⁺	171.0 mg g ⁻¹	Cui et al. [49]
9.	Fe(III)-Al(III)	As ⁵⁺	54.5 mg g ⁻¹	Basu et al. [50]
10.	Fe-Zr	As ⁵⁺ , As ³⁺	46.1 and 120.0 mg g ⁻¹	Ren et al. [51]
11.	Fe-Zr	PO ₄ ⁻	13.65 mg g ⁻¹	Long et al. [53]
12.	Fe-Zr binary oxide	Sb ⁵⁺	51.0 mg g ⁻¹	Li et al. [54]
13.	Goethite	As ⁵⁺	23.47 mg g ⁻¹	Velčković et al. [55]
14.	Fe-MWCNT	As ⁵⁺ , As ³⁺	1723 and 189 mg g ⁻¹	Nim and Mitra [56]
15.	Fe ₃ O ₄ and MnO ₂ nanoparticles modified graphene oxide	As ⁵⁺ , As ³⁺	14.0 and 12.2 mg g ⁻¹	Luo et al. [58]
16.	Chitosan-functionalized MWCNTs-CoFe ₂ O ₄ -NH ₂	Pb ²⁺	140.1 mg g ⁻¹	Zhou et al. [59]
17.	Amidoximated magnetite/graphene oxide	U ⁶⁺	1.197 mmol g ⁻¹	Zhao et al. [60]
18.	Bio-based α -Fe ₂ O ₃ impregnated chitosan beads	As ³⁺	9.3 mg g ⁻¹	Liu et al. [64]

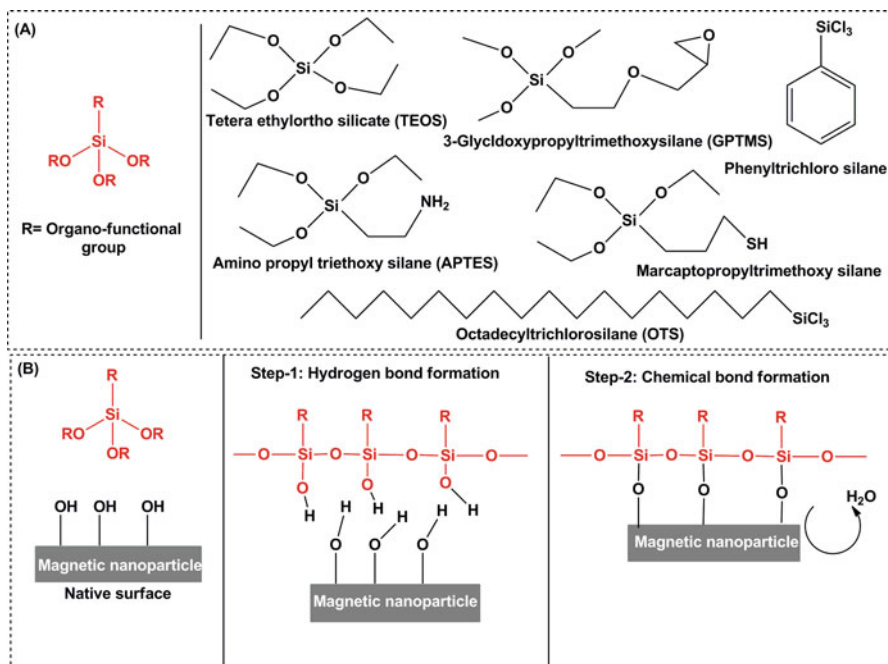


Fig. 8.4 Schematic representation showing various silanes and their interaction with magnetic nanoparticles

Uranium is a radioactive metallic element that is chemically active in its pure form. However, uranium and its compounds are highly toxic to humans and lead to kidney failure or even death. The WHO has established that the maximum uranium concentration in drinking water should be less than $15.0 \mu\text{g L}^{-1}$, while this value in spring waters should be less than $20.0 \mu\text{g L}^{-1}$ [27]. However, depending on the location, the level of uranium in water varies. It is difficult to determine directly the extremely low concentration of uranium in the presence of relatively high concentrations of other diverse ions. Therefore, a refined analytical method must be used to detect such low concentrations [31]. Sadeghi et al. reported on 3-aminopropyl triethoxysilane (APTES)-coated MNPs modified with quercetin as a new solid-phase sorbent for the extraction of uranyl ions from water [27]. The absorption was explained by Langmuir isotherm, and the maximum monolayer adsorption capacity was found to be 12.33 mg g^{-1} . The synthesized sorbent was applied to the extraction of uranyl ions from different water samples. Fan and coworkers reported on the use of magnetic $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ composite particles to remove uranium ions from aqueous solution [28]. The experimental results were well fitted by a pseudo-second-order model and adsorption process was well described by Langmuir isotherm model and the maximum uranium sorption capacity onto magnetic $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ composite particles was estimated to be about 52.0 mg g^{-1} at 25°C . The aforementioned

composite materials showed a good selectivity for uranium from aqueous solution in the presence of other interfering ions.

Another important, common, and harmful metal ion is chromium, which exists in the environment as Cr(III) and Cr(VI). The existence of a metal-ion oxidation state depends on the pH and redox conditions of the environment. Cr(III) is much less soluble and therefore less mobile than Cr(VI). Because of the greater solubility of Cr(VI), it can penetrate into plants, animals, and microorganisms, so exposure to certain levels of Cr(VI) can result in significant risks for human health [32]. Based on the significance of chromium metal ions on human health, their detection is very important, and several studies have been reported on the analysis of chromium ions in aqueous and solid samples. Prakash et al. reported on iron oxide-reduced graphene oxide hybrid materials. This material was used to detect Cr(III) in aqueous solution. The linear range of detection of Cr(III) is 0.2–2.0 nM [33]. Cui et al. reported on chitosan-modified MNPs used to detect Cr(III) and Cr(VI) in water, and the limits of detection were 0.02 and 0.03 ng mL⁻¹ for Cr(III) and Cr(VI), respectively [34]. Cheng et al. reported on dithizone-modified MNPs, which used trace amounts of Cr(III) in environmental and biological samples. The linear range of detection of Cr(III) is 0.1–100.0 µg L⁻¹, with a limit of detection of 35.0 ng L⁻¹ [35].

Arsenic (As) is a very toxic element. Pollution from As is mainly due to human activities that include the production of wood preservatives, agricultural uses such as pesticides and herbicides, and mining activity, burning coal, and copper smelting [36]. Industrial activities also contribute to As pollution. Arsenic exists in water in two main chemical forms, As(V) and As(III). The arsenite ion is more soluble in water and approximately 50 times more toxic than arsenate ions [37]. The total As level in drinking water should be below 10 ppb as established by WHO. In the literature, several works have been reported for the detection and removal of arsenite and its conversion to arsenate [37]. Saiz et al. reported a magnetic Fe₃O₄@SiO₂ composite nanoparticle functionalized with aminopropyl groups incorporating Fe³⁺ as adsorbents for removing arsenate from polluted groundwater. This material was easily regenerated under alkaline conditions and showed adsorption yields of arsenic of around 90% [38]. Kokate et al. reported a novel one-pot single-step synthesis of magnetite–silica nanocomposites that has various applications such as in tagging (attachment of fluorophores to rhodamine), entrapment matrices (zinc loading), and the removal of As for water purification [39].

In addition to these metal ions, other metal ions are also known for their toxic nature in the everyday life of living organisms, that is, copper, lead, cadmium, mercury, and zinc metal ions. MNPs were reported to be very effective for sensing and removing them from water samples. Mahmoud et al. have reported on nanosorbents, synthesized from the direct surface impregnation of magnetic iron oxide nanoparticles (nano-Fe₃O₄) with nano-silicon oxide (Nano-SiO₂) for the formation of (nano-Fe₃O₄–SiO₂) sorbents. They were further modified with target nitrogen donor atoms via covalent surface binding and immobilization of triethylenetetramine (TETA) for the formation of a (nano-Fe₃O₄–SiO₂–TETA) sorbent that selectively removes some heavy-metal ions such as Cu(II) and Pb(II) from water samples [40].

Wei et al. have reported on novel adsorbent γ -AlOOH (boehmite)@SiO₂/Fe₃O₄ porous magnetic microspheres with high adsorption capacity toward heavy-metal ions. The nanomaterial was found to be very useful for the simultaneous and selective electrochemical detection of five metal ions, Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II), in drinking water [41].

8.2.1.2 Polymer-Modified MNPs

To increase the stability and sorption capacity of Fe₃O₄ nanoparticles, a variety of natural (e.g., cellulose, chitosan) and synthetic polymers (e.g., polyacrylamide, polydopamine, polystyrene) were also used as grafting/coating agents. Song and coworkers synthesized polyacrylamide-coated Fe₃O₄ magnetic composites applied as adsorbents to remove U(VI) from aqueous solutions and were able to separate it by a simple magnetic separation method [42]. The sorption isotherms were well fitted in the Langmuir sorption isotherm model, and the maximum sorption capacity of uranium (VI) at pH 5.0 was calculated to be 220.9 mg g⁻¹. Savina et al. reported a poly(ethylene glycol)diacrylate containing α -Fe₂O₃ and Fe₃O₄ nanoparticles prepared by cryopolymerization, and the resulting monolithic structure containing material showed a higher efficiency for the removal of As(III) from aqueous solution [43]. The experimental results revealed that the nanocomposite showed an excellent capability for the removal of trace concentrations of As(III) from solution, with a total capacity of up to 3.0 mg As/g of nanoparticles. Wei et al. [44] reported a polystyrene (PS)-supported nano-Fe₃O₄ for the removal of As from water [44]. The maximum adsorption capacity of this PS-Fe₃O₄ was 139.3 mg g⁻¹. Zhang and coworkers synthesized the polydopamine (PDA) modified MNPs (Fe₃O₄/PDA) and applied the nanomaterial for removal of multiple pollutants like methylene blue, tartrazine, Cu(II), Ag(I) and Hg(II) from water. The synthesized nanomaterial follow the Langmuir adsorption isotherm during binding study and shows the maximum capacity of 204.1, 100.0, 112.9, 259.1, and 467.3 mg g⁻¹ for methylene blue, tartrazine, Cu(II), Ag(I) and Hg(II) respectively [45].

8.2.1.3 Bimetallic MNPs

Bimetallic MNPs (BMNPs) can also be used as substitutes to enhance the stability of nanoparticles. Bimetallic nanoparticles are prepared using iron as the principal metal to which a thin layer of transition metals such as palladium (Pd), copper (Cu), nickel (Ni), or platinum (Pt) is deposited by chemical reaction. Bimetallic nanoparticles have considerable potential in the removal of contaminants from water and have several potential advantages over single MNPs, such as faster reaction kinetics and slower deposition of corrosion products on the particle surface. The representative studies dealing with contaminant removal by BMNPs in water are summarized in what follows.

For example, Wen and coworkers reported on magnetic mesoporous iron cerium (MMIC) bimetallic oxides with large surface area and pore volume via a hard

template approach. The MMIC could separate As(III) very easily from water with an external magnetic field and was also proposed as a heterogeneous Fenton-like catalyst for the oxidation of As(III) [46]. The same group also synthesized mesoporous iron manganese (OMIM) bimetallic oxides via the hard template approach. The material showed excellent performance for As(III) removal owing to its large surface area and pore volume. The pH was significantly affected by the removal efficiency of As(III) and As(V), and the greatest removal occurred in acidic solutions for both As species. The adsorption isotherms for the aforementioned materials were well described by a Freundlich model, and the calculated adsorption capacities of As(III) and As(V) were 67.89 and 93.54 mg g⁻¹, respectively [47]. Kong and coworkers prepared an Fe–Mn binary oxide-laden zeolite (MFM), which was used in the removal of As from contaminated groundwater [48]. This bimetal is produced by an improved precipitation method and was easily separated from water by an external magnetic field after As adsorption. The adsorption kinetics was well fitted with a pseudo-second-order and Weber–Morris model, and this material can also be used to remove more than 99.0% As from water at a pH of 7.0. Cui et al. have also reported on magnetic porous Fe–Mn binary oxide nanowires with superior capability for the removal of As(III) from water [49]. The magnetic porous Fe–Mn binary oxide nanowires with an initial Fe:Mn molar ratio of 1:3 exhibited the highest absorption capacity for As(III), and the maximum adsorption capacity value was found to be 171.0 mg g⁻¹ at pH 7.0. Basu and coworkers reported on agglomerated iron(III)–aluminum(III) mixed oxide nanoparticles (NIAO) for As(V) adsorption in the presence/absence of some common ions [50]. This nanomaterial showed the highest As(V) adsorption efficiency, 54.5 mg g⁻¹ at pH = 7.0 and 30 °C. This nanocomposite was able to detect As(V) in a qualitative and quantitative way in groundwater. Ren and coworkers have reported on an Fe–Zr bimetallic type nanoparticle that was used as an adsorbent material for the removal of As from drinking water [51]. This adsorbent material was easily prepared using a coprecipitation method and shows the maximum adsorption for As(V) and As(III), 46.1 and 120.0 mg g⁻¹. Fu et al. reported on iron/aluminum (Fe/Al) bimetallic nanoparticles that are highly efficiency in the removal of Cr(VI) from aqueous solution [52]. The particles showed high stability and high removal efficiency for Cr(VI) in acidic, neutral, and alkaline solutions. Long et al. reported on a magnetic Fe–Zr binary oxide as adsorbent for removing phosphate from aqueous solution [53]. The specific surface area of the reported material was 106.2 m² g⁻¹. The result presented here follows pseudo-second-order kinetics and was well executed using a Langmuir isotherm model. The maximum adsorption capacity was found to be 13.65 mg g⁻¹ at a pH value of 4.0. Additionally, the magnetic Fe–Zr binary oxide adsorbent could be regenerated using a 0.1 M NaOH solution as eluent, and the adsorption capacity reached as high as 66.7% of the original adsorption capacity after the fifth cycle. Li and coworkers synthesized an Fe–Zr binary oxide adsorbent

by the coprecipitation method that was able to remove antimonate [Sb(V)] from water [54]. The material showed a maximum adsorbent capacity of 51.0 mg g^{-1} at pH 7.0 with an initial Sb(V) concentration of 10.0 mg L^{-1} .

8.2.1.4 Magnetic Nanoparticles Modified with Carbonaceous Nanomaterials

Recently carbonaceous nanomaterials, like carbon nanotubes (CNTs) [single-walled (SWCNTs) and multiwalled carbon nanotubes (MWCNTs)], graphene, and others, were investigated as promising adsorbents for various organic pollutants and metal ions thanks to their large surface area, hollowness, and layered structure. They can be easily modified by chemical treatment to increase their adsorption capacity. To increase the unique surface property of the aforementioned carbonaceous nanomaterials, their modification with inorganic nanoparticles has been reported, in which MNPs are the most common materials. The modification of MNPs with carbonaceous nanomaterials not only increases the surface property but also enhances the adsorptive capacity and lifetime of prepared nanocomposites.

Veličković and coworkers [55] reported on ethylenediamine-functionalized MWCNTs laden with iron(III) oxide in goethite form, and these adsorbent materials were used to adsorb As from drinking water [55]. The adsorption procedure for As(V) was described by a pseudo-second-order kinetic model, and adsorption data were best fitted in the Langmuir adsorption isotherm model; the maximum adsorption capacity for As(V) was found to be 23.47 mg g^{-1} . Ntim and Mitra [56] reported the removal of trace-level arsenic from drinking water using an iron oxide (Fe-MWCNT) hybrid as a sorbent [56]. The Fe-MWCNT was effective in arsenic removal below standard drinking water levels of $10.0 \text{ } \mu\text{g L}^{-1}$. The absorption capacity of the aforementioned composite was $1723.0 \text{ } \mu\text{g g}^{-1}$ and $189.0 \text{ } \mu\text{g g}^{-1}$ for As(III) and As(V), respectively. Vadahanambi et al. reported a highly versatile and one-pot microwave route for the production of 3D graphene–CNT–iron oxide nanostructures for the efficient removal of arsenic from contaminated water [57]. Here, a unique 3D nanostructure shows that CNTs were stood vertically on graphene sheets and MNPs were tinted on both the graphene and CNTs. The material with MNPs showed excellent absorption performance toward arsenic removal from contaminated water due to its high surface-to-volume ratio and open pore network of the graphene–CNT–iron oxide 3D nanostructures. Similarly, a nanocomposite of graphite oxide (GO), MNPs, and manganese dioxide (MnO_2) nanoparticles was synthesized by Luo et al. using a coprecipitation method [58]. The nanocomposite was used for the removal of both As(III) and As(V) from water samples, and their maximum adsorption capacity for As(III) and As(V) was found to be 14.04 and 12.22 mg g^{-1} , respectively. Zhou and coworkers reported on MWCNTs coated with magnetic amino-modified CoFe_2O_4 ($\text{CoFe}_2\text{O}_4\text{-NH}_2$) nanoparticles via a simple one-pot polyol method. This MNP composite was further modified with chitosan (CTS) to obtain a chitosan-functionalized MWCNT- $\text{CoFe}_2\text{O}_4\text{-NH}_2$ hybrid material [59]. The adsorption of tetrabromobisphenol A was well represented by

the Freundlich isotherm model, and the absorption of Pb(II) was better described by the Langmuir model. This composite material showed maximum adsorption capacities for both tetrabromobisphenol A and Pb(II) of 42.48 and 140.1 mg g⁻¹, respectively. Zhao et al. reported on amidoximated modified magnetite/graphene oxide composites for the removal of uranium from wastewater and seawater. The sorption isotherm agreed well with the Langmuir model, and the maximum sorption capacity was found to be 1.197 mmol g⁻¹ at pH = 5.0 and a temperature of 298 K [60].

Fu et al. reported on a water-dispersible MNP–graphene oxide (MGO) composite that was applied to remove selenium ions [both Se (IV) and Se (VI)] in an aqueous system [61]. They showed that for 1.0 g L⁻¹ of metal ions the MGO showed >99.9% removal percentage for Se (IV) and approximately 80% for Se (VI) within 10 s. This material can be separated effectively under an external magnetic field and recycled for reuse in water treatment. Cong et al. reported on a facile one-step approach for the fabrication of macroscopic graphene/iron oxide hydrogels with 3D interconnected networks under the synergistic effects of the self-assembly of GO sheets. Metal oxide nanoparticles such as FeOOH nanorods and magnetic Fe₃O₄ nanoparticles were simultaneously in situ deposited on graphene sheets. This induced metal nanoparticles to act as a reducing agent to reduce the GO sheets under mild conditions. In this case, the compositions of graphene hydrogels could be easily changed by adjusting the pH value of the initial GO suspension with other conditions remaining constant. Low-cost graphene/metal oxide hydrogels exhibit an excellent capacity for the removal of heavy-metal ions and oils from water [62].

8.2.1.5 Molecularly Imprinting Polymer–Modified MNPs

Molecularly imprinted polymers (MIPs) containing tailor-made recognition sites exhibit the ability to rebind a target molecule with high specificity and selectivity in preference to analogous compounds. To fabricate specific binding sites, the copolymerization of functional and cross-linking monomers around a template molecule in a suitable porogenic solution is first conducted, which creates a 3D polymeric matrix. When the template is removed from the polymeric matrix by extraction or chemical reaction, a cavity is created in the polymer matrix that is highly specific and selective for the target analog. The schematic representation for the synthesis of MIPs is shown in Fig. 8.5.

Due to its high specificity and selectivity, as well as favorable thermal, mechanical, and chemical stability, MIPs have been widely used as artificial receptors in various applications, for example, solid-phase extraction [29], chromatography separation [63], and chemical sensing [30]. Additionally, they are also very popular in the field of environmental analysis or pollutant detection owing to their high selectivity and specificity toward their template molecules. It has been reported that nanosized MIPs perform better for the removal of organic pollutants from environmental samples at trace levels because their small particle sizes and high specific surface area could produce a large adsorption capacity and fast adsorption rate [30]. To further increase their adsorption capacity and removal efficiency, MNPs

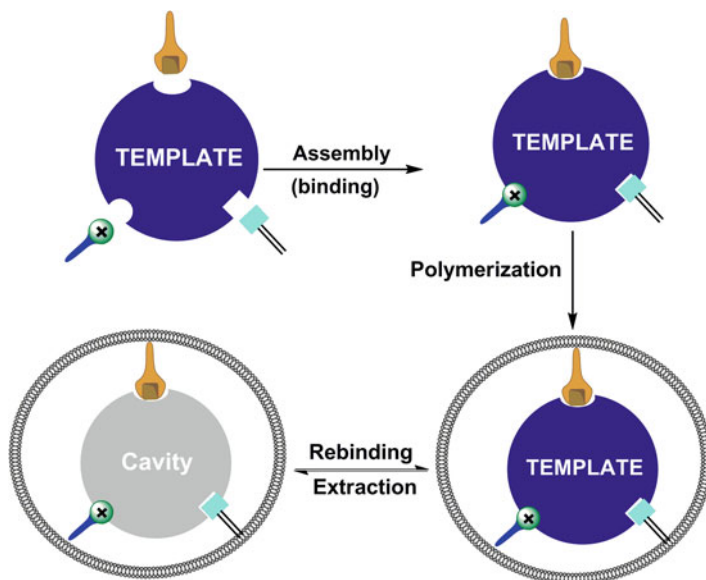


Fig. 8.5 Schematic representation showing synthesis procedure of molecularly imprinting polymer

have been incorporated into MIPs. Several works have reported on the combination of MIPs with MNPs to detect and remove pollutants and heavy-metal ions from water samples. Liu and coworkers reported on As(III)-imprinted bio-based α -Fe₂O₃ impregnated chitosan beads for the adsorption and removal of As(III) ions from aqueous solutions [64]. The kinetic data, obtained at the optimum pH of 5, could be fitted with a pseudo-second-order equation and the adsorption process could be well described by Langmuir adsorption isotherms. The maximum adsorption capacity calculated from the Langmuir equation was found to be 9.355 mg g⁻¹. Roy et al. have reported on the novel synthesis of reduced GO dendrite kind of nanomaterial that was used to detect europium metal ions in water [30]. The same research group also reported on the synthesis of GO and silane-modified MNP-based dendritic monomers for the synthesis of Eu(III)-imprinted polymers. This Eu(III)-imprinted polymer was developed on vinyl group-modified silica fiber and used as a substrate for solid-phase microextraction. The modified fiber was used for the extraction or separation of Eu(III) from the soil of coal-mining areas and the removal of Eu(III) contamination from wastewater [29].

8.2.1.6 Nanoscale Zero-Valent Iron

Since 1991, the nanoscale zero-valent iron (Fe⁰ or nZVI) has been known for the removal of toxic metal ions like Pb(II), As(III), Cr(VI), Ni(II), Cu(II), and Co(II) [8], owing to their ability to reduce them, either directly or indirectly. Iron is present

in the environment in their most stable (thermodynamically) oxide form. But, in normal conditions, the nZVI is not very stable and is easily oxidized. The reduction of metal-ion contaminants involves several steps, and the prescribed pathways are given as follows [12, 65]:

1. By the direct reduction of metal ions at the surface of nZVI,
2. By catalytic reduction via Fe(II) at corrosion product surfaces,
3. By adsorption onto the surface of corrosion products.

It has been reported in the literature that nZVI have a core and shell type structure [66] in which the core is made up of metallic iron (α -Fe) and the shell is formed by oxides and hydroxides, resulting from the oxidation of iron. Here, the core is responsible for the reduction of metal ions. As the contaminants is reduced, the core becomes oxidized and several other reactants like iron (II), its oxides, and hydroxides, are produced [67]. On the one hand, iron oxides help to prevent contaminants from migrating to the core; on the other hand, they also form an electroconductive layer for better electron flow/migration [67]. Therefore, many research groups have reported the synthesis of differentially modified nZVI and explored their role in water purification and wastewater management. Torrey and coworkers reported nZVI mixed matrix membranes for water treatment applications. Upon oxidation of metallic iron to iron oxide hydroxide, FeO(OH), particles, a significant transformation in size and morphology had occurred. Spherical particles 100 nm in diameter are transformed into platelike crystalline particles with a hydrodynamic diameter greater than 450 nm. These nanoparticles are incorporated to the membrane at the time their synthesis and remain intact during filtration to ensure the production of safe drinking water [68]. Vernon et al. conducted a series of experiments on the interactions of nZVI and mercury (Hg) dissolved in aqueous solution [69]. Huang and coworkers reported on hybrid nZVI technology for removing selenium (Se), mercury (Hg), and nitrate from the wastewater of a coal-fired power plant. The hybrid was prepared by interaction between nZVI and magnetite or other Fe(II) species. The hybrid nZVI technology creates a self-sustaining highly reactive mixture that can achieve rapid reduction, transformation, immobilization, and mineralization of various heavy metals, oxy anions, and other impurities from aqueous streams in a neutral or near-neutral pH environment [70]. Ling et al. reported that nZVI is an effective agent for the treatment and removal of selenium (IV) from water [71]. The experimental results showed that Se(IV) was separated from water by nZVI via chemical reduction to Se(II) and Se(0). Herein, 1.3 mM selenite was quickly removed from water within 3 min using only a 5.0 g L⁻¹ suspension of nZVI. Kim et al. have reported a composite of zeolite and nZVI that shows good potential to remove Pb(II) from water [72]. The surface area of the composite was found to be 80.37 m² g⁻¹, which was much greater than normal zeolite (1.03 m² g⁻¹) or nZVI (12.25 m² g⁻¹) alone. Moreover, 96% of the Pb(II) was removed from 100.0 mL of solution containing 100.0 mg L⁻¹ Pb(II) within 140 min of mixing with 0.1 g composite material. Almeelbi and Bezbaruah have used nZVI particles for the removal of phosphate from aqueous solution [73]. They reported that the efficiency of the nZVI in phosphate removal was found to

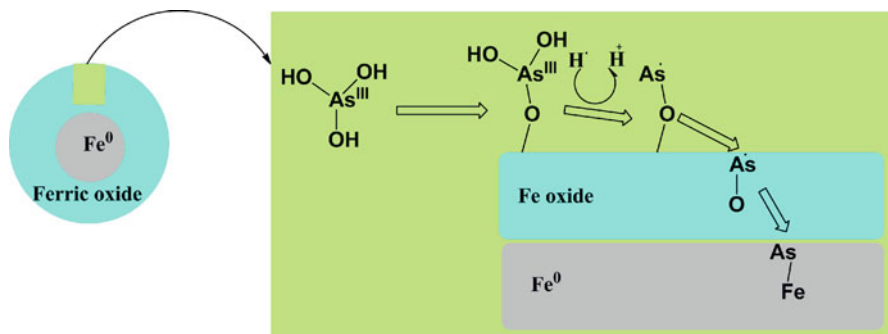


Fig. 8.6 Proposed reaction mechanism for removal of As(III) using nano zero-valent iron (nZVI)

be 13.9 times higher than micro-ZVI particles at the same concentration. Su et al. reported a magnetic sulfide-modified nZVI for the removal of cadmium from water [74]. Sulfide-modified nZVI had an optimal Cd(II) removal capacity of 85.0 mg g^{-1} , which was 100% higher than normal nZVI, with a 95% removal efficiency. Petala and coworkers reported a Mobil Composition of Matter No. 41 solid (MCM-41)-supported nZVI used for the removal of Cr(VI) from water [75]. The MCM-41 belongs to the M41S family and shows a regular hexagonal shaped arrangement of pores that looks like a cylinder and has a variable pore diameter in a range of 1.5–20 nm. The material shows high crystallinity as well as high thermal stability. Its large surface area ($1000 \text{ m}^2 \text{ g}^{-1}$) as well as its high loading capacity towards metal cations, makes it ideal for catalytic applications. nZVI is also very popular in As removal owing to its specific and selective interaction with arsenic ions. The interaction mechanism of arsenic with nZVI is shown in Fig. 8.6. Thus, a number of research papers have been published on the removal and determination of different forms of arsenic using nZVI.

Zhou et al. reported on magnetic cellulose nanomaterials using nZVI for the removal of arsenite [76]. They reported that composites could be easily separated from solutions in 30 s through an external magnetic field. The experimental results showed that arsenite adsorption followed the pseudo-second-order kinetic model and Langmuir isotherm model. A maximum removal of 99.27% was observed for an initial concentration of 10.0 mg L^{-1} at pH 8.0 and an adsorbent dose of 1.0 g L^{-1} . The researchers stated that the maximum adsorption capacity of As(III) was approximately 19.93 mg g^{-1} at pH 6–7 at 25°C . Chauhan et al. described the synthesis of chitosan/PVA/nZVI nanofibrous material that was used for the removal of As from water [77]. The experimental results showed that the aforementioned nanofiber was biodegradable and capable of removing $200.0 \pm 10.0 \text{ mg g}^{-1}$ As(V) and $142.9 \pm 7.2 \text{ mg g}^{-1}$ As(III) from aqueous solution of pH 7.0 under ambient conditions. In another work, the fabrication of nZVI nanoparticles was reported using two polymers, carboxymethyl cellulose and starch, as stabilizers [78]. The fabricated nanoparticles were able to remove both As(III) and As(V) from aqueous water samples in just 5 min. The pseudo-second-order kinetics and Langmuir

equation were followed by the adsorption phenomenon. Along with these, the maximum adsorption capacity for As(V) and As(III) was found to be 14.0 and 12.2 mg g⁻¹, respectively. Similarly, a GO-modified nanocomposite of nZVI was synthesized by Wang and coworkers for the removal of both forms of arsenic (III and V) with maximum adsorption capacities of 35.83 and 29.04 mg g⁻¹ for As(V) and As(III), respectively [79].

8.2.1.7 Miscellaneous Magnetic Nanoparticles

In addition to popular methods of MNP modification, some different modifiers have also been used to enhance the stability of bare MNPs and remove heavy-metal ions from water. Zhang and coworkers synthesized Fe-coated bamboo charcoal for the removal of Pb(II) from water [80]. The material was easily synthesized by microwave-assisted reaction, and the resultant material showed an excellent porosity and absorption capacity for Pb(II). In this study, the researchers used bamboo charcoal as a low-cost supporting material for Fe oxides coated by a novel and simple synthetic approach. The proposed Fe-coated bamboo charcoal material follows the Langmuir adsorption isotherm model and showed the maximum adsorption capacity of 200.38 mg g⁻¹. Thanh and coworkers reported on a novel composite adsorbent by successfully incorporating α -MnO₂ nanorods and γ -Fe₂O₃ nanoparticles into the ball-milled expanded perlite carrier material for As(V) removal from aqueous solution [81]. The adsorption capacity of this material for As(V) was found to be highly pH dependent, and the adsorption kinetics followed the pseudo-second-order kinetic model. The Langmuir isotherm was found to be the best fitted to describe the adsorption of As(V) on both composites, and the adsorption capacity was found to be 4.64 and 7.09 mg g⁻¹ for γ -Fe₂O₃- and α -MnO₂-containing adsorbents compared to 0.0025 mg g⁻¹ for perlite alone, confirming that these composites retain the constituent nanomaterial properties.

Lee and coworkers fabricated unique sea-urchin-like magnetic iron oxide (mixed-Fe₂O₃/Fe₃O₄ phase) nanostructures (called u-MFN) with large surface areas (94.1 m² g⁻¹) and strong magnetic properties (57.9 emu g⁻¹), and the material was used in wastewater treatment [82]. The u-MFN had excellent removal capabilities with respect to the heavy-metal ions such as As(V) (39.6 mg g⁻¹), Cr(VI) (35.0 mg g⁻¹), and the organic pollutant Congo red (109.2 mg g⁻¹). Biswal et al. have reported the use of an inexpensive and natural seed based hydrogel. They have shown that natural seeds sabja (*Ocimum basilicum*) can absorb water to about 30 times their weight and can be easily loaded with nanoparticles of functional metal oxides such as visible light photo-catalyst N-doped TiO₂ or magnetite (Fe₃O₄). The material can be used for effective multiple water purification objectives such as efficient photocatalytic degradation of toxins or bacteria, heavy metal ion (As³⁺, Cr⁶⁺, Pb²⁺, Cd²⁺) removal or simple particulate filtering [83]. Rao et al. have examined the removal of hexavalent chromium [Cr(VI)], an important groundwater pollutant, by phyto-inspired Fe⁰/Fe₃O₄ nanocomposite-modified cells of *Yarrowialipolytica*. The maximum adsorption capacity was found to be

137.31 mg g⁻¹ for a 1000.0 mg L⁻¹ concentration of Cr (VI) [31]. Han and coworkers have investigated the removal of Hg(II) from water using FeS(s) with batch and continuous contact filtration systems. The results showed that in batch kinetic tests, FeS(s) was a good scavenger for Hg(II) and could rapidly remove the bulk of the Hg [84]. The material was also able to achieve complete Hg(II) removal after sufficient contact time, regardless of initial Hg concentration in the range studied (500–1250 μM).

Yuan et al. reported a new synthesis strategy for Fe₂O₃–ceramsite using sintering bentonite, iron powder, and activated carbon [85]. The materials showed a maximum removal efficiency of 17.5 and 7.4 mg g⁻¹ for Pb(II) and Zn(II) at pH 5.0, respectively. Fan et al. described a nano-iron/oyster shell composite by an in situ synthesis method to detect the arsenic in wastewater [86]. The composite showed a good acid/alkali resistance and thermal endurance for the removal of As(III). Zelmanov and Semiat [87] reported iron oxide/hydroxide nanoparticles solution for removal of selenium from water [87]. The experimental results showed maximum adsorption capacities of 95.0 and 15.1 mg g⁻¹ for Se(IV) and Se(VI), respectively. Cheng et al. have discussed the synthesis of MNPs by a dispersion–precipitation method involving acetone-promoted precipitation of colloidal hydrous MNPs and subsequent calcination of the precipitate at 250 °C [36]. This material was successfully used to remove arsenite from water. The experimental results showed that the adsorption obeyed pseudo-second-order kinetics and the data were well fitted in the Langmuir adsorption isotherm model, and the maximum adsorption found for arsenite was 46.5 mg g⁻¹ at pH 7.0. Zhang et al. described a composite of arginine and lysine-modified Fe₃O₄ nanoparticles by a coprecipitation process used to remove trace arsenate [As(V)] from river water [88]. The modified adsorbents had maximum adsorption capacities of arginine MNPs and lysine MNPs of 29.14 and 23.86 mg g⁻¹ and were found to be greater than the normal adsorption capacities found for bare MNPs (12.12 mg g⁻¹). Jing Wang and coworkers synthesized MNP-impregnated chitosan beads for the removal of As from water. It shows maximum adsorption capacities of 35.7 and 35.3 mg g⁻¹ for As(V) and As(III) [89].

Jin and coworkers synthesized a cetyltrimethyl ammonium bromide–modified MNPs which has higher As(V) adsorption capacity from 7.59 to 23.07 mg g⁻¹ [37]. Almost 95% of the As(V) (100.0 μg L⁻¹) was removed with 0.1 g L⁻¹ modified composites within 2 min at pH 6. This composite could be regenerated with a simple alkalization–acidification process and more than 85% As(V) removal rates could be achieved even in the fifth adsorption/desorption cycle. Feng et al. reported on ascorbic acid–coated superparamagnetic iron oxide nanoparticles (SPIONs) by an environmentally friendly hydrothermal route [90]. The composite was used as an absorbent to remove As from wastewater and adsorption data well fitted in the Langmuir adsorption isotherm with a maximum adsorption capacity of 16.56 mg g⁻¹ for As(V) and 46.06 mg g⁻¹ for As(III).

Badruddoza et al. described novel nanoadsorbent, carboxymethyl-cyclodextrin-modified MNPs for the removal of copper ions from aqueous solution. The maximum adsorption capacity for these MNPs for Cu(II) was estimated and found

to be 47.2 mg g^{-1} at $25 \text{ }^\circ\text{C}$ [91]. Liu et al. reported on ethylene diamine tetracetate (EDTA)-functionalized MNPs as novel magnetic nanoadsorbents for the removal of Cu(II) from aqueous solution. Studies on the adsorption revealed that the adsorption process obeyed the pseudo-second-order kinetic model. The data were well fitted in the Langmuir adsorption isotherm model and the maximum adsorption was found to be 46.27 mg g^{-1} at pH 6.0 and 298 K [92]. Recently, a green synthesis approach was reported for the synthesis of MNPs using natural precursors. Prasad et al. described a new approach to synthesizing MNPs using the leaf extract of a mint plant (*Menthaspicata* L.) [93]. These green MNPs were used to remove arsenite and arsenate from aqueous solution. The sorption process fitted well with the Langmuir model and followed pseudo-second-order kinetics, and the maximum adsorption capacity of the prepared sorbent was found to be 86.53 for As(III) and 94.67 mg g^{-1} for As(V), respectively, at optimal experimental conditions.

8.2.2 Microbial Contamination

Contamination in drinking water by bacteria or viruses causing diarrheal disease is the most important aspect of drinking water quality. The bacteria and viruses that are mainly responsible for this type of diseases are *Escherichia coli*, *P. aeruginosa*, *Salmonella*, *B. subtilis*, polio virus, retro virus, and others. The common pathogenic species and their detection methods are portrayed in Fig. 8.7. Thus, in many parts of

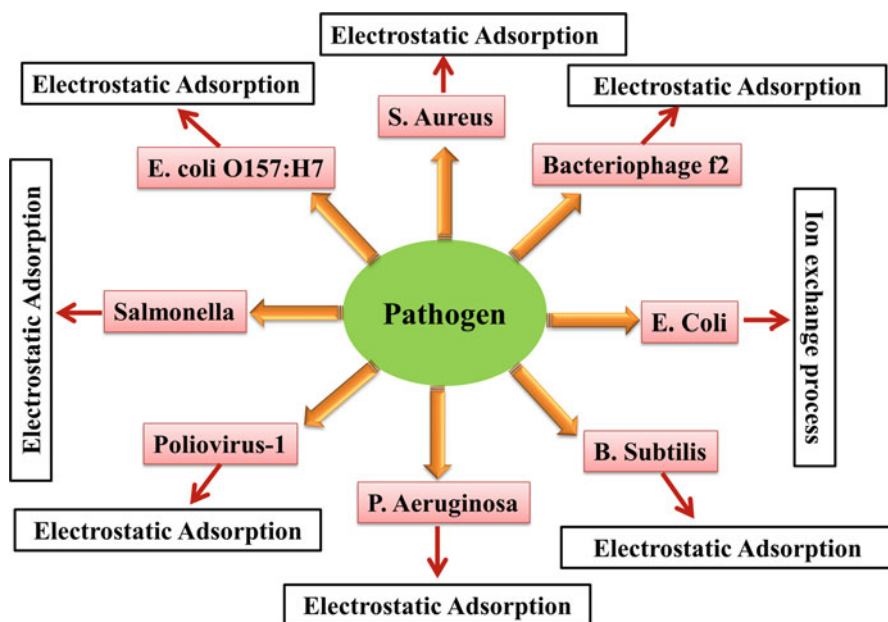


Fig. 8.7 List of popular analytical techniques used for detection of pathogens

the developing world contamination by pathogens remains a major cause of disease. It is therefore essential to prevent such pathogens from entering water sources or to treat drinking water to kill the pathogens. Many works have been published where bare or modified MNPs play an important role in the purification of drinking water from pathogens.

Zhan and coworkers synthesized aminosilane-functionalized MNPs (NH_2 -MNPs) using a layer-by-layer method for the rapid removal of both pathogenic bacteria and viruses from water [94]. These prepared MNPs were able to capture a wide range of pathogens, including bacteriophage ϕ 2 and a virus (Poliovirus-1), as well as various bacteria, such as *S. aureus*, *E. coli* O157:H7, *P. aeruginosa*, Salmonella, and *B. subtilis* from wastewater. Sarika and coworkers reported on-COOH, $-\text{NH}_2$, and $-\text{SH}$ group-modified MNPs by facile soft-chemical approaches for the removal of toxic metal ions [Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), and As(III)] and bacterial pathogens (*E. coli*) from water [95]. Depending on the surface functionality ($-\text{COOH}$, $-\text{NH}_2$, or $-\text{SH}$) magnetic nanoadsorbents can capture the different metal ions either by forming chelate complexes or undergoing an ion-exchange process or electrostatic interaction. Wei et al. have described $\text{Ag}@\text{Fe}_2\text{O}_3$ -Gluyolk-shell multifunctional nanoparticles that provide a new platform for the simultaneous rapid detection of bacteria and safe decontamination treatment, which may have applications in water purification and food safety [96]. Nangmeny et al. described an Ag-modified Fe_2O_3 nanoparticle impregnated fiberglass by an aqueous hydrothermal synthetic approach [97]. The experimental results showed that the material was used to kill bacteria and viruses in water, and these new systems are less costly since a lower amount of nanoparticles is needed to achieve the same disinfection efficiency.

8.2.3 Other Widespread Water Pollutants

MNPs have been used in the purification or treatment of groundwater and wastewater contaminated with different types of materials besides heavy metals, like anions (nitrate) [98], chlorinated organic compounds [99], nitroaromatic compounds (NACs) [100], dyes [101], and phenol [102]. Recently, there has been great interest in the use of MNPs for the removal of contaminants from groundwater and wastewater, and many articles have been published recently on this topic. A summary of studies reported for removal of other water pollutants using MNPs is given in Table 8.2.

8.2.3.1 Anions as Water Contaminant

Recently, nitrate pollution in ground and surface water has become a serious problem in developing countries. The source of NO_3^- is the use of chemical fertilizers, pesticides, animal-feeding operations, petroleum products, and waste

Table 8.2 Estimation of anions, industrial dyes, pesticides, and aromatic organic contaminants using magnetic nanoparticles as adsorbent

Serial number	Material	Detection or adsorption	Adsorption capacity	Reference
1.	nZVI	Nitrate	–	Xu et al. [104]
2.	nZVI	Nitrate	–	Hwang et al. [98]
3.	Fe–Ti bimetallic oxide Fe ₃ O ₄ particles	Fluoride	57.2 mg g ⁻¹	Zhang et al. [106]
4.	γ -AlOOH@CS-MNPs	Fluoride	67.5 mg g ⁻¹	Wan et al. [107]
5.	Polypyrrole (PPy)/Fe ₃ O ₄	Fluoride	–	Bhaumik et al. [108]
6.	Mg–Fe–La tri metal composite	Fluoride	112.1 mg g ⁻¹	Wang et al. [109]
7.	Fe–GAC	Bromate and perchlorate	–	Xu et al. [110]
8.	Fe ³⁺ oxide/hydroxide nanoparticles	Phosphate	–	Zelmanov and Semiat [111]
9.	Chitosan MNPs	Humic acid	32.6 mg g ⁻¹	Dong et al. [84]
10.	nZVI	Remazol Blue R, Acid Black I	–	Chang et al. [118]
11.	nZVI	Acid Blue 129	–	Shirin and Balakrishnan [101]
12.	nZVI–UASB	Brilliant Red X-3B	–	Zhang et al. [119]
13.	nZVI and anaerobic sludge	Azo dye	–	Li et al. [54]
14.	Fe ₃ O ₄ @C core-shell nanoparticle	Methylene blue, Cresol red	44.3, 11.2 mg g ⁻¹	Zhang and Kong [117]
15.	Fe ₃ O ₄ @HHSS	Methylene blue, Fuchsin dye	147.0, 124.6 mg g ⁻¹	Zhang et al. [122]
16.	Magnetic TiO ₂ /montmorillonite/Fe ₃ O ₄	Methylene blue	–	Zhang et al. [124]
17.	Graphene nanosheet-Fe ₃ O ₄	Methylene blue	43.8 mg g ⁻¹	Ai et al. [125]
18.	Polydopamine-graphene–Fe ₃ O ₄	Methylene blue	365.3 mg g ⁻¹	Han et al. [127]
19.	Fe ₃ O ₄ /MWCNTs/RGO	Rhodamine B	–	Pawar et al. [128]
20.	nZVI	2,4-Dichlorophenoxyacetic acid	–	Zhu et al. [131]
21.	Chitosan-Fe ₃ O ₄	Carbamazepine	–	Zhang et al. [132]
22.	SPION	Tetracycline	12.1 mg g ⁻¹	Dai et al. [133]
23.	Chitosan-Fe ₃ O ₄	Alizarin red	40.1 mg g ⁻¹	Fan et al. [134]
24.	Iron-polyphenol complex	Acid black 194	1.6 g g ⁻¹	Wang [129]
25.	Fe ₃ O ₄ @SiO ₂ @TiO ₂ /graphene oxide	Rhodamine B	–	Chen et al. [114]
26.	ZnFe ₂ O ₄ –C ₃ N ₄ hybrids	Orange II	–	Yao et al. [123]
27.	Magnetic ionic liquid modified MWCNTs	Aryloxyphenoxy-propionate	–	Luo et al. [130]
28.	nZVI	<i>p</i> -Nitrophenol	–	Nakatsuji et al. [113]

contamination through storm and urban runoff. Because of nitrate contamination, serious health problems like methemoglobinemia, carcinoma, malformation, and mutation defects have been observed. According to WHO, the minimum limit of nitrate in drinking water is 10.0 mg L^{-1} [103].

Although the chemical reduction of nitrate by MNPs was reported as early as 1964, it has not gained popularity until the last 10 years [103]. In recent years, MNPs have been intensively studied for their ability to reduce NO_3^- in water and groundwater. Nitrate can be reduced to NH_3 , N_2 , and NH_4^+ , and iron may be oxidized to Fe^{2+} , Fe^{3+} , Fe_2O_3 , or Fe_3O_4 depending on the reaction conditions. Several papers have been published where nitrate reduction was carried out using MNPs (Table 8.2). Xu et al. have reported that 95% of nitrate was rapidly removed by MNPs under strongly acidic conditions ($\text{pH} < 2-3$), while less than 50% of nitrate was removed at $\text{pH} > 5$ [104]. When Fe^{2+} is added, the reductive efficiency of nitrate by MNPs at neutral pH initially increased, accompanied by the generation of Fe_3O_4 , which favored electron transfer on the surface of iron particles and accelerated the reductive denitrification rate of nitrate. Hwang and coworkers investigated the fate of nitrogen species during nitrate reduction by MNPs and related reaction mechanisms [98]. They reported that ammonia was the major product of nitrate reduction by MNPs and the nitrate was absorbed onto the surface of the nanoparticles, followed by reduction and desorption in sequential steps. On the other hand, some studies have concentrated on seeking a solution where nitrate was converted into N_2 . Pan and coworkers investigated nitrate removal from solution by single (TiO_2 and Fe) and composite (Nano- TiO_2 - Fe^0 composite) systems under UV illumination [105]. They found that the composite system could satisfactorily transform nitrate into N_2 .

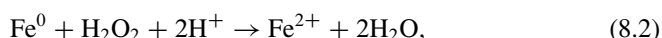
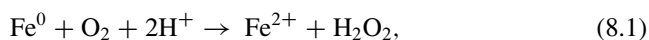
Similarly, MNPs were also used to remove fluoride contamination from drinking water. In this regard, Zhang and coworkers prepared a novel adsorbent by coating Fe-Ti bimetallic oxide on magnetic Fe_3O_4 particles by a coprecipitation method. The synthesized material was added to fluoride-containing water, and after adsorption, the material was easily separated within 2 min by an external magnet. The experimental data showed that the adsorption process should follow the Langmuir adsorption isotherm model, and the maximum adsorption capacity was found to be 57.22 mg g^{-1} [106]. Wen and coworkers synthesized a novel adsorbent of γ - $\text{AlOOH}@$ CS (pseudoboehmite and chitosan shell) MNPs with magnetic separation capabilities to remove fluoride from drinking water, and the calculated adsorption capacity of the ACMN for fluoride was found to be 67.5 mg g^{-1} [107]. Bhaumik and coworkers prepared a polypyrrole (PPy)/ Fe_3O_4 magnetic nanocomposite as a novel adsorbent via in situ polymerization of a Py monomer with FeCl_3 as oxidant in aqueous medium for fluoride removal from drinking water [108]. The equilibrium data were well described by Freundlich and Langmuir-Freundlich isotherm models, while the adsorption kinetics followed the pseudo-second-order model. The thermodynamic parameters confirmed the spontaneity as well as endothermic nature of the fluoride adsorption. Wang et al. described a novel Mg-Fe-La trimetal composite by coprecipitation for the removal of fluoride ions from water [109]. The adsorption process was fitted well with the Langmuir isotherm and pseudo-second-order kinetic models and showed a maximum absorption capacity of

112.17 mg g⁻¹ toward fluoride. Xu and coworkers published a comparative study of nano-iron hydroxide-impregnated granular activated carbon (Fe-GAC) for bromate or perchlorate removal from water [110]. The experimental results showed that Fe-GAC exhibited a much greater removal capacity for bromate than perchlorate. Furthermore, Fe-GAC could remove bromate first through adsorption and then reduction to bromide, and it removed bromate (optimal pH 6–8) completely after 50 h. Zelmanov and Semiat [111] reported on an iron oxide/hydroxide nanoparticle-based agglomerate (AggFe) suspension that was used to remove phosphate ions from water [111]. The effect of inorganic ions on the removal of phosphate ions using AggFe, like HCO₃⁻, Cl⁻, and SO₄⁻², which were usually present in municipal and industrial wastewater, was also reported.

8.2.3.2 Aromatic Compounds

Aromatic compounds, mainly phenol and their derivatives, are common organic pollutants in water that are discharged by petrochemical and chemical companies, coking plants, oil refineries, and pharmaceutical companies. Similarly, carcinogenic organic compounds, such as chlorophenol and polychlorophenols, are produced during the chlorination process of drinking water. Waters containing aromatic compounds are highly toxic for most aquatic life and, indirectly, for humans as well. Therefore, the removal of phenol and other organic contaminants from wastewater is of central concern.

Shimizu and coworkers investigated the removal of phenol by MNPs. For this, the concentration of hydroxyl radical (•OH) was quantified via a Fenton reaction [102]. The Fenton reaction was mainly responsible for the removal of phenol. In the Fenton reaction, H₂O₂ or oxygen species (in acidic medium) reacts with Fe²⁺ and produces hydroxyl radicals (•OH) that have a strong oxidizing capability toward a variety of organic compounds:



To reduce the presence of ferrous ions in solution, the role of nZVI was also studied by Babuponnusami et al. nZVI was used to advance the oxidation processes in Fenton reactions and remove phenol from water [112]. Nakatsuji and coworkers have also reported on nZVI to remove p-nitrophenol and its derivatives from aqueous solution [113]. Chen and coworkers have synthesized a quaternary nanocomposite of Fe₃O₄@SiO₂@TiO₂/graphene oxide for simultaneous adsorption and photocatalytic degradation of aromatically structured chemical pollutants [114].

Dong and coworkers prepared novel chitosan MNPs for the removal of humic acid from water using the Langmuir isotherm model, and the maximum absorption capacity was shown to be 32.6 mg g^{-1} at 25°C [84].

8.2.3.3 Industrial Dyes

Dyes are widely used in various fields, mainly in the textile industry, and heavily implicated in water pollution. Dyes used for industrial purposes are toxic, carcinogenic, and teratogenic, and unfortunately most of them are stable and resistant to photodegradation, biodegradation, and other oxidizing agents [115, 116]. Based on their numerous advantages, such as high separation efficiency, simple manipulation process, benign operating conditions, and easy modifications, recently, magnetic nanoparticle loaded adsorbent materials have attracted special attention of the researcher for water purification [11, 117]. The reduction of nZVI in anoxic conditions has received much attention for the decolorization of the most used azo and anthraquinone dyes, and representative studies dealing with heavy-metal removal have been published. However, under anoxic conditions, the reduction of dyes by nZVI often has a low chemical oxygen demand (COD) removal ability. Numerous studies have reported that nZVI under aerobic conditions can generate strong oxidants and degrade dyes. Chang et al. reported that an nZVI/air process can decolorize remazol brilliant blue R and acid black 1 dyes more rapidly and significantly. Higher COD removals for both dyes were achieved (compared to Fenton oxidation) [118]. Shirin and coworkers have investigated the reduction of acid blue 129 dye by nZVI under aerobic conditions and identified novel reaction intermediates and products, including a genotoxic end product, 2,4,6-trimethylaniline [101].

Zhang et al. have developed an nZVI packed upflow anaerobic sludge blanket (ZVI-UASB) reactor to treat azo dye reactive brilliant red X-3B in wastewater that showed greater removal of COD and color [119]. Li et al. combined nZVI and anaerobic sludge to decolorize reactive blue 13 dyes and found that the wastewater treatment of azo dye was enhanced in an acidogenic reactor by nZVI dosing [120]. Zhang et al. have described novel magnetic $\text{Fe}_3\text{O}_4@\text{C}$ core-shell nanoparticles as adsorbents for the removal of organic dyes such as MB and cresol red from polluted water [117]. The maximum adsorption capacities for MB and cresol red were found to be 44.38 and 11.22 mg g^{-1} , respectively. In another year, Zhang and Kong [121] examined magnetic $\text{Fe}_3\text{O}_4@$ hierarchical hollow silica spheres ($\text{Fe}_3\text{O}_4@$ HHSS) by a microemulsification method that had a high specific surface area, huge interior space, and robust magnetic properties. The $\text{Fe}_3\text{O}_4@$ HHSS material showed good adsorption performance for the removal of MB from aqueous solution [121]. The same research group also developed a magnetic microsphere with an Fe_3O_4 core and a $\text{SiO}_2\text{-TiO}_2$ hybrid hollow shell by an aerosol process and subsequent etching treatment. This material showed maximum adsorption capacities of 147.0 mg g^{-1} for MB and 124.6 mg g^{-1} for fuchsin dye [122]. The adsorption should follow the pseudo-second-order model and the dye-saturated microspheres can be easily

recycled using an external magnet. The nanomaterial could be easily regenerated by 1–3 wt% aqueous NaOH solution. Yao et al. reported on magnetic $\text{ZnFe}_2\text{O}_4\text{-C}_3\text{N}_4$ hybrids through a simple reflux treatment of ZnFe_2O_4 nanoparticles (ca. 19.1 nm) with graphitic C_3N_4 sheets in methanol at 90 °C. This hybrid material exhibited stable performance without losing activity and holds promise as an application for the photo-oxidative degradation of organic contaminants [123].

Zhang et al. described a magnetic $\text{TiO}_2/\text{montmorillonite (MMT)/Fe}_3\text{O}_4$ nanocomposite prepared by a single-step hydrolysis method. This material showed adsorption and photocatalytic activity toward MB as contaminant. The results showed that 94% of the MB was decomposed by the aforementioned nanocomposite, and this material maintained a high degradation rate and revealed good reusability [124]. Ai et al. presented a facile one-step solvothermal method for the synthesis of a graphene nanosheet (GNS)/magnetite composite for the removal of MB from water [125] with a maximum adsorption capacity of 43.85 mg g^{-1} . Wang et al. described a magnetic hybrid nanomaterial ($\text{Fe}_3\text{O}_4\text{-MWCNT}$) for water purification. The prepared $\text{Fe}_3\text{O}_4\text{-MWCNT}$ nanocomposites can be used as an effective catalyst in Fenton-like reactions for the purification of methylene blue-polluted water in a wide pH range [126]. Han et al. described polydopamine-functionalized graphene- Fe_3O_4 nanocomposites by a simple solution mixing method that has high adsorption capacities and easy separation ability. The synthesized nanocomposite was easily separated from polluted water and the adsorption capacity of these nanocomposites for MB was found to be 365.39 mg g^{-1} , which is much higher than that of graphene- Fe_3O_4 nanocomposite [127]. Pauer and coworkers synthesized an $\text{Fe}_2\text{O}_3/\text{MWCNT}/\text{RGO}$ composite by a hydrothermal process. It exhibits photocatalytic activity in terms of the degradation of rhodamine B under visible irradiation [128]. In 2013, Wang [129] prepared iron-polyphenol complex nanoparticles (Fe-PNPs) using eucalyptus leaves. This material has an excellent adsorption-flocculation capacity and might have potential in the removal of acid black 194 from water [129]. The maximum adsorption-flocculation capacity of this material for acid black 194 has been observed at 1.6 g g^{-1} of Fe-P nanoparticles.

8.2.3.4 Pesticides

As the name suggests, pesticides are compounds used to kill pests, that is, organisms that are harmful to plants, animal, or humans. These are chemicals that are intentionally added to the environment to kill pests. They can be classified based on the type of organism they are used to kill:

1. Herbicides: used to kill weeds,
2. Insecticides: used to kill insects,
3. Fungicides: used to kill fungi,
4. Rodenticides: used to kill rodents and others.

Due to the effectiveness of these chemicals, they have become very popular in agricultural activities throughout the world. Their use is not restricted to agriculture; they are also very common in residential homes, on college campuses, in forests, and even on roadsides. As a consequence, pesticides are present in air, food, and drinks and inhaled, eaten, and drunk by all humans in the course of daily life. In the literature, several studies have been reported on the removal as well as detection of pesticides from groundwater and drinking water using MNPs. The role of MNPs in the removal of such toxic materials is discussed in the next section. Mai Luo and coworkers have reported a sensitive, rapid, and environmentally friendly analysis procedure for the simultaneous detection of aryloxyphenoxy-propionate herbicides and their metabolites in water using magnetic ionic liquid-modified MWCNTs [130]. The limits of detection of herbicides and their metabolites were in a range of 2.8–14.3 and 9.8–43.2 $\mu\text{g L}^{-1}$, respectively. Zhu and coworkers have described nZVI particles, prepared by an in situ chemical reduction method, that were employed for 2,4-dichlorophenoxyacetic acid (2,4-D) hydrodechlorination. To do this, the researchers used a palladium/nickel foam (Pd/Ni foam) electrode [131]. The combination of electrochemistry and nZVI is a promising technology for the degradation of 2,4-D, which could control environmental pollution.

8.2.3.5 Other Toxic Chemicals

Other than these water pollutants, MNPs have also been applied to remove estradiol, aniline, phenolic estrogens, diclofenac (DFC), and carbamazepine (CBZ) from contaminated and sources of water. Zhang and coworkers reported a novel magnetic MIP based on chitosan- Fe_3O_4 for the fast separation of CBZ from water samples. This study can be regarded as a combination of selective adsorption and magnetic separation, and the obtained magnetic MIP exhibited higher specific recognition and selectivity to CBZ in the presence of various interferents [132]. Dai and coworkers have reported a novel effective technique for the preparation of MIP@SPION via atom transfer radical emulsion polymerization (ATREP). The as-prepared magnetic molecularly imprinted nanoparticles were evaluated as adsorbents for the selective recognition of tetracycline (TC) molecules from aqueous medium [133]. Fan et al. have reported a novel chitosan coating on the surface of magnetite for the adsorption and removal of alizarin red from aqueous solutions. It should follow the pseudo-second-order equation, and the adsorption process was well described by the Langmuir adsorption model. The maximum adsorption capacity was found to be 40.12 mg g^{-1} at pH 3 and 30 °C [134].

8.3 Toxicity of MNPs

The toxicity of MNPs to biological entities is highly dependent on its size and on a combination of factors related to the properties of the MNPs themselves, such as structural properties, dosage, and the intended use [135]. The chemical

composition of MNPs is naturally toxic. MNPs could elicit a cytotoxic response by interfering with the biological function of the cells but not when attached to the cell membrane [136]. However, when MNPs are attached to the surfaces of cells, they may interfere with cell surface interaction [136]. Furthermore, according to the size and shape of MNPs, they become aggregated and coagulate, which will evoke a toxic response in the physical properties like particle size, shape, and surface coating [137]. However, another issue arises when MNPs become degraded and the outcome of MNPs or MNP byproducts accumulate in various tissues and organs [137]. These degraded products are thought to react with various components of tissues or cells in the body. When MNPs enter a body, they come into direct contact with biological macromolecules such as proteins, lipids, and enzymes, which are found within biological fluids. These biological molecules interact with the surfaces of MNPs and form a complex layer over them called a *corona* [138]. The physical and chemical properties of MNPs, like surface coating, size, or functionalization, result in the formation of either a hard or weak corona [138]. When protein molecules are bound to a corona, various toxic outcomes could result. According to the literature, approximately 10–50 protein molecules could bind to the surfaces of MNPs simultaneously with high affinity [139]. The parameters affecting MNP–protein interactions include various physiochemical properties like surface properties, particle size, shape, charge, surface area, surface defects, smoothness or roughness, and functional groups of MNPs and the composition of the biological fluid [139]. The interaction of proteins with the surfaces of MNPs with different types of coatings is also an important factor when assessing in vitro toxicity. When MNPs are added to culture media, media proteins and other nutrients may be adsorbed onto the MNPs and thus be unavailable for cellular activities. In connection with the toxicity of MNPs, another effect is observed with MNPs, called *cell vision*, and was presented by Laurent et al. [140]. It occurs when the membrane constituents of cells, like proteins, sugars, and phospholipids, come into contact with MNPs. Different type of cells bind in different ways to MNPs. As a result, the binding of exogenous objects to MNPs may cause different responses and affect uptake and metabolism depending on cell type. Furthermore, another problem is posed by the sedimentation of MNPs, as this phenomenon effectively occurs when there is an apparent increase in MNP concentration at cell surfaces and so should be taken into account when performing toxicity assays [141].

8.4 Future Aspects of MNPs in Water Purification and Treatment

The application of nanotechnology to water and wastewater treatment is attracting significant attention. The unique properties of MNPs and their convergence with current treatment technologies present great opportunities to revolutionize water and wastewater treatment. The multifunctional applications of MNPs have been estab-

lished. However, the different structure of MNPs, like their micro- or nanoporous structures with nanometer SPIONs embedded within these structures, could offer alternative applications in different fields. They could be successfully applied to the remediation or treatment of drinking water, groundwater, and wastewater contaminated with chlorinated organic compounds, nitroaromatic compounds, arsenic, heavy metals, nitrate, dyes, fluoride, and phenols.

Although several aspects of MNPs were highlighted in this chapter, most of them are still at the laboratory research stage. Among them, very few are used as a guide in testing or have been commercialized. The stages in their research and development, commercial availability, the cost of nanomaterials involved, and their compatibility with the existing infrastructure will determine their full-scale application for the general population. The challenges faced in water or wastewater treatment by nanomaterials are important, but many of these challenges are only temporary, including technical handling, and high cost. To overcome these challenges, collaboration among research institutions, industry, government, and other stakeholders is essential. It is expected that advancing nanotechnology by careful handling to avoid unintended consequences can continuously provide robust solutions to water and wastewater treatment challenges.

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