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Nanomaterials and Water Purification: Opportunities for Improving and Protecting Water

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Abstract

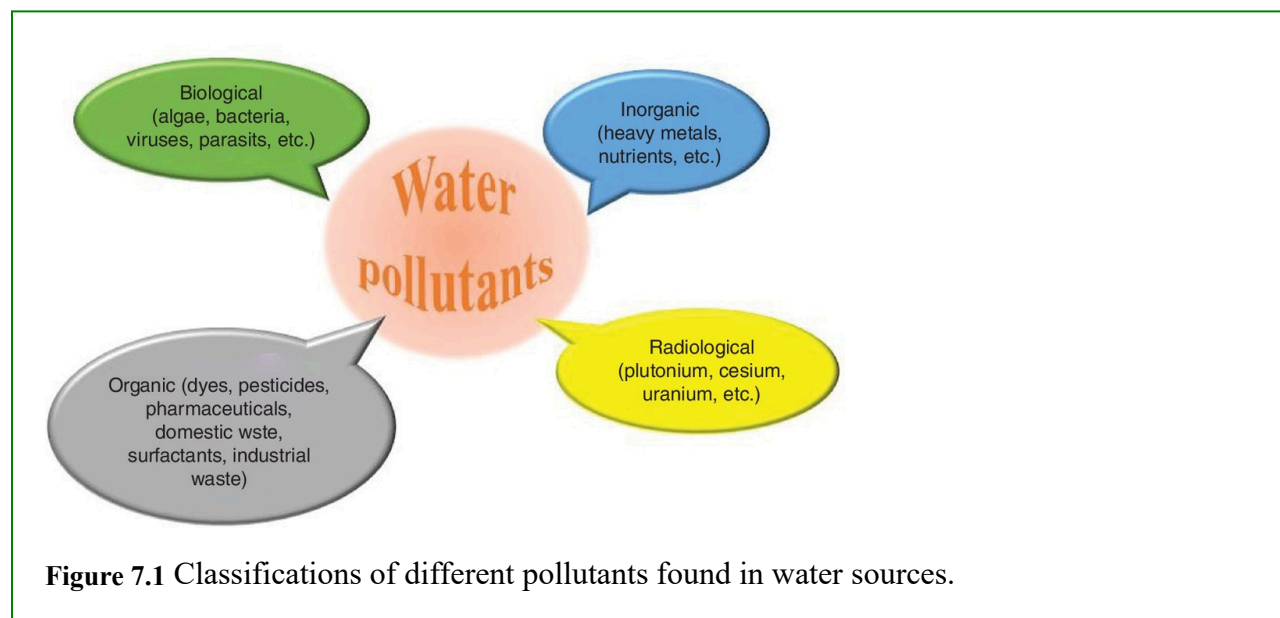
Water purification has become a significant challenge in the last decades due to the increase of pollutants present in water sources. Inorganic contaminants, as well as organic compounds, have received special attention due to their impact on human health and the environment. The presence of these species in aquatic ambient is increasing within the last few years due to industrialization and population growth. For this reason, it is necessary to create an environment of human conscience and develop methodologies for protecting and remediating the ambient. In this sense, the development of novel technologies is emerging. Nanotechnology appears as a recourse for the development of new nanomaterials, which could be implemented in different methodologies for environmental remediation and especially for water purification. In this chapter, an overview of the most novel nanomaterials based on inorganic nanoparticles and bio-based nanocomposites was reviewed, and their methodology of synthesis, characteristics, and properties for water remediation was exhaustively analyzed due to give knowledge in terms of their impact on environmental remediation.

Keywords: water purification; inorganic nanoparticles; biopolymer nanocomposites; synthesis; adsorption properties

7.1 Introduction

In the last few decades, nanotechnology has been studied and applied in different areas by researchers. The great variety of applications of nanotechnology gives this discipline great potential for the economic transformation of countries and the modification of the production processes of their industries. Hence the interest of government agencies and also the private sector, which is promoting research centers, the launch of *I + D + i* programs for the development of nanomaterials (NMs) for multidisciplinary uses. In this sense, in the last few years, the continuous industry growth and population growth all over the world have impacted water supplies. Since the increase of all human activities the quality of water sources has been declining continuously. So, nanotechnology and the implementation of novel NMs and/or nanoparticles (NPs) have emerged as good tools for water purification in conditions suitable for consumption [1]. Nanotechnological strategies can be applied both for the remediation of natural water sources and for

anthropogenically polluted waters. Figure 7.1 exemplifies the various types of contaminants that can be found in water resources and the extent to which the different nanotechnological methodologies are efficient in their remediation.



When we are talking about NMs, we refer to materials that include natural or manufactured particles with at least one dimension of 100 nm or less. In contrast, nanoparticles (NPs) include those with at least two dimensions between 1 and 100 nm [2]. One of the most important characteristics of NMs is related to their surface. In this sense, the NMs and nanoparticles display a higher surface/volume ratio, which allows improvement in their applications such as nano-sensors, nano-adsorbents, among others. This special characteristic gives the NMs used in environmental remediation the affinity to retain in their surface or structure the pollutants found in water media by a different mechanism of interaction. In a review of NMs and the environment, it was informed that in the period between 2006 and 2009, according to the Project and Engineering Nanotechnologies, 212 new nanotechnology-based products have been added to the consumer product list [3].

The investigation is continuously growing around NMs and the researchers have dedicated their work to developing novel nanoparticles for the application, especially in water remediation. So, we can overview the nanoparticles that have been studied: (i) inorganic nanoparticles, (ii) metal-organic frameworks (MOFs), (iii) nanomembranes, and (iv) organic polymer-based NMs. Among all the aforementioned nanoparticles employed for prepared NMs, special attention is given in this chapter to inorganic nanoparticles. This selection was done based on the fact that the methodologies of synthesis of these inorganic nanoparticles involve available reagents, and the use of environmentally friendly solvents; the techniques employed are usually easier to implement and the control of size and surface structure at the nanoscale could be done by modifying variables of synthesis. Table 7.1 shows the most inorganic nanoparticles used for water purification and their principal characteristics considering the application.

Table 7.1 Characteristics of Inorganic Nanoparticles for water purification.

Inorganic nanomaterials					
Carbon-based nanomaterials	Characteristic	Transition metal nanoparticles	Characteristic	Transition metal oxides nanoparticles	Characteristic
CNT	Easy synthesis; high external surface area; high stability in vigorous low or high pH conditions	Fe(0)NPs	– Cheapest of transition metals, – high reactivity	TiO ₂ NPs	Different catalytic reactivity, chemical behavior due to different surface planes
G, GO, and rGO	High sorption capacity; easy surface modification; sufficient functional groups; large surface area; easy modification	Cu NPs, Au NPs	– good performance	Fe ₂ O ₃ NPs, Fe ₂ O ₄ NPs	– active sites for reaction with pollutants, – particle size controllable, – large surface area for interaction
CNT: Carbon nanotubes G: Graphene GO: Graphene oxide rGO: Reduced graphene oxide NPs: nanoparticles		Bimetallic NPs	Higher removal efficiency than monometallic NPs	ZnO NPs	– eco-friendly material, – cheap, – simple way methodology of synthesis

The aforementioned NMs and nanoparticles have been extensively studied in recent years. In particular, the researchers focus their work on the development of novel nanomaterials that could be applied to water and wastewater remediation or purification. In this context, the Section 7.2 presents the most relevant nanoparticles and NMs synthesized for this application. The description was especially focused on the material stabilization in the media, the performance of pollutants removal, and a critical point of view about the possibility of scalability of these materials and the development of a system of purification applied in the pollutant sites. In this sense, zero-valent metal-based NMs; silver nanoparticles (Ag-NPs); metal-oxide NMs; nanosized-zeolite; polymer carbon nanocomposites and derivatives were described below.

7.2 Zero-Valent Metal-Based Nanomaterials

In recent decades, researchers from various areas have extensively studied zero-valent metal-based nanomaterials (nZVM), with a particular focus on water purification. The use of different nZVM-based materials has been reported for their application in removing different contaminants, with most of the studies dedicated to the elimination of heavy metals and organic pollutants from water. For example, Ag⁰ nanoparticles have been extensively studied for their application in water disinfection, owing to their known antimicrobial properties [4]; Zn⁰ nanoparticles have been widely reported for the degradation of numerous organic pollutants [5, 6]. On the other hand, nanosized zero-valent iron (nZVI) has been successfully used for the elimination of a wide range of pollutants, including aromatic compounds [7], heavy metals [8], and inorganic anions [9].

Generally, nanoparticles of zero-valent metals are obtained from the reduction of their metal salts in an aqueous solution. The reducing agent and the synthesis conditions used (e.g. stabilizing agents, temperature, and solvents) determine the size and shape of the nanoparticles. In this sense, the higher the surface area/volume ratio, the higher their reactivity and thus their efficiency in removing contaminants. However, the increase in reactivity, associated with the increase in surface energy, leads to aggregation and surface oxidation of the nZVMs, reducing their photocatalytic properties or adsorption capacity. Additionally, the decrease in size at nanometric scales can decrease the stability of these compounds in aqueous media, causing the leaching of metals into the medium.

The main challenges associated with applying these materials lie in their potential toxicity; rapid surface oxidation, which limits their storage; and their tendency to agglomerate, which significantly decreases their efficiency. Additionally, the separation of nZVMs from the medium is a complex process, and their direct application in columns generates very high internal pressures. The Section 7.2.1 will detail the uses, types of mechanisms, and applicability of ZVM-based NMs in water and wastewater treatment.

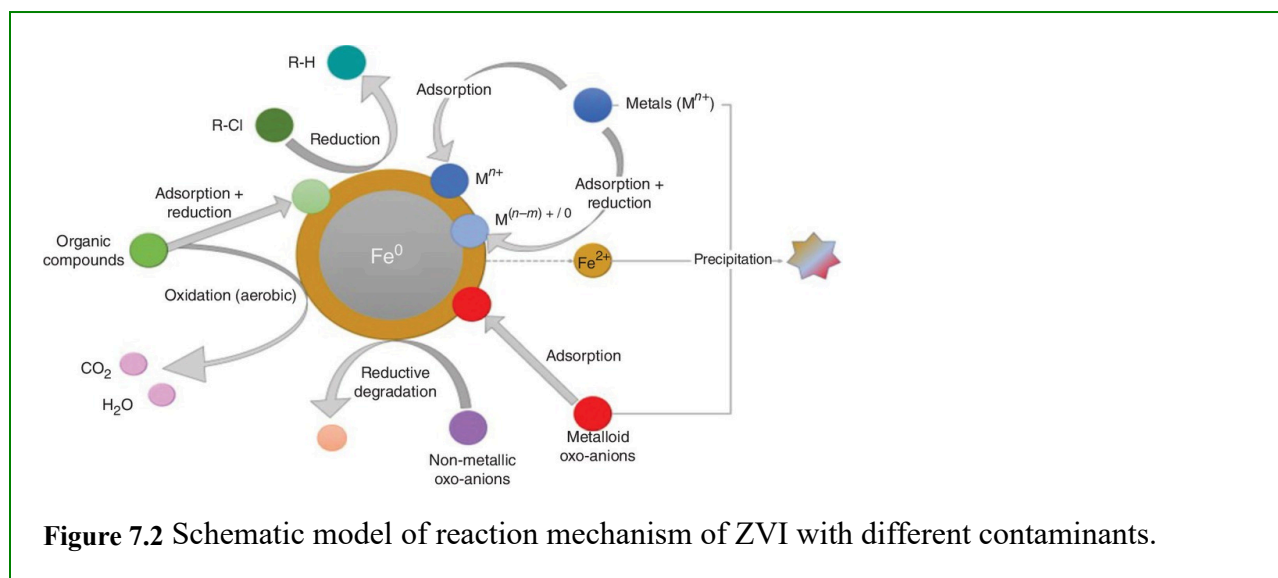
7.2.1 Nanosized Zero-Valent Iron

nZVI is an emerging material widely studied for water remediation. Its moderate reduction potential gives it stability in an aqueous medium, making it an ideal material for removing many redox-sensitive contaminants, such as halogenated hydrocarbons, organic dyes, antibiotics, and heavy metal ions [10]. Also, due to its small size and thus large specific surface area, nZVI presents excellent adsorption, precipitation, and oxidation properties. In this sense, nZVIs are estimated to be between 10 and 1000 times more reactive than granular zero-valent iron. However, the reactivity of nanoparticles does not depend only on their size but also on factors such as their shape, oxide layer, or surface coatings, among others. The synthesis methodology determines these

factors. So then, the synthesis methodology used will depend on the field of application of nZVI.

Nowadays, numerous synthetic methodologies have been developed to obtain nZVI, including chemical co-precipitation, ball milling, liquid-phase reduction, carbothermal method, and green synthesis [11]. Among them, the liquid-phase reduction method has been widely reported in the literature. Normally, iron salts are reduced with sodium borohydride in an aqueous medium under anaerobic conditions (inert atmosphere). However, this type of methodology requires large amounts of expensive reagents, such as NaBH_4 , that hamper their large-scale industrial application [11].

Bare nZVIs are highly reactive in an oxygen environment. When the nZVI is exposed to air, a thin iron oxide layer forms on its surface. Thus, nZVIs are considered a composite consisting of a core of Fe^0 and a layer of iron (hydr)oxides, as shown in Figure 7.2. In water, this layer appears to be a $\text{Fe}(0)/\text{Fe}(\text{II})/\text{Fe}(\text{III})$ mixed-phase with a surface stoichiometry close to FeOOH [12], whose main crystalline phase would be lepidocrocite ($\gamma\text{-FeOOH}$) [13]. If the surface oxide layer is thin enough to allow electron transfer, its presence is advantageous from a practical point of view, as it gives the material greater stability than bare zero-valent iron nanoparticles. Besides, this core-shell structure gives the material adsorption and reduction functions for removing and transforming various contaminants.



The use of nZVI with a typical core-shell structure have been successfully applied for the elimination of numerous water contaminants: heavy metal ions, including lead, cadmium, copper, nickel, zinc, and silver [14]; metalloids, such as arsenic; inorganic anions, like nitrates [15]; dyes [16]; and organic compounds, such as phenol and halogenated organic compounds [17].

It is important to note that the removal mechanisms will depend essentially on the pollutant but also on the conditions of the reaction medium, such as pH. For example, the interaction mechanism for the removal of heavy metals will depend on the standard potential E^0 of the metal pollutant. For metals whose E^0 is very close to or more negative than the potential of $\text{Fe}^{2+}/\text{Fe}^0$, such as Zn and Cd, the predominant mechanisms will be adsorption and surface complexation without reduction. Meanwhile, ion metals whose E^0 is far more positive than Fe^0 , such as Cu, As, and Hg, are typically reduced, and the reduced form can precipitate on or close to the nZVI

surface. Finally, metals whose standard reduction potentials are slightly higher than E^0_{Fe} , such as Ni and Pb, could be immobilized on the surface by both adsorption and reduction processes [10]. The removal of inorganic oxo-anions (NO_3^- , ClO_4^- , and BrO_3^-) is generally by reduction mechanism.

On the other hand, the removal of organic pollutants is based on the adsorption and reduction capacity of nZVI. nZVI nanoparticles are able to reduce and modify the functional groups of organic compounds, transforming them into derivatives with lower toxicity and even adsorbing them on their surface. Additionally, nZVI can be used as catalysts in the Fenton reaction, degrading the pollutants to mineralization.

The application of nZVI has excellent potential for the remediation of various water sources, such as groundwater and wastewater. However, its use has some drawbacks: (i) the easy oxidation of their surface prevents their long-term storage; (ii) the agglomeration of the nanoparticles produces a notable decrease in their removal efficiency; (iii) difficult separation from the remediation medium; and (iv) leaching of iron into the medium, as a result of the redox processes involved in the removal mechanisms.

To overcome these drawbacks, many researchers have proposed the modification of nanoparticles. Modification strategies mainly include doping with other metals, surface coating, encapsulation in the matrix, and deposition of nZVI on a carrier or support [18]. The approaches used depend on the objective to be achieved. Doping with other metals, such as Pd and Pt, aims to increase their reactivity [19]. Both surface coating [20] and deposition of nZVI on a carrier [21] are usually used to prevent aggregation and enhance dispersibility. Also, the deposition of nZVI on a support and the encapsulation in a matrix are intended to reduce the agglomeration of nanoparticles, retard oxidation, and provide a higher surface area favoring the adsorption processes [22–25].

Another aspect to consider is the toxicity of nZVI. Studies have shown that the toxicity of nZVI is limited compared to other types of nanoparticles. However, modifications of nZVI may not only lead to the generation of more efficient adsorbents but may also cause increased accumulation in living organisms and the ecosystem. For this reason, it is important to study the toxicity of modified and unmodified nZVI to determine the potential effects on living organisms and the ecosystem when applied for contaminant removal in the field [26].

7.2.1.1 Practical Application of nZVI in Macro-Scale

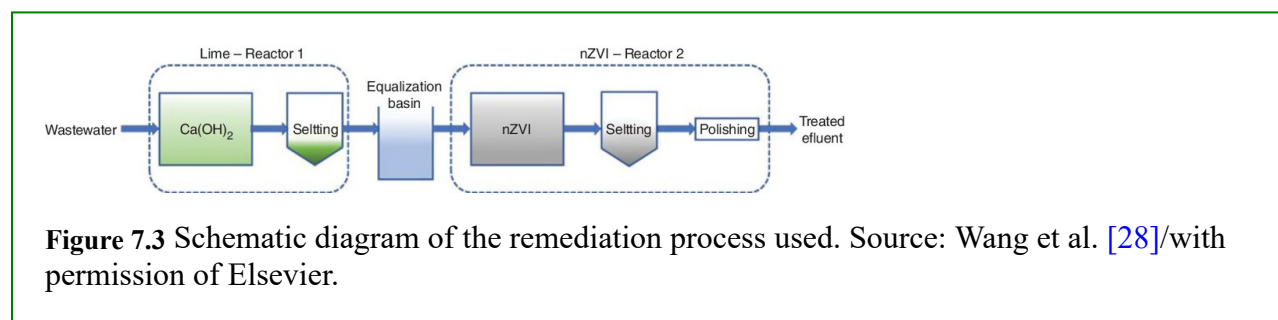
Despite the drawbacks mentioned above, the effectiveness of nZVI in removing various pollutants has been extensively demonstrated on a laboratory scale [27]. In this sense, the studies consist mainly of batch and column tests under ideal laboratory conditions, i.e. model solutions are used where only the pollutant of interest is present, usually at very high concentrations, and pH values that in many cases do not match the values that occur in a real medium. For this reason, the results of laboratory experiments do not always reflect the effectiveness of nanoparticles in natural water or wastewater conditions. In order to know the feasibility of the practical application of nZVI, it is necessary to carry out experiments under real conditions, previously considering the advantages and limitations inherent to the application of this material [18].

The first step to applying any adsorbent on a large scale is conducting pilot-scale tests. The main objective of these tests is the study of different variables to maximize the efficiency of the pollutant removal process. In addition to studying typical variables, such as contact time, water injection flow rates, and dosage, pilot-scale tests also allow a cost study to be carried out.

Consequently, with all this information, it is possible to find the combination of variables that will allow a process to have the best cost/efficiency ratio.

Numerous studies of the application of nZVI on a pilot scale can be found in the literature. Li et al. used nZVI in a pilot-scale process to remediate wastewater from the metallurgical industry [8]. The process consisted of a first adsorption step in a two-stage reactor, followed by a polishing treatment. Each nZVI reactor consisted of a reaction zone, a gravity separator, and a recirculation system. The treated water contained high concentrations of heavy metals (Au, Cu, Co, Ni, Tl, Zn, and Pb) and metalloids (As and Se). The treated water matrix had extremely high concentrations of Cu (103 mg l^{-1}) and As (110 mg l^{-1}). Long-term monitoring of the system (>12 months) showed that it achieved $>99.5\%$ removal of Cu, As, and other toxic contaminants.

Another pilot-scale study was conducted by Wang et al. to remove Zn and Pb from metallurgical wastewater [28]. A continuous, sequential process was used, consisting of the first stage of treatment with lime ($\text{Ca}(\text{OH})_2$) as adsorbent, followed by the second stage of treatment with nZVI. Figure 7.3 shows the flow diagram of the process. The first stage aimed to reduce the concentration levels of the pollutants, which, after treatment with nZVI, were brought into compliance with the established standards for their elimination. The results of this combined process show that the concentrations of Pb and Zn were reduced from 610 and 195 mg l^{-1} to values below 0.8 and 0.5 mg l^{-1} after treatment with nZVI.



This type of ex situ treatment for groundwater is costly and slow. So then, the use of in situ groundwater treatment technology is increasing [29]. The literature shows that many in-situ applications have been carried out, both pilot and full-scale [30]. This method mainly consists of the injection of nZVI, which degrades or adsorbs the pollutants as the groundwater comes into contact with the material.

Germany was the first European country to use this technology to remove chlorinated organic pollutants on a large scale in the town of Borheim. The site was contaminated with politetetrachloroethylene (PCE) <<Query: As per author response we have updated expansion for "PCE". Kindly confirm this is fine. Ans: I confirm this fine.>> from a former industrial laundry [31]. Initially, the contaminated area was treated with another type of technology, such as ex-situ treatment and soil vapor extraction. However, these treatments were not efficient due to the high cost and time required. The injection of nZVI and micro-sized ZVI was able to remove more than 90% of the contaminant at a significantly lower cost than previous treatments used [30]. It is important to note that the success of the treatment cannot be attributed to nZVI alone, as micro-sized ZVIs were also used.

The Czech Republic has also successfully applied this technology on a large scale in Horice and Pisečna [32]. In particular, the area to be treated in Horice was approximately 7.2 km^2 in size, with

a depth of 3–10 m. The area was contaminated with different organochlorine compounds, reaching concentrations above 70 mg l^{-1} . About 82 injection wells were used, through which 600 kg of nZVI were injected in two stages. The reduction of the different pollutants ranged from 60% to 90% after treatment. Similar results were obtained in the locality of Písecna, where the extent of the contaminated area was 2 km^2 [30].

7.2.2 Silver Nanoparticles

Ag-NPs have been mainly used for the disinfection of contaminated water. Among the various NMs with disinfectant capacity, Ag-NPs are the most widely used due to their high antimicrobial and antibacterial activity and low toxicity in humans [33]. It has been reported for use against a wide range of microorganisms, including viruses [34], bacteria [35], and fungi [36]. The biocidal mechanism of Ag-NPs is still under discussion. To explain this process, researchers have proposed many action mechanisms, which can be summarized in three action pathways: (i) alteration of membrane properties due to the adhesion of Ag-NPs to cell walls, increasing their permeability (ii) irreversible damage to the cell membrane by the generation of free radicals (iii) release of the Ag^+ ion in the cellular environment, capable of destroying the bonds that involve the S and P atoms of vital enzymes and/or DNA/RNA [1].

The antimicrobial properties of Ag-NPs increase with decreasing size and depend on the shape of the nanoparticles. In this regard, it has been shown that, at equal concentrations, the antibacterial activity of Ag-NPs is considerably higher than that of dissolved Ag^+ and micro-sized Ag [35, 37]. Moreover, the efficacy of the bactericidal properties of Ag-NPs depends on their size and shape [38]. The size and shape of Ag-NPs depend on the synthesis methodology used.

Ag-NPs can be obtained by many methods that can be classified into three main groups: physical (thermal decomposition, laser ablation, and ball milling), chemical (chemical reduction, electrochemical, and photochemical), and biological (plant extract reduction and microbial reduction) methods. The most commonly used methods are those involving chemical or physical synthesis routes. Nevertheless, the choice of synthesis method will primarily be determined by the shape, size, and stability of the nanoparticles required but will also be affected by factors such as cost and complexity.

The direct application of Ag-NPs has some associated disadvantages, such as their tendency to aggregate, surface oxidation, and the release of Ag^+ ions into the medium, reducing their reactivity toward their different applications. On the other hand, uncontrolled release of Ag^+ ions into the environment can have eco- and cytotoxicological effects. Ag-NPs are usually stabilized or supported in different polymeric and ceramic matrices to overcome these drawbacks.

Ag-NPs impregnated in porous ceramic filters for point-of-use (POU) water treatment are a promising option for expanding access to clean water, especially in rural areas. Several studies have demonstrated the effectiveness of this technology in filtering and sterilizing water [39–42]. It has been shown that the addition of Ag-NPs to ceramic filters using different methodologies (painting and immersion) improves the performance of the filters and provides them with the ability to remove *Escherichia coli* in the range of 97–100% [42]. Mellor et al. [43] studied the efficacy of these long-term treatments compared to the traditional method of sterilization, which involves the use of sodium hypochlorite. The researchers found no statistically significant differences in water quality over time between the sterilization methods tested. Additionally, there are no cost differences in applying both technologies [44]; however, evidence of overchlorination

has been found when using the traditional methodology. It is important to note that commercial treatment devices already use this type of system, such as Aquapure® and MARATHON®.

Other low-cost POU water disinfection systems can be generated from the immobilization of Ag-NPs on the cellulose fibers of a filter paper. Several studies showed that filter papers with deposited Ag-NPs showed excellent antibacterial properties against *E. coli* and *Enterococcus faecalis* [45–47]. Therefore, this type of system has great potential to be used as a personal or household water treatment method.

In addition to using Ag-NPs as disinfecting agents, recent publications have reported their potential application as sensors for aqueous pollutants, such as heavy metals and various organic pollutants. Additionally, the use of Ag-NPs for the oxidative degradation of pollutants has been studied on a laboratory scale.

7.3 Metal Oxide-Based Nanomaterials

Ideally, adsorbent materials used in water treatment should be effective, reusable, multifunctional, stable, nontoxic, economically viable, and environmentally friendly. In this sense, metal oxide nanoparticles (nMO) are excellent candidates, since they have a good capacity for adsorption and reuse against many contaminants. Due to the abundance of their precursor materials, the ease of synthesis, and the simple possibility of surface functionalization, the nMO represent an economically viable option. In addition, as they are compounds naturally present in the earth's crust, their toxicity is considered very low or null. A wide range of nMO have been used as adsorbents. Among them, the most common nMOs used as adsorbents are mainly oxides of iron (Fe), titanium (Ti), aluminum (Al), silicon (Si), and zinc (Zn).

The nMOs have proven effective in removing heavy metals, metalloids, and various organic contaminants, even at low concentrations. Factors such as pH, initial concentration, and the presence of coexisting species govern the adsorption processes, determining the removal efficiency of the materials. However, most applications of metal oxide-based NMs have been studied under laboratory conditions, using model solutions of contaminants or simulated water. Furthermore, nMOs separation currently remains a critical challenge for its large-scale application. The Section 7.3.1 will detail the uses, and types of removal mechanisms, focusing on the practical applicability of nMOs in water and wastewater treatment.

7.3.1 Iron Oxide Nanoparticles

The separation and recovery of adsorbents from water remain a major challenge with an important prospect for research and development in the area of water science and technology. Due to their superparamagnetic behavior, iron oxide nanoparticles (IONPs), such as magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), have a great advantage over other adsorbents as they can be easily separated from the medium by applying an external magnetic field. Here, magnetic nanoadsorbents appear promising not only because they can be easily separated but also recovered and thus reused.

The IONPs can be synthesized by physical, chemical, and biological methods. Chemical-based synthesis methods are the most widely used due to their low production cost and high yield [48]. This method includes a wide range of techniques, such as hydrothermal, co-precipitation, solvothermal, and sol–gel synthesis. Each methodology will have its advantages and disadvantages, depending on the purpose and application required.

IONPs are widely used as adsorbent materials due to their fast kinetics and exceptional removal efficiency of various pollutants. Their application has been reported for the adsorption and degradation of heavy metals and metalloids, such as As, Pb, Cu and Ni; non-metallic oxo-anions, NO_3^- and PO_4^{3-} ; and various organic micropollutants, such as dyes, pesticides and pharmaceuticals. Due to the enormous variety of contaminants, the removal capacity of IONPs has been explained by several types of mechanisms, including adsorption, complexation, ion exchange, electrostatic attraction, chemical reduction, precipitation, and co-precipitation processes mediated by the surface of the oxides.

IONPs can remove several species simultaneously, which significantly reduces their efficiency compared to empirical model tests. For this reason, it is essential to study the performance of these materials in a real-water environment to have a more realistic perspective on the possibility of their practical use in groundwater or wastewater treatment. Castelo-Grande et al. studied the application of micro-sized magnetite for wastewater remediation [49]. The adsorption performance was investigated at three different points in a wastewater treatment facility. In general terms, the magnetite particles showed good efficiency in removing the vast majority of the pollutants analyzed (heavy metals, detergents, and chemical oxygen demand [COD]). The influence of the type of wastewater sample (i.e. sampling point) proved to be an important parameter, especially in the case of high contaminant concentration.

Despite the promising results of laboratory-scale trials regarding magnetic IONPs for real water treatment, several limitations still delay their industrial-scale application in water purification systems [50]. These limitations mainly involve their chemical stability, toxicity, regeneration, and reusability [51]. Some of the most commonly used strategies to improve these aspects are coating nanoparticles with polymeric materials or generating nanocomposites based on IONPs. The generation of these types of materials will be further discussed in Sections 7.3.2 and 7.3.3.

On the other hand, the separation of magnetic IONPs by large-scale magnetic decantation is still a challenge to overcome. Ideally, it is intended that these technologies can be integrated into existing wastewater treatment facilities. Figure 7.4 shows the synergistic combination of both technologies schematically to improve process efficiency. Thus, after the first treatment stage, the effluents are treated with IONPs to remove residual pollutants. In the second stage, the IONPs, loaded with various pollutants, are separated from the effluent using a magnetic settling system in a second stage. The IONPs can then be regenerated and recovered for subsequent reuse.

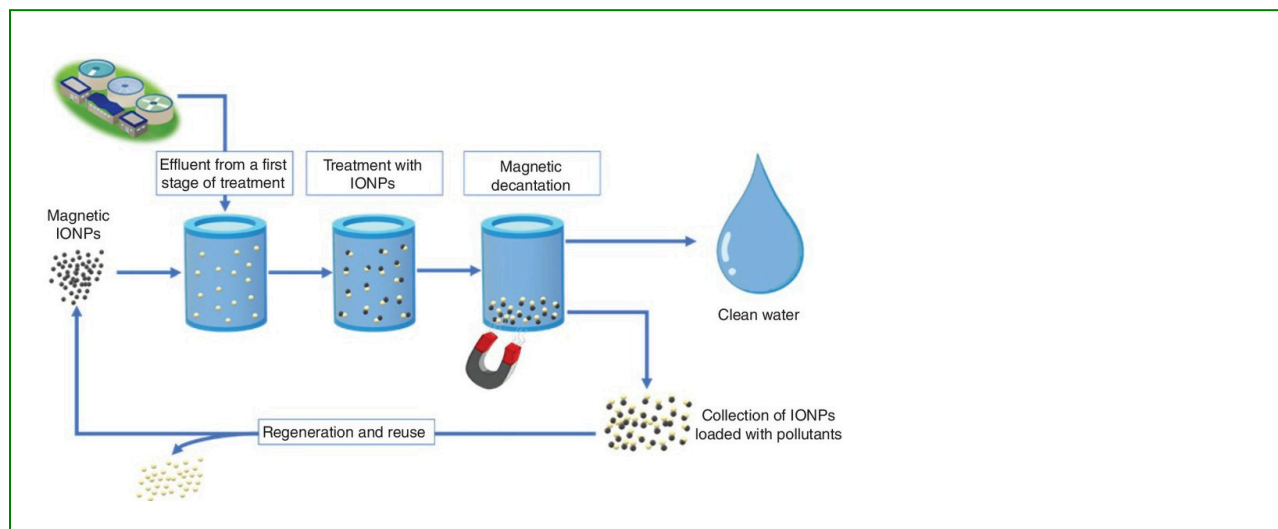


Figure 7.4 Schematic representation of the synergistic combination of adsorption and magnetic settling technologies with existing water treatment plants.

Under this concept, Powell et al. developed and operated a device called MagNERD to separate and reuse magnetite nanoparticles from treated water under online and continuous flow, in relevant conditions at pilot scale [52]. MagNERD removed 94% of arsenic in a simulated drinking water medium. Furthermore, the MagNERD device efficiently separated magnetite nanoparticles (>95%) in different water matrices (e.g. ultrapure water and brackish water). Recovery of the adsorbent was performed by hydraulic backwashing.

Drenkova-Tuhtan et al. conducted pilot-scale tests for phosphate removal from wastewater using a magnetic $\text{ZnFeZr@Fe}_3\text{O}_4/\text{SiO}_2$ nanocomposite as an adsorbent [53]. Almost total removal was obtained after the first cycle, which included adsorption, magnetic separation, desorption, and reuse of the nanocomposite. However, a gradual decrease in removal efficiency was recorded in the following cycles. The authors reported that this decrease in efficiency was consistent with the loss of adsorbent particles throughout each cycle.

7.3.2 Titanium Dioxide Nanoparticles

Titanium dioxide nanoparticles (TiO_2 -NPs) have been widely reported for water purification due to their low cost and toxicity. In virtue of its photocatalytic properties, TiO_2 -NPs have been studied mainly to degrade a wide variety of organic pollutants, such as pesticides, herbicides, dyes, and products from the pharmaceutical industry [54]. The photocatalytic degradation reaction is initiated because light irradiation of TiO_2 -NPs induces charge separation, causing them to become highly unstable and react with water, generating free radicals. These free radicals are mainly responsible for the degradation process. On the other hand, its application in the removal of heavy metals and metalloids has also been demonstrated [55]. Also, TiO_2 -NPs serve as disinfectant against a broad spectrum of microorganisms [56].

The efficiency of using TiO_2 -NPs has been tested both at the laboratory and pilot scales. In Argentina, scientists designed an economic POU-type system for water purification in critical areas where resources are very limited [57]. The systems evaluated consisted of the immobilization of TiO_2 -NPs inside PET soft drink bottles by different procedures. Different methodologies for the immobilization of the nanoparticles were studied. The efficiency of these devices was tested in different simulated and groundwater samples. The results showed a good photocatalytic efficiency of the tested devices, significantly reducing the organic matter present. However, TiO_2 particles were released into the medium when the bottles were shaken.

A wide variety of reactor designs have been reported, varying in factors such as the irradiation source and how the TiO_2 -NPs are used (powder or immobilized). In this regard, Benotti et al. evaluated the performance of a pilot system using UV/ TiO_2 photocatalysis for a total of 32 contaminants of pharmaceutical origin in enriched lake water samples [58]. The results showed that 29 of the pollutants were removed by 70%, while the remaining three pollutants were degraded by 50%. These results show the great potential of these technologies for water treatment.

Because TiO_2 -NPs require ultraviolet radiation to overcome their bandgap, their photocatalytic capacity is limited under ambient conditions. Only 5% of the solar energy reaching the earth is

within this range. The doping of TiO₂-NPs with metals and nonmetals is one of the widest strategies used to reduce the bandgap and, therefore, increase their efficiency in the degradation processes. Doping of TiO₂-NPs with iron, palladium, silver, nitrogen, carbon, and nitrogen, among others, has been reported to achieve photodegradation of various pollutants using visible light successfully. For example, Park et al. investigated the efficiency of TiO₂ nanofibers and Ag-doped TiO₂ nanofibers in the photocatalytic degradation of 2-chlorophenol under UV irradiation [59]. Ag-doped TiO₂ nanofibers showed higher performance in pollutant photodegradation than TiO₂ nanofibers. In this regard, the degradation rate constant of Ag-doped TiO₂ nanofibers was almost 50% higher than that of its undoped counterpart.

Although the application of TiO₂-NPs is mainly focused on the photocatalytic degradation of organic pollutants, they can also be used as adsorbents for various types of inorganic pollutants, such as heavy metals, metalloids and nonmetallic oxo-anions. One of the most studied lines is the use of TiO₂-NPs and its derivatives for arsenic removal. In this sense, the adsorption mechanisms of TiO₂-NPs can be divided into two types: in the presence of UV/Visible light, TiO₂-NPs function as adsorbents and as photocatalysts, promoting the oxidation of As(III)/organic arsenic to its less toxic As(V) species; while in the absence of irradiation, TiO₂-NPs function only as adsorbents. In addition to TiO₂-based materials, the application of titanates and TiO₂-based materials for water removal has been reported. However, most studies were performed at a laboratory scale under empirical model test conditions.

7.3.3 Zinc Oxide Nanoparticles

The use of zinc oxide nanoparticles (ZnO-NPs) in water treatment has been widely reported. Their good adsorptive and photocatalytic properties give them great potential for application in water purification processes. Due to their adsorptive capacity, ZnO-NPs have been mainly used to remove heavy metals such as Cd, Cr, Hg, and Pb [60]. Some research shows that ZnO-NPs have better heavy metal removal efficiency than TiO₂ [61]. Their application as adsorbents for methyl orange and amaranth has been reported recently [62].

Like titanium dioxide, due to their photocatalytic properties, ZnO-NPs can be used to degrade a wide variety of organic compounds, such as dyes, phenolic compounds, fungicides, pesticides, and pharmaceuticals. Several investigations have focused on comparing the photocatalytic activity of ZnO-NPs with that of TiO₂-NPs. Sakthivel et al. compared the photocatalytic activity of ZnO-NPs and TiO₂-NPs to degrade acid brown 14 [63]. From comparing the performance results of the different semiconducting materials, it emerged that ZnO-NPs have higher photocatalytic activity for the degradation of acid brown 14 using sunlight as the energy source. The authors explained this result were obtained because zinc oxide can absorb a large fraction of the solar spectrum, which is not the case for titanium oxide. Similar results for the degradation of naproxen and methylene blue by Štrbac et al. [64].

7.4 Nanosized Zeolite as Adsorbent and Support Material

Zeolites are low-cost, highly porous aluminosilicates with great potential to be used as adsorbents for various pollutants. Over other inorganic adsorbents, zeolites stand out for their large surface area and exceptional ion exchange capacity, which gives them high adsorption capacity. Due to their high stability and intrinsically low toxicity, these materials have been studied for different applications. Nanosized zeolite can be obtained both by synthetic methods, from their chemical precursors, and by physical methods, from milling the naturally present mineral in the earth's crust.

Because zeolites in aqueous media have a negative surface charge, these materials have been studied mainly to remove cationic pollutants, such as heavy metals and cationic dyes [65]. However, their surface modification using different multivalent metal cations has been reported to apply them as adsorbents of anionic species, such as fluorides [66, 67]. On the other hand, the scientific community has used zeolites as support materials to stabilize and immobilize various nanoadsorbents. For example, nZVI nanoparticles have been supported on zeolites to avoid agglomeration and increase the removal efficiency of pollutants such as As, Cd, and Pb [68]. Similarly, it has been reported that the generation of zeolite-magnetite nanoparticle nanocomposites leads to an increase in stability, in terms of iron release to the medium, concerning the application of bare magnetite nanoparticles [69].

The application of nanosized zeolites generates excessive pressure drops when used directly in fixed bed and continuous flow systems. For this reason, bulk zeolites rather than nanosized zeolites are often used for this type of application.

7.5 Nanocomposites

The abovementioned nanoscale materials have exceptional physicochemical properties; nevertheless, some exhibit potential risks to human and animal organisms and hazards to the environment. They could be introduced to human and animal organisms by inhalation, ingestion, and dermal penetration through potable water, air, food, and personal products [70]. When NMs are discharged into the environment, they are chemically and structurally modified, increasing, or decreasing their toxicity. Their dynamic in the environment is complex due to several factors that must be considered: temperature, pressure, humidity, and pH. The toxicity of NMs is directly dependent on their size, shape, surface area, and surface chemistry [71]. The size of the NM is one of the significant physicochemical properties that should be assessed since a small size (comparable to some biomolecules) allows fast absorption in the organism. As the size decreases, the surface area increases, enhancing reactivity and interaction.

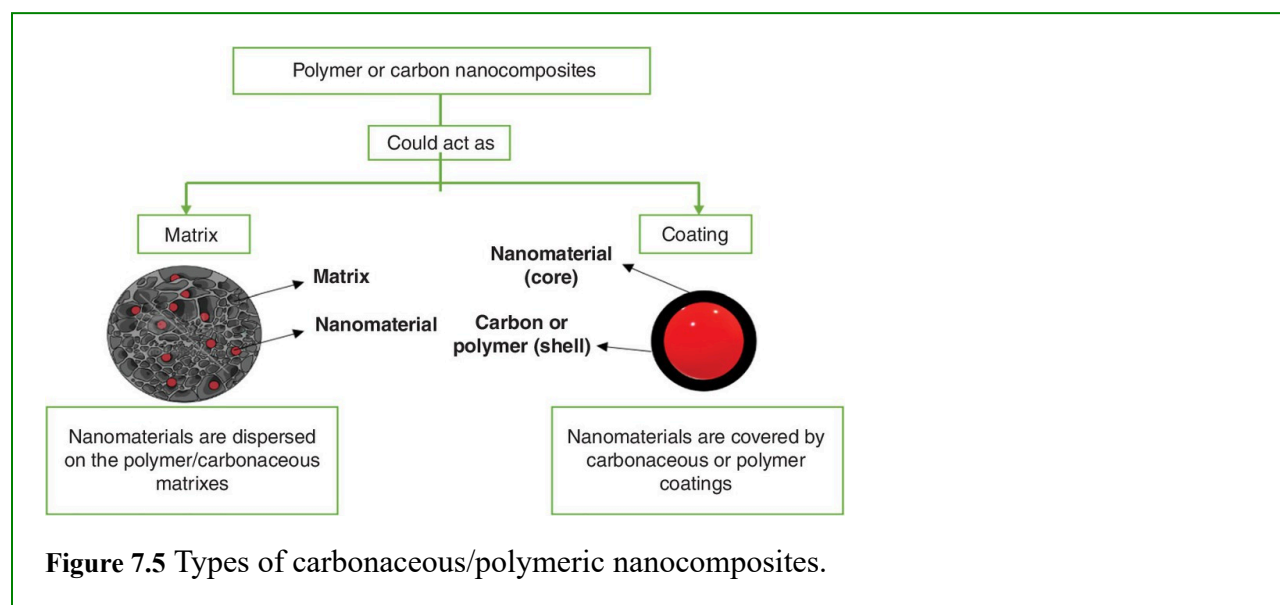
The NMs small size facilitates their entrance into the cell membranes and other biological barriers; thus, they could spread through the whole body, reaching biological tissues, and accumulating mainly in the liver, kidney, and spleen [72]. Furthermore, some NMs induce reactive oxygen species (ROS) production, resulting in oxidative stress [73]. For example, Ag nanoparticles are a well-known type of metal nanoparticle widely used as efficient antimicrobial, antibacterial, and antiprotozoal agents [74]. Toxicological studies of Ag⁰ have demonstrated that they exhibit cytotoxic and genotoxic effects (oxidative stress, DNA damage, and modulation of cytokine production) against several cell lines [75]. TiO₂-NPs are another favorite type of nanoparticle that have been employed in the preparation of sunscreens, toothpaste, and nutritional supplements, also as pollutants degradation agents in water remediation. Therefore, it is a compound that has been gaining considerable attention; therefore, it is pivotal to study its interaction with biological systems. Recent studies on rats and mice have shown that skin, pulmonary, and oral absorption could be exposed. The results suggested that the tiny TiO₂ nanoparticles of <0.1 μm show pulmonary inflammatory responses. Affections in different organs like kidneys, brain, spleen, and liver have been impacted by NMs uncontrolled use [76].

On the other hand, NMs tend to aggregate due to their high surface energy and large surface area [77]. Furthermore, NMs such as iron oxides (magnetite, maghemite, and hematite) could be easily oxidized by air and alter their physicochemical properties. For these reasons, newly developed materials with low or nontoxicity, oxidation resistance, and low or nonaggregation have been

synthesized. As a result, nanocomposites have been widely reported in the literature, and diverse classifications have been suggested depending on various factors.

The classification of carbonaceous or polymer nanocomposites has been intensely investigated. Polymers can be natural or synthetic, including cellulose, starch, chitosan, polyethylene, polyester, Teflon, and epoxy [78]. On the other hand, carbonaceous matrixes or coatings could be obtained from natural sources or residues through a thermal treatment followed by an activation process.

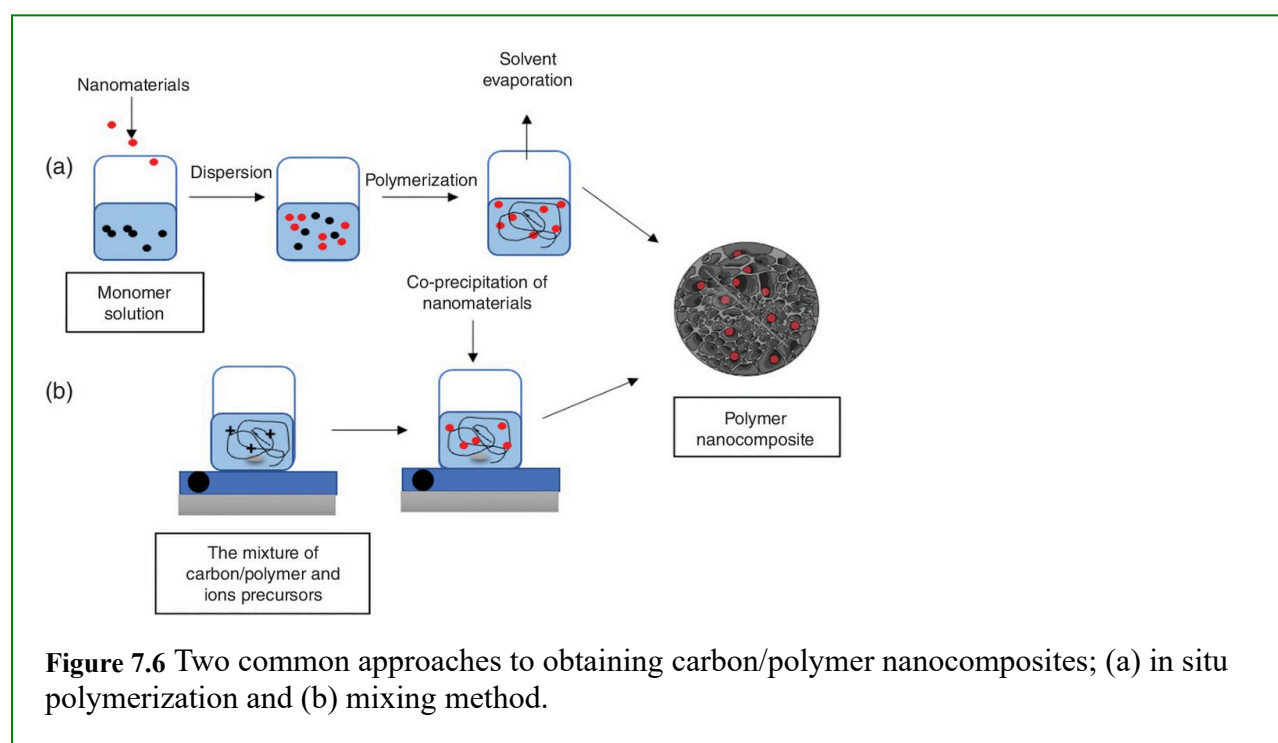
As seen in Figure 7.5, the carbon or polymer could act as a (i) matrix where NMs are introduced or supported into the carbonaceous/polymeric matrix (it acts as binding reinforcement) or as an (ii) coating where the carbon/polymer coats the inorganic core. The hybridization between NMs and carbon/polymer matrix or coating could improve essential properties, including colloidal, chemical, and mechanical stability [79]. Colloidal stability is a crucial factor that can be enhanced by introducing a carbonaceous/polymeric coating or matrix that could, in some cases, decrease the zeta potential to a negative magnitude, which could stimulate the steric and electrostatic (repulsion between particles) stabilization [80]. Regarding matrix nanocomposites, the NMs are considered fillers that could achieve different shapes and sizes depending on the interaction between the NMs and the matrix. Nonetheless, sometimes the matrix does not guarantee to prevent agglomeration of NMs. Sometimes, Van Der Waals forces contribute to creating nanoparticle aggregates in the matrix. This issue can be solved by employing coatings that will functionalize and modify the surface of the NMs.



In coatings nanocomposites, the system is deemed a core-shell structure where NMs are in the core part, and the carbon/polymer acts as a shell where protection of the nanocore is induced. The nanosized fillers and the carbon/polymer matrixes or coatings could interact by physical (electrostatic and London dispersion forces) or chemical forces (covalent bonds), depending on the porous structure and chemical nature (exposed functional groups), or a combination of both. Core-shell structures are systems applied in diverse fields; however, the focal point is biomedicine (especially in controlled drug delivery systems and hyperthermia treatment) and water remediation [81]. For example, carbon-coated magnetite nanoparticles have been widely applied in hydrometallurgy under very aggressive operating conditions (low pH and high temperatures). In addition, water remediation in acid mine sources is another well-known application. These acid

conditions ($\text{pH} < 3$) could disaggregate some metal nanoparticles (iron oxide) and change their properties by altering their structure [82]. These inconveniences could be solved by employing nanocomposites. The mentioned drawbacks of NMs have led to the search of new alternatives to biocompatible and nontoxic coatings or supporters to avoid the toxic effects of NMs and chemical perturbation.

Many synthesis methods of carbonaceous/polymeric nanocomposites, such as chemical, biological, and physical, have been investigated. However, core-shell systems are more complex to obtain. Usually, their preparation consists of a two-step procedure where NMs are obtained via bottom-up or top-down approaches. After that, each nanocomposite could be obtained by chemical vapor deposition, solution plasma processing, hydrothermal methods, spray pyrolysis, solid-phase, or slow pyrolysis treatment [83–85]. On the other side, as shown in Figure 7.6, NMs supported on carbonaceous/polymeric matrixes can be prepared by two main methods: in situ NMs deposition into the matrix by (i) the in situ polymerization or (ii) mixing method [86, 87].



7.6 Classification of Carbon/Polymer Nanocomposites

7.6.1 Metal/Polymer or Carbon-Based Nanocomposites

7.6.1.1 nZVI (Nanosized Zero-Valent Iron) Nanocomposites

Water treatment technologies have been increasing due to the requirement to follow the accepted limits on maximum permitted concentrations of pollutants in water. However, the constant search for efficient technologies for the degradation or removal of pollutants: metalloids, heavy metals, and organic pollutants has been challenging. One of the most explored elements is iron, the fourth most abundant element in the earth's crust. Therefore, magnetic carbonaceous nanocomposites are being researched because of their vast range of applications. They are usually composed of nZVI

(nanoscale zero-valent iron) or iron oxides (magnetite, maghemite, and hematite) supported or coated on/by various polymers or carbon solids.

Furthermore, IONPs are nontoxic, biocompatible, and exhibit a substantial magnetization property, which gives them an added value property that will be advantageous when removing the material from a particular water source by applying an external magnetic field. One of the most commonly used NMs at laboratory and industrial scales are nZVI. Its immobilization should be comprehended to prevent the loss of nZVI and avoid iron pollution. When supporting nZVI, it could achieve different shapes highlighting the beads, which show remarkable potential to be implemented in continuous flow systems, filter columns, domestic filters, and fixed bed reactors [88]. To take into consideration, during the NMs immobilization process, they could suffer oxidation. Thereby, it is advised to carry out the synthesis in anaerobic conditions.

Application of immobilized nZVI focuses on adsorption and degradation (employed as reductants in heterogeneous Fenton oxidation processes) of organic and inorganic pollutants. nZVI has been supported or coated on/by different matrixes, standing out the activated carbon (a popular adsorbent material used in water treatment plants), biochars, hydrochars, diatomite, PEG (Polyethylene), and PVP (Polyvinylpyrrolidone) [89]. nZVI/carbon core-shell and nZVI/diatomite/organosilane nanocomposites have been employed to degrade organic compounds such as phenol (aromatic organic compounds), bisphenol A (BPA), and pharmaceuticals (amoxicillin, metronidazole, tetracycline) by a Fenton-type reaction [90, 91]. Fenton reactions are suggested to reach high percent removal efficiencies and were used to promote the oxidation rate of organic compounds in the presence of some radicals such as $\cdot\text{OH}$ and $\cdot\text{O}_2$. In some cases, both degradation and adsorption co-occur where the degradation process of the pollutants leaves functional groups in the aqueous medium, and the nanocomposite could adsorb the degradation products [92].

Another application of these nZVI nanocomposites is removing toxic, nonbiodegradable organic dyes such as methylene blue, malachite green, and methyl orange [93]. They are used in the textile and leather industries. The dyes impart color to the effluents and remain stable in water sources due to their stabilization owing to the auxotrophic and chromophoric groups. Removing dyes could involve degradation, adsorption, reduction, or precipitation [94]. Cellulose, montmorillonite, and bentonites are other popular coatings and supporters of nZVI to remove dyes. Moreover, cellulose could be used in the form of cellulose nanocrystals, and it enhances the amount of active and reactive sites that will facilitate the interaction with nZVI [95]. Clays are other types of supporters or coatings that have been attractive due to their outstanding cation exchange capacity (CEC), surface hydrophilicity, and surface electronegativity [96].

On the other side, heavy metals and metalloids are some of the most dangerous pollutants released into the environment due to industrial activity. Therefore, they have great potential to accumulate in living organisms. One of the widespread nanocomposites is carbon/polymer. The interaction between nZVI carbon/polymer nanocomposites and the heavy metals could be through reduction, adsorption, oxidation/reoxidation, co-precipitation, and precipitation of Cr, As, Cu, Pb, Se, Pd, Hg, and Ag ions [97]. Some of the processes mentioned previously can be combined depending on the redox potential of the system and the capping or support agent of the nZVI. The carbon supporters are gaining considerable attention, highlighting biochars (carbon-rich solids obtained from materials that are considered residues) that possess great potential as water remediation agents. Biochars could be obtained by thermochemical processes, including pyrolysis (slow, fast, and flash), torrefaction, or gasification [98]. They are converted into carbon-rich solids through cellulose, hemicellulose, and lignin chemical transformations [99]. The main functional groups present in the lignocellulosic framework are mostly oxygen-containing ones (C–O, C=O, and OH)

that are capable of interacting with inorganic or organic molecules [100]. Depending on the pH and the point zero charge (PZC), those functional groups can change into their ionized forms: COO^- and OH^- forming strong electrostatic bindings with cationic organic or inorganic molecules. nZVI/biochar nanocomposites can also be used in the removal of Cd(II), Co(II), As(V), and Cr(VI) [101]. From these heavy metals, Cr(VI), a pollutant found in industrial effluents, appears in various chemical forms (trivalent and hexavalent) [102]. It exhibits carcinogenic effects on organisms; therefore, depuration technologies, including chemical precipitation, membrane process, electrodialysis, and ion exchange, have been applied [103]. Nevertheless, they are time- and energy-consuming. The use of nZVI nanocomposite as a reduction agent is preferred because of its efficient degradation through chemical reactions of electrochemical corrosion [104].

7.6.1.2 Silver Nanocomposites (Ag^0)

Silver has been used since ancient times as an antibacterial agent. Its demand has increased over time due to its unique optical, chemical, physical, antibacterial, conductive, and catalytic properties [105]. It has been estimated that 320 tons/year are produced worldwide [106]. Nowadays, AgNPs carbon/polymer nanocomposites have been employed in engineering products, clothing, sprays, and detergents [107]. The use of carbon or polymer reduces the toxic risks that AgNPs intrinsically have and stabilize the thermodynamically unstable AgNPs. It has been compared AgNPs crystal surfaces to other nanoparticles, and it has been noticed that AgNPs possess higher atom density. This characteristic permits easy adhesion to cell membranes [108]. The size of AgNPs influences the antibacterial effect. AgNPs have broad-spectrum effects against gram-positive and gram-negative bacteria by releasing silver ions [109]. As mentioned in the introduction to the nanocomposite section, AgNPs could be harmful at high concentrations, altering live organisms (oral, reproductive, neurotoxic, and immunotoxic) and the environment [110]. Subsequently, AgNPs nanocomposites have been developed to control and slow silver ions release into the aqueous medium.

Chitosan, a polysaccharide obtained naturally by deacetylation of chitin, has gained high interest due to its distinct chemical and physical properties. Chitosan has two main functional groups within its structure corresponding to amine (NH_2) and hydroxyl (OH) that promote the formation of intra and intermolecular interactions [111]. Chitosan, by itself, was found to have a poor surface area [112]. To enhance and activate its surface area, several nanostructures have been introduced into chitosan, including nanoparticles, nanosheets, nanorods, and nanowires [113]. Ag-NPs can be added to their chitosan matrix due to the high affinity for the chitosan functional groups [114]. Different authors have implemented AgNPs chitosan nanocomposite in the remediation of metal ions by ultrafiltration, dyes, antibiotics, and pesticides. The excellent heavy metal adsorption is related to its high chemical reactivity due to active functional groups and a flexible polymer structure [115].

AgNPs cellulose is another type of nanocomposite considered an eco-safe, versatile, and efficient water treatment agent. Cellulose is a polysaccharide composed of chains of glucose monomers [116]. Its structure is rich in hydroxyl groups which actively interact with AgNPs. This nanocomposite has been reported to serve as a plasmonic sensor of heavy metals and organic compounds [117]. Furthermore, it is also employed as a photocatalyst for oxidative degradation [118]. Besides their utilization as an adsorbent and degradation agent, AgNPs cellulose nanocomposite has shown high antibacterial activity by inactivating *E. coli* and *E. faecalis* [119]. Another water treatment system that is gaining much attention is membranes. For example, AgNPs have been supported on polyethersulfone (PES) microfiltration membranes, showing solid

antimicrobial properties and prolonged silver release, enhancing the lifetime of water treatment membranes [120].

7.7 Metal Oxides/Polymer or Carbon-Based Nanocomposites

7.7.1 Iron Oxide (Magnetite) Nanocomposites

IONPs, especially Fe_3O_4 (magnetite), exhibit high adsorption capacities against many pollutants, including heavy metals, metalloids, dyes, pesticides, and care products. IONPs are gaining significant attention due to their remarkable physicochemical properties, including nontoxicity, biocompatibility, superparamagnetism, and high reactivity [121]. It is crucial to point out their substantial magnetization property due to their easy recovery from the applied aqueous medium by an external magnetic field [122]. Plenty of matrixes or coatings are available; however, carbonaceous ones have been employed because of their simplicity and availability. The carbonaceous matrix or coating can be obtained through chemical, physical, or biological treatments. Nevertheless, thermochemical treatments, including pyrolysis, hydrothermal carbonization, torrefaction, and gasification, have been widely used due to their high efficiency and yields, low cost (capital, operational, and maintenance), and accessibility [123].

Nowadays, the circular economy plays an essential role in industry and our daily lives [124]. For this reason, the reuse or recycling of materials generated throughout an agro-industrial process could be employed as a feedstock to prepare added-value products. This is the case with lignocellulosic residues. Some of the most common agricultural wastes are husks: rice, sunflower, and coffee [125]. Lignocellulosic residues are considered agricultural wastes that can be transformed into carbonaceous materials by thermochemical treatments. The transformation employing a specific temperature, pressure, and activating agent will condition the final porous characteristics. Activated carbons and biochars usually possess well-developed pores and a large surface.

IONPs supported on carbonaceous matrixes or coated by a carbon layer have been investigated. They have been applied to remove different pollutants such as heavy metals, dyes, and pharmaceuticals [126]. The removal efficiency is dependent on the medium pH, the initial dose of adsorbent, ionic strength, the initial concentration of the pollutant, temperature, and stirring rate. The metal oxide carbonaceous nanocomposites reveal synergism of properties. For example, magnetic biochars are well-investigated nanocomposites to remove arsenic, a toxic metalloid found in groundwater aquifers mainly in two anionic forms: As(III) and As(V). Biochar has a negative surface charge, and the interaction with the anionic forms of As provokes a low sorption efficiency. For this reason, modified biochar with magnetite could induce a stronger interaction between the sorbate and sorbent [127].

Another well-known application of magnetite nanoparticles supported on a biochar matrix is the removal of Cr(VI). The presence of the biochar matrix enhances adsorption and reduction, which results in an efficient, reusable, and cost-beneficial nanocomposite [128]. Besides, other nanocomposites involve two phases and three or more phases, generating trifunctional or multifunctional nanocomposites, such as Fe_3O_4 -Ag nanocomposite, which has catalytic antibacterial activity effects, and adsorption capacity [129]. Furthermore, other nanocomposites involve microorganisms, such as a developed iron oxide biochar loaded with photosynthetic bacteria. Each component interacted synergically and played an essential role in the nanocomposite; biochar and IONPs were helpful in the adsorption and catalysis, and on the other

side, the photosynthetic bacteria were employed as biodegradation agents to control COD, ammonia (NH_4^+), and phosphate (PO_3^{4-}) in an aqueous medium [130].

7.7.2 Titanium Oxide (TiO_2) Nanocomposites

As early mentioned, TiO_2 is involved in the photocatalytic degradation of various pollutants and can damage the function of various gram-positive and gram-negative cell lines [131]. Both effects can occur under UV light, which promotes the generation of OH radicals, which are the ones in charge of degrading arsenic, heavy metals, pesticides, dyes, and polycyclic aromatic hydrocarbons (PAHs). These processes are called advanced oxidative processes (AOPs) and are efficient tools utilized in the last years [132].

Heterogeneous photocatalysis is when the degradation of pollutants is carried out using a nanocomposite (composed of a semiconductor TiO_2 and a carrier) and a light source [133]. TiO_2 has been supported on clays, which are minerals including montmorillonite and bentonite made up of silica, alumina, water, and weathered rock [134]. TiO_2 immobilization enhances its activity by increasing active surface sites. In addition, it prevents the agglomeration and release of TiO_2 into the environment. Another example could be the preparation of TiO_2 into bacterial cellulose, which is a biocompatible matrix. It is characterized as having high mechanical strength, crystallinity, water retention, and adsorption capacity. The use of bacterial cellulose as a matrix helps to prepare a well-organized nanostructure due to the exposure of hydroxyl functional groups [135].

7.7.3 Zinc Oxide (ZnO) Nanocomposites

ZnO nanoparticles are interesting due to their strong oxidation ability and photocatalytic property. Nevertheless, they present almost the same disadvantage as TiO_2 due to their considerable bandgap energy that demands the use of UV light. Compared to TiO_2 , ZnO is less toxic and cost-effective [136]. However, ZnO undergoes photocorrosion; consequently, new strategies are being searched for, such as metal doping or immobilization of ZnO in polymers to enhance the photodegradation of pollutants. Metal doping and ZnO immobilization are two strategies that have been applied. Starch, cellulose, and chitosan are examples of biopolymers employed as carriers of ZnO [137]. In some studies, two or three compounds are added to enhance photocatalytic activity. ZnO supported on chitosan/polypyrrole (conductive polymers) has been reported to exhibit great potential as a photodegradation agent of different dyes, including orange-16, methylene blue, and brilliant blue R-250. The presence of amino groups in chitosan could interact with the anionic part of the dyes improving the degradation of pollutants [138].

Moreover, other conductive polymers are embedded with ZnO , such as polyaniline, polyphenylendiamine, and poly(1-naphthylamine) [139]. The energy levels of the conductive polymers match those of ZnO , thus increasing the sensitiveness of absorption of visible light [140]. The use of sunlight is preferred over ultraviolet radiation due to the harmful effects caused by the artificial source. On the other side, ZnO could also act as membrane antifouling material. To cite, polyvinylidene fluoride (PVDF)- ZnO composite membranes are prepared. The addition of ZnO into the membrane promotes smaller contact water angles and enhances antifouling characteristics [141].

7.8 Silicate/Polymer or Carbon-Based Nanocomposites

7.8.1 Nanosized Zeolites Composites

Nanosized zeolite (a microporous aluminosilicate material) is well-known for being an excellent ion-exchange agent [142]. Owing to its characteristic negative surface charge on the framework, it possesses a high affinity for cationic molecules or cationic metal ions. Adding zeolites to carbonaceous or polymer matrixes will improve stabilization in an aqueous solution, easier reusability, and high adsorption capacities. There has been investigation related to finding supporters such as natural and synthetic polymers and carbonaceous matrixes, including activated carbons, cellulose, chitosan, alginate, polyvinyl chloride (PVC), polycaprolactone (PCL), polyacrylamide (PAA), polyvinyl alcohol (PVA), polypropylene (PP), polypyrrole (PPy), PVP, polyamide (PA), polyacrylonitrile (PAN), and polysulfone (PSF) [143]. Zeolite nanocomposites have been prepared in various forms, including beads, films, and hydrogels. One of the most compelling applications of nanocomposites is the removal of radioactive ions from water sources. For example, magnetic zeolite nanocomposite (nZVI-zeolite) was used as strontium (Sr^{2+}) sorbent in a real seawater sample [144]. This is quite challenging since real water sources present a high amount of ions and compounds that could compete for the active sites of the nanocomposite. Other similar work used a natural zeolite supported on PAA to remove UO_2^{2+} , Tl^+ , Pb^{2+} , Ra^{2+} , Bi^{3+} , and Ac^{3+} [145].

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