PART

II

Nanoremediation with processes

2

Applications of nanomaterials for adsorptive removal of various pollutants from water bodies

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1. Introduction

With a human population approaching eight billion by 2023, and the global increase in urbanization, industrialization, and consumption, natural resources are facing serious challenges [1–3]. Pollution of air, water, and soil is a worldwide concern that poses a threat to human and animal lives. Because of its significance to living beings, freshwater resources are endangered by lack of equal distribution, misuse, and pollution. New policies are currently added to address water pollution problems at different levels. In Europe, for example, the "zero liquid discharge" (ZLD) and "minimal liquid discharge" (MLD) policies have been introduced to limit or eliminate intentional contamination of freshwater resources [4–6].

Over the last decades, several technologies have been introduced to address water pollution through either control or removal. This includes coagulation and flocculation, membrane separation, adsorption, ion exchange, and advanced oxidation—to name only a few [7,8]. With the help of nanotechnology, researchers have developed several materials that are more efficient in treating wastewater than conventional technologies. Some of these materials have been also developed to address emergent pollutants, such as organic dyes, heavy metal ions, and pharmaceuticals, that conventional methods fail to treat.

In addition, smart materials are needed to help resolve the water crises in remote areas. It is astonishing to know that around 1.8 billion humans have no access to safe drinkable water [9]. With

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the help of nanotechnology, mobile and versatile nanofiltration equipment can provide clean water to whom in need. Nanomaterials exhibit novel properties that make them an excellent choice for environmental applications. These materials are characterized by their [7,10]:

1. Small size in the range of 1–100 nm.
2. High surface area per unit volume, leads to higher removal capacities.
3. Unique physical properties such as thermal stability and dispersibility.
4. Chemical activity such as their adsorption affinity and selectivity, and catalytic ability to degrade pollutants.
5. Integrability, where the nanomaterials can be easily combined and integrated in conventional processes.

Fig. 2.1 shows some examples of the most important nanomaterials that have been developed for the purpose of nanoremediation over the last 20 years. The data represent the number of journal articles and patents published between 2002 and 2021 according to the Web of Science [11]. As seen, the list includes iron oxides, graphene, silica, carbon nanotubes (CNT), alumina, titania, and zinc oxide. Graphene followed by iron oxide are among the most researched nanomaterials, probably due to their ease of preparation, high removal efficiency, stability, and availability.

Adsorption is one of the leading advanced technologies to treat polluted water from both organic and inorganic pollutants. The process relies on the adhesion of contaminants (adsorbate) to a solid surface (adsorbent) [12,13]. Adsorbents such as activated carbon (AC) have been used in the removal of organic and inorganic contaminants for several years, in a limited capacity [13,14]. However, such conventional adsorbents have several limitations, including slow adsorption rates owing to the irregular porous structure, high cost owing to the severe preparation conditions (high temperature), inapplicability of the materials to remove some emerging pollutants from water bodies, and unsuitability of the materials for in situ treatment. Alternatively, novel adsorbents have been developed to overcome these drawbacks and some are depicted in Fig. 2.2. The list involves:

1. Zero-valent metals such as Zn, Fe, and Al, where iron is the most popular due to its availability and low cost.
2. Inorganic materials such as zeolites, silicon nitride (SiN), and layered double hydroxides (LDH).
3. Natural materials, such as wood, peat, fruit shells, clay, and sawdust.
4. Carbon-based materials such as CNT that demonstrate high adsorption efficiency due to their altered chemical,

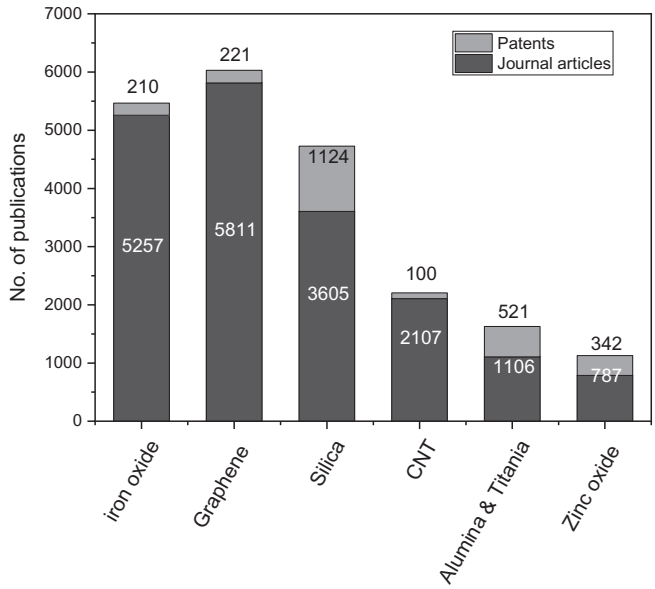

Fig. 2.1 A histogram for the literature review on the research of different nanomaterials in the period of 2000–21 according to Web of Science [11].

mechanical, and thermal properties originating from their 2D and 3D crystallinity as well as their high specific surface area [7,15,16].

5. Metal oxides and their modified magnetic materials.

This chapter focuses on metal oxides and their modified composites, in addition to carbon-based materials such as AC and CNT. Other materials such as items 2 and 3 mentioned before are discussed in Chapter 9 of this book. This chapter covers: (a) the synthesis procedure for nanomaterials, (b) adsorption mechanisms, and (c) advantages and disadvantages along with the potential applications of each nanomaterial as a promising solution to the global crisis of water pollution. The chapter also presents the main factors and experimental conditions that affect the adsorption process. In the end, the chapter addresses the future of nanomaterials and current pilot- or full-scale water treatment applications.

2. Synthesis of nanomaterials

There are several methods that have been reported in open and closed literature for nonmaterial preparation. These methods can be classified into two categories, namely [10]:

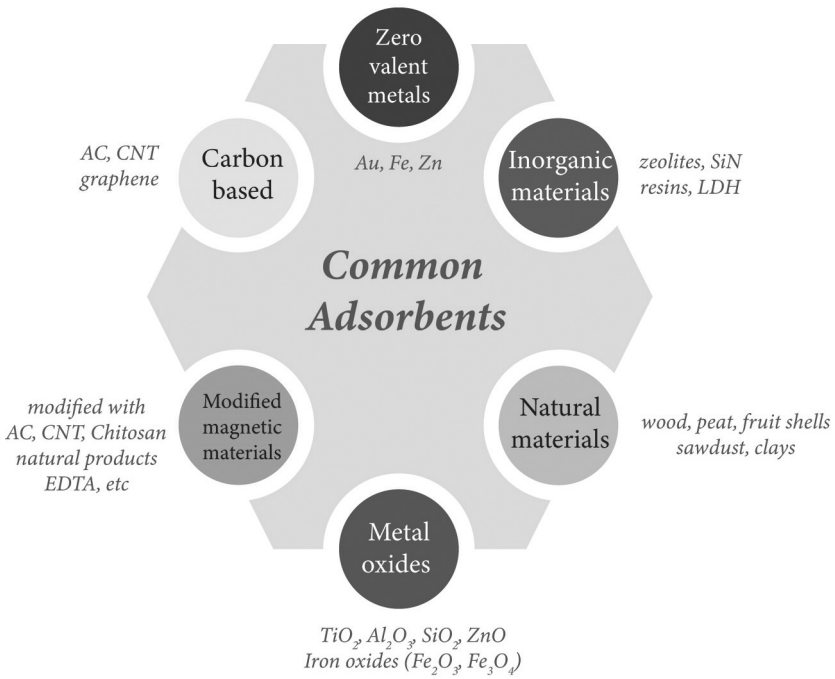

Fig. 2.2 Schematic representation of the common nanoscale-based adsorbents reported in the literature. For abbreviations, see the corresponding text. Own source.

a) Top-down: this includes physical methods such as mechanical fabrication, grinding, or polishing. It also involves technologies that use physical methods, such as laser ablation, physical vapor deposition (PVD), or chemical vapor deposition (CVD).

b) Bottom-up: this involves wet chemical techniques such as coprecipitation, sol-gel, hydrothermal, self-assembly, or electrochemical methods.

The coprecipitation method is the classical, cost-effective, fast, scalable, and simplest chemical method to synthesize metal oxides, and iron oxides in particular [17,18]. Typically, salts of Fe^{2+} and Fe^{3+} (e.g., chlorides, nitrates, and sulfates) are mixed and treated with a base (e.g., NH_3OH) and the pH is brought to >10. This leads to the precipitation of the iron oxides as shown in Fig. 2.3 [17,18]. Depending on variations of the iron salts, Fe^{2+}/Fe^{3+} ratios, temperature, pH, and the base used, the magnetic phase and particle size can be controlled [19].

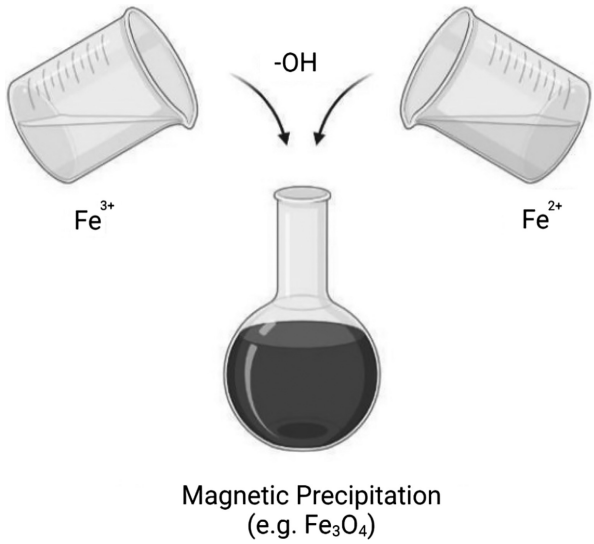

Fig. 2.3 Schematic representation of the synthesis of Fe_3O_4 MNPs by coprecipitation method. Own source.

Another common preparation technique is the sol-gel method. This is a wet-chemical technique where a sol (colloidal solution) gradually evolves from a gel-like system containing both a solid and liquid phase. The method is widely used to fabricate metal oxides, especially ZnO and TiO_2. The advantage of this technique is the fabrication of highly pure, nanoscale, and crystalline material at relatively low temperatures [20]. The method has its own drawbacks. One problem is the possible formation of amorphous or poor crystalline structures. Thus modified sol-gel techniques such as ultrasonic-assisted sol-gel and aerogel methods have been developed [20].

The hydrothermal method is also common in preparing high-quality crystalline nanoparticles. The term "hydrothermal" is of geologic origin where crystalline materials are formed based on their pressure-temperature phase diagrams [21]. The method involves mixing the chemical precursors in an aqueous solution, followed by ultrasonication to ensure homogeneous dispersion of the constituents. Next, the mixture is transferred to a Teflon-lined stainless-steel autoclave where it is heated to high temperature, typically in the range of 120–200°C. The nanoparticles can be then separated by centrifugation, washed, and dried [22–24]. Inside the autoclave, a temperature gradient is maintained between its opposite sides. At the hot end, the high vapor pressure of the liquid allows melting, diffusion, and reactions of the constituents,

where the crystals are diffused and collected at the cold end [22–24]. The method was used to prepare highly stable MnO_2/gelatin composites for the sake of removing Pb and Cr ions from water. The adsorption capacities were 318.7 mg/g for Pb(II) and 105.1 mg/g for Cd(II) with removal efficiencies approaching 100% [23]. In other studies, the hydrothermal method was used to prepare Fe_3O_4/zeolite [24], Fe_3O_4/MnO_2 [25], ZnO/graphene [22], and nanopyroxene [26–29] in which the nanomaterials demonstrated excellent performance in removing heavy metal ions, organic pollutants, and dyes.

3. Metal oxides

Metal oxides are one of the most researched adsorbents due to their low cost, availability, and ease of preparation. They are generally characterized by their large surface area per unit volume, crystalline chemical structure, and surface activity [30]. The high adsorption capacity of metal oxides is due to their surface ability to adsorb different pollutants through electrostatic interactions. It was found that the size of the nanoparticle affects both the mechanism and efficiency of adsorption [10,31]. For instance, the decrease of Fe_3O_4 nanoparticle size from 300 to 11 nm has improved the adsorption capacity of metal ions by more than 100 times [7]. Examples of metal oxides that have been used for wastewater treatment are SnO_2, ZnO, TiO_2, Fe_3O_4, Fe_2O_3, and ZrO_2. In this chapter, we will focus on iron oxides as they are the most commonly used adsorbents. Oxides of iron come in different forms and oxidation numbers. The most important are as follows [32]:

- FeO: iron(II) oxide, wüstite
- α-Fe_2O_3: iron(III) oxide, alpha phase, hematite
- β- Fe_2O_3: iron(III) oxide, beta phase
- γ- Fe_2O_3: iron(III) oxide, gamma phase, maghemite
- Fe_3O_4: Iron(II, III) oxide, magnetite
- $Fe(OH)_2$, Iron(II) hydroxide
- FeOOH, iron(III) oxide-hydroxide, goethite

While most of these oxides have been investigated as potential adsorbents, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are the most studied because of their high specific surface area which ranges between 30 and 100 m^2/g and magnetic feature as these two forms exhibit strong magnetic responses (M_s: 50–150 emu/g) [7]. The magnetic property of iron oxides serves two purposes: (a) it allows easy separation of the adsorbent at the end of the adsorption and (b) it generates more channels for pollutant

diffusion through the bulk that leads to higher adsorption efficiency [7,30,32]. The motivation force of using iron oxides in nanoremediation is their high availability in earth curst and metal wastes, as there are the final product of iron rusting. Thus metallic wastes can be recycled and used to treat water. The exact mechanism of adsorption on the iron oxides surface is explained next.

4. Adsorption mechanism

In general, adsorption is a process in which a molecule is transferred from a fluid bulk to an adsorbent solid surface [13]. Conversely, desorption denotes the release of the adsorbate's molecules from or through a surface. The general adsorption mechanism is depicted in Fig. 2.4. Depending on the type of interactions between the surface of the adsorbent and the molecule adsorbed, the adsorption process can be classified into two classes: (a) *physical*, where the molecular interactions between the adsorbate molecules and the adsorbent are generally driven by van der Waals forces, or (b) *chemical*, whereas strong chemical bonds such as covalent bond forces govern. The surface phase can be considered as a monolayer or multilayer. Chemisorption

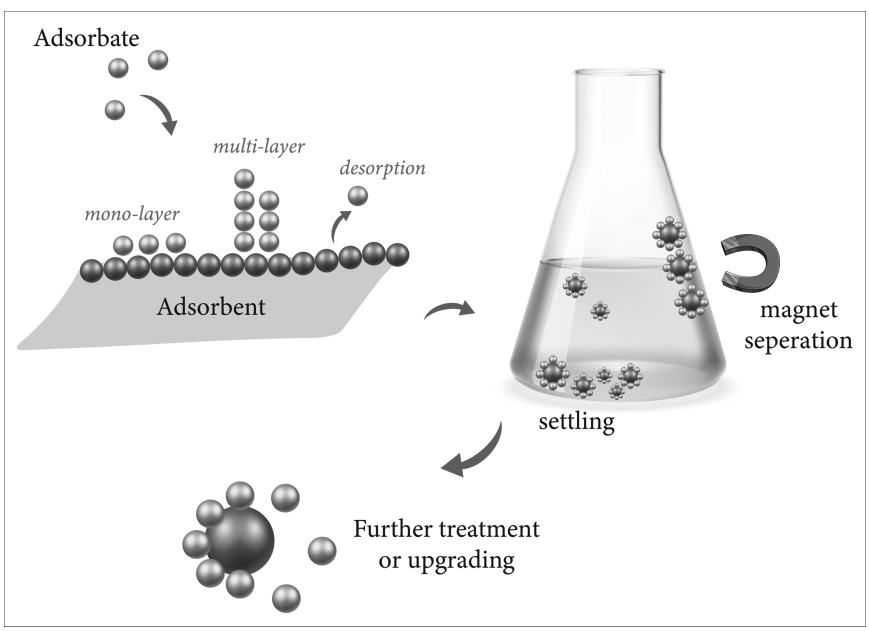

Fig. 2.4 Schematic representation of the adsorption-desorption of pollutants from water. For the case of magnetic adsorbent, separation can be assisted by a magnetic field for regenerating the adsorbent. Own source.

usually involves the formation of a monolayer (mono-molecular layer). However, in the case of physisorption, a multilayer is formed on the adsorbent surface [13,33]. It is noteworthy to mention that conventional adsorption methods target the treatment of wastewater through concentrating the pollutant species on the adsorbent surface. However, this leads to a secondary environmental problem formulated in the "sludge" formed as a result of the adsorption process. Modern technologies, however, focus on upgrading this sludge either by recycling the adsorbent and/or upgrading the organic matter into new commodity chemicals or fuels [34–36]. Upgrading can be achieved either by thermal oxidation, advanced oxidation, oxy-cracking, or catalytic cracking [37–43].

The adsorptive removal of pollutants on metal nanoparticles depends on several factors, including:

1. *The nature of the adsorbent/adsorbate*: adsorption is not limited by the physical adhesion of the pollutant species on the adsorbent surface. Rather, it might involve redox or photochemical reactions that enhance the removal of certain pollutants. For instance, as illustrated in Fig. 2.5, zero-valent iron

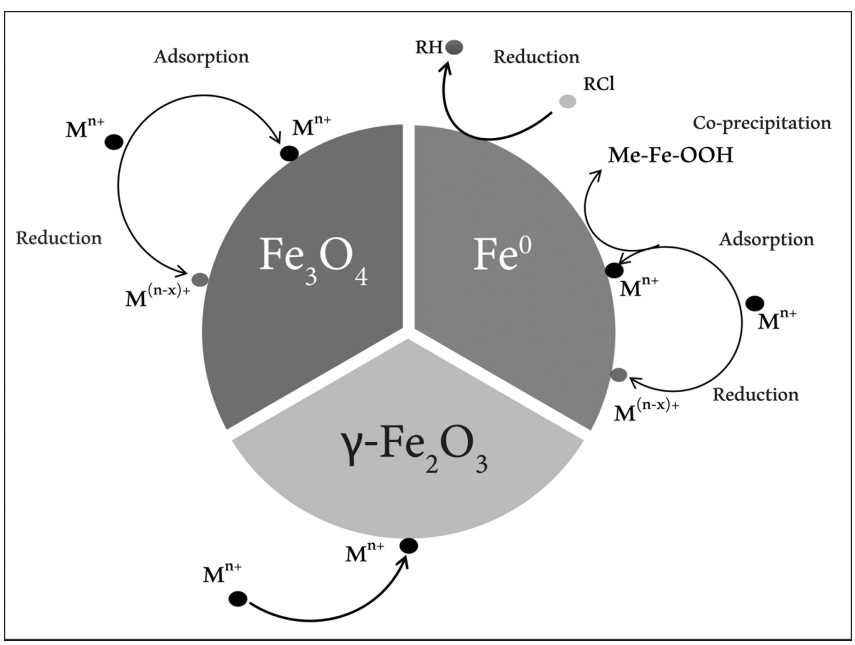

Fig. 2.5 Schematic representation of the removal mechanisms of pollutants by iron-based nanoparticles (i.e., nZVI, Fe_3O_4, and γ-Fe_2O_3). M refers to metal. Reproduced from S.C. Tang, I.M. Lo, Magnetic nanoparticles: essential factors for sustainable environmental applications, Water Res. 47 (8) (2013) 2613–2632. Copyright 2013, Elsevier.

(Fe^0) was found to oxidize into iron oxides/hydroxides shell upon contacting with air or water, while metal ion pollutants reduce to their free forms [44]. On the other hand, Fe(II)/Fe (III) adsorbents have the ability to reduce metal ion pollutants. For example, it was found that the removal of toxic chromium from water using Fe_3O_4 caused the reduction of Cr(VI) to Cr(III), followed by surface precipitation onto the magnetic nanoparticles (MNPs) [44].

2. *The medium pH*: The effect of pH on adsorption is an important parameter that affects its mechanism and efficiency. However, there would be no general rule that governs the relationship between the solution pH and the removal efficiency, as this depends on the nature of the adsorbent/adsorbate species and the functional groups involved in both. The solution pH can affect the solubility of the metal oxide as well as the pollutant species. Also, positive or negative surface charges can form on the metal oxide depending on the pH of the solution. This is governed mainly by the point of zero charge (PZC) of the adsorbent [10,13,45]. Generally speaking, the surface would carry a net positive charge below its PZC and a net negative charge above that value. Thus adsorption of anionic dyes would be preferred in acidic solutions. For example, Fayazi et al. [46] found that the adsorption of alizarin red S (anionic dye) on γ-Fe_2O_3 nanoparticles supported on AC was decreasing with increasing pH. But the effect of the pH depends on the functionalization of the metal oxide too. For example, the adsorption of methylene blue, which is well known to be a cationic dye, was maximum at a pH of 5.2. This is because of the nature of functional groups attached to the adsorbent surface [47].
3. *Exposure to light*: Some metal oxides have a photocatalytic ability to degrade organic pollutants. For instance, the removal of alizarin dye from an aqueous medium using maghemite nanomaterials was increased from 40% to 90% upon the radiation of UV light for 2 h [36]. This takes place when the metal oxide adsorbent acts as a photocatalyst or the pollutant molecules themselves undergo photo degradation. Typically, the photocatalytic oxidation reaction utilizes a semiconductor material to harvest light to induce the formation of reactive species. These are capable of degrading pollutants such as organic dyes and pharmaceuticals. The mechanism is initiated by the excitation of one electron (e^-) from the valance band (VB) to the conduction band (CB) in the semiconductor. This results in the generation of a positive hole (h^+) in the VB. It is well agreed that the

mechanism proceeds by the reduction of oxygen from the air to form a superoxide radical ($^{\bullet}O_2^{-}$), per the following reactions [48–52].

$$\text{Photocatalytic} + h\nu \rightarrow e^- + h^+ \quad \text{(R2.1)}$$
$$O_2 + e^- \rightarrow {}^{\bullet}O_2^{-} \quad \text{(R2.2)}$$

Consequently, and with the presence of water molecules adsorbed on the nanomaterial surface, chain reduction-oxidation reactions take place forming other reactive species, including hydroxyl ($OH^{\bullet}$) and hydroperoxyl ($^{\bullet}OOH$) radicals. Titanium oxide, TiO_2, is the most common photocatalyst with a band gap of ~3.2 eV (anatase) or 3.0 eV (rutile) [53,54]. This implies the need for light in the UV range (375–420 nm) to activate the catalyst. However, this range can be shifted to the visible region by doping TiO_2 with other materials [49,53,55].

4. *Effect of contact time*: this effect plays an important role in the feasibility and large-scale applicability of pollutant adsorptive removal using nanomaterials [56]. In the initial contact phase, the adsorbed amount increases due to the availability of vacant binding sites. As the contact time increases, adsorption will eventually reach an equilibrium between the adsorbate and the adsorbed amount, as a result, plateaus [57]. Studying the contact time also serves to understand the kinetics of the adsorption and determine the kinetic parameters such as the rate constant and the equilibrium adsorption capacity. The adsorption can be followed over time, and a plot of q_e against time can be constructed. The data can then be fitted to different adsorption kinetics models. The most common ones are the pseudo first-order (PFO) model given by [58,59]:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (2.1)$$

and the pseudo second-order (PSO) model that is defined by:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (2.2)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively, and k_1 and k_2 are the rate constants for the PFO and PSO models, respectively.

The kinetic model of adsorption can help reveal important facts about the nature of adsorption. The physical meaning of the PSO model, for instance, lies in its relationship with the vacant

sites [59]. Once the kinetic model is determined, information on the adsorption mechanism can be revealed. The present understanding of the PFO model is that it represents the following conditions [59]:

a. At high initial concentrations of the adsorbate.
b. At the initial stage of adsorption.
c. Few active sites are available on the adsorbent surface.

On the other hand, the PSO could represent the 1st and 2nd conditions but assumes plenty of active sites on the surface. Because adsorption is a complex process and the adsorbent might contain different types of functionalities and morphologies, the adsorption kinetics can be described by more complex models, such as the mixed-order, Elovich, or Ruchie models [59].

5. *The effect of temperature*: this can affect the adsorption rate and efficiency. While increasing the temperature should decrease the solution viscosity and enhance the diffusion rate of adsorbed molecules [10], this does not necessarily lead to enhancing the adsorption rate. This is because the adsorption equilibrium is also affected by thermodynamical consideration. For exothermic adsorption, the adsorption capacity would decrease as the temperature rises. Alternatively, endothermic adsorption would rather favor high temperatures. It is common to observe endothermic adsorption with metal oxides [10], but that also depends on the nature of the adsorbent/adsorbate species and the type of interactions between the two. Studying the temperature effect can lead to a better understanding of the adsorption mechanism and the determination of some important thermodynamic parameters. It is known that the change in Gibb's free energy (ΔG) is related to the equilibrium constant (K) through the Van't Hoff equation [60,61]:

$$\Delta G^{\circ} = -RT \ln K \tag{2.3}$$

where R is the universal gas constant and T is the temperature in K. The fundamentals of thermodynamics, on the other hand, state that:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{2.4}$$

where ΔH° and ΔS° are the changes in standard enthalpy and entropy, respectively. Eqs. (2.3), (2.4) rearrange to:

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{2.5}$$

Thus a plot of ln$K$ against $1/T$ (in K^{-1}) should yield a linear relationship with a slope $= -\Delta H^{\circ}/R$ and an intercept $= \Delta S^{\circ}/R$.

According to a recent critical review by Lima et al. [60], several studies were reported to misuse these equations in order to obtain the thermal properties through applying a simplified Arrhenius plot that contains only the equilibrium constant K. In other words, by plotting the natural logarithm of concentration against $1/T$ for a single experiment. This was shown to introduce large errors in determining the thermodynamical parameters. It is stated that the correct way to evaluate the value of K is to "obtain isotherms of adsorption at different temperatures and making the nonlinear fitting of the isotherms" [60,62].

The importance of ΔH° lies in its sign and magnitude; while its sign signifies if the adsorption is either exothermic or endothermic, its magnitude can help to understand the mechanism. Low values (<20 kJ/mol) of ΔH° refer to physisorption, while greater values refer to chemisorption. As presented in Table 2.1, most adsorption studies using metal oxides are associated with an endothermic

Table 2.1 Thermodynamical values determined by some adsorption studies.

Adsorbent	Adsorbate	Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1} K^{-1})	ΔS° (J K^{-1} mol^{-1})	Ref.
Graphene oxide-SiO_2-SWCNTs	Congo red (CR)	293	−24.3	200	30.6	[63]
Polypyrrole-MWCNT	Potassium diclofenac (PD)	298	−20.6	52.7	246	[64]
MWCNT-Alumina	Methylene blue (MB) and Cr(VI)	298	−36.4 and 24.9	18.2 and 19	200	[65]
γ-Fe_2O_3	Alizarin	298	−6.8	−27.8	−71	[36]
Fe_3O_4	Ni(II) and Cr(VI)	298	−5.4	33.7	131.4	[66]
Magnetic goethite	Cr(VI)	323	−1.6	3.7	20	[67]
Al_2O_3	As(III)	298	−3.8	−26.1	−0.08	[68]
γ-Fe_2O_3	Diclofenac	298	−29	67.3	96.3	[69]
MgO	Cu(II)	333	−1.66	46.6	140	[70]
ZnO	Cu(II)	333	−94.9	8.5	40	[70]
MnO_2	Hg(II)	313	−7.2	5.3	40	[71]
ZnO-graphene	Ni(II)	298	−6.1	53.3	199.5	[22]

process. Thus performing the water treatment at a higher temperature would be in the favor of the process. Also, most cases demonstrate physisorption, as the forces between metal oxide nanoparticles and most pollutants in aqueous media are weak intermolecular forces. As for ΔS°, negative values are explained by a decrease in entropy because of accumulating the adsorbate molecules on the adsorbent surface. However, most studies demonstrated positive values as presented in Table 2.1. This can be explained by the tendency of the system to increase its disorder and randomness at the solid-solution interface during the adsorption process due to adsorption and subsequent desorption. As for ΔG°, it refers to the spontaneity of the process. As per Table 2.1, most adsorption studies have reported slightly negative values indicating spontaneous adsorption. Although adsorption is endothermic in general, the process is still spontaneous with negative values of ΔG°. This is because the high magnitude of ΔS° causes the $T\Delta S^\circ$ term in Eq. (2.4) to increase, leading to negative ΔG°.

5. Magnetic nanoparticles

MNPs have attracted much attention due to their wide scope of technological applications. In addition to their ease of synthesis, abundance, and low cost, MNP offers environmentally friendly and low toxic solutions to wastewater treatment [72,73]. Besides being pointed out as a game changer in several fields such as military, energy, magnetic separation, biomedical applications, catalysis, and magnetic sensors [74], MNP also demonstrated high performance in pollutant removal from water bodies including toxic heavy metal ions [75–78]. Likewise, it has been established that they are effective in membrane separation for water treatment and purification operations [79,80]. This is due to the high activity levels caused by the size quantization effect and vast surface areas to which a large number of contaminants adsorbed [75]. In the context of water treatment, MNP has many exceptional properties, such as high removal capacity, recycling potential with the aid of magnetic field, fast adsorption kinetics, and magnetism. The magnetism property makes MNP preferable over conventional materials [81]. The separation process of the adsorbent/adsorbate solution becomes a cost-effective and convenient method with one single step by exposing the solution to a magnetic field.

Environmental impacts are another crucial factor to be considered to evaluate the feasibility of using the MNP in wastewater treatment. During the synthesis of MNP, the ratio of surface to bulk atoms increases due to the size reduction of the particle from micrometer to nanometer scale, thereby increasing the energy of

the system as a whole which leads to poor system stability [72]. Accordingly, MNP tends to agglomerate resulting in the reduction of the surface energy due to van der Waals forces [45]. Furthermore, bare MNP are chemically active and easily oxidized in air, leading to a loss of magnetism and dispersibility in most cases. To overcome these limitations, the functionalization technique has been proposed. Functionalization is a practical technique that can be described as the addition of functional groups to the MNP surface that permits further chemical interactions with the environment. MNP are typically covered or grafted by organic species, including surfactants or polymers, or coating with inorganic materials. This grafting will not only improve their thermodynamical stability but also their surface functionalities and maximize dispersity. Hence, the adsorption properties would be improved. However, a perquisite of the functionalization technique is needed in the form of supplying the surface with a binding agent to act as a bridge between the MNP surface and the functional group [29].

Table 2.2 presents the typical reported experimental and adsorption parameters of recently published adsorption studies that employed different families of metal oxide nanomaterials for the removal of different pollutants from water. As seen, the selected metal oxide-based nanoadsorbents may differ in type, particle size, structure, and surface chemistry. Such differences may affect the adsorption characteristics and behavior. The pollutants themselves vary between being toxic heavy metals such as Cu(II), Pb(II), Hg(II), and Cd(II) and organic dyes such as methylene blue, acid red, and alizarin. The removal process also targets new emergent pollutes such as pharmaceutical drugs, which were reported to pose risks to the human, animal, and aquatic life if misadministered or existed in water resources above certain limits [1,2,15]. Generally, metal oxides and MNP demonstrate excellent removal efficiencies that might reach 99% as seen in the table. Due to their nanoscale sizes, their structures are able to reach excellent adsorption capacities, with values close to 1 g of adsorbent for each 1 g of adsorbate. Typical pollutant concentrations range between 1 and 50 ppm, but some studies have reached a few hundred ppms as shown in the table. As for the optimum pH of adsorption, there is no common trend as shown in the table. Some systems are more efficient at high pH, while others work best in an acidic medium. This again depends on the surface acidity of the adsorbent, the PZC, the type of functional groups on the surface, and the structure of the adsorbate itself, as discussed earlier in Section 3. In most of the cases, the reported adsorption isotherms are either of the Langmuir or Freundlich type. Where the first model assumes homogeneous monolayer coverage on the adsorbent surface, the latter model suggests a heterogeneous coverage

Table 2.2 Adsorption parameters for the removal of different pollutants by metal oxide nanomaterials.

Adsorbent	Adsorbate	Adsorbent particle size (nm)	Adsorption capacity (mg/g)	Concentration range (ppm)	Optimum pH	Equilibrium time (min)	Removal (%)	Isotherm model	Ref.
γ-Fe_2O_3-coated chitosan-α-ketoglutaric acid	Cu(II)	30	96.2	40–800	6	60	89.8	Langmuir model	[82]
γ-Fe_2O_3	Alizarin	–	23.2	2.4–96.1	11	60	95	Langmuir	[36]
γ-Fe_2O_3	Diclofenac	–	261	–	7	120	–	Langmuir and Sips	[69]
γ-Fe_2O_3-zeolite 5A	Pb(II)	5–15	265	–	> 6	5	99.9	Sips	[83]
γ-Fe_2O_3EDTA	Pb(II)	4–8	–	0–50	–	7 h	99.9	–	[84]
γ-Fe_2O_3-FMWCNTs-alginate	Methylene blue	–	905.5	30–230	5.2	24 h	–	Freundlich	[47]
Magnetic-α-FeOOH	Cr (VI)	–	4.3	10–50	2	240	88.2	Langmuir	[67]
α-FeOOH	As(V) and Se(IV)	–	6.2 and 7.7	0.1–0.3	2–5	24 h	–	Langmuir	[85]
α-FeOOH	Ni(II), Cd(II), and Zn(II)	–	0.9, 1.1, and 1.1	10	5–6	120	78.1, 89.1, and 85	Langmuir and Freundlich	[8]
β-FeOOH	Cd(II)	2.6	17.1	500	8	24 h	100	Langmuir and Freundlich	[86]
Fe_3O_4-EDTA	Ag(I), Hg(II), Mn(II), Zn(II), Pb(II), and Cd(II)	35	71–169	–	7.9	10	96	–	[87]
Fe_3O_4-Zeolite NaA	Methylene blue	–	40.4	–	–	240	96.8	–	[24]

Continued

Table 2.2 Adsorption parameters for the removal of different pollutants by metal oxide nanomaterials—cont'd

Adsorbent	Adsorbate	Adsorbent particle size (nm)	Adsorption capacity (mg/g)	Concentration range (ppm)	Optimum pH	Equilibrium time (min)	Removal (%)	Isotherm model	Ref.
Fe_3O_4-MWCNTs	Hg(II)	5–10	238.8	10–50	2	60	–	Langmuir	[88]
Fe_3O_4	Cr(VI) and Ni(II)	10–15	3.6 and 11.5	5–15	2 and 8	60 and 60	100 and 94.3	Langmuir and Freundlich	[66]
Ash-graphene oxide-Fe_3O_4	Pb(II) and Cd(II)	<20	47.1 and 43.7	5–70	6	60	99.7 and 98.7	Langmuir	[89]
MnO_x/PC	Pb(II)	9–40	254.8	–	2.2–4.5	240	98.7	Langmuir model	[90]
MnO_2/gelatin	Pb(II) and Cd(II)	50	318.7 and 105.1	–	–	–	100 for Pb(II)	Langmuir	[23]
nMnO_2	Tl(II)	–	672	–	7	15	–	Langmuir	[91]
MnO_2	Hg(II)	5–10	199.5	10–40	6–9	2.5	–	Langmuir	[71]
Fe_3O_4-MnO_2	Cd(II)	60	53.2	10–50	4–6	30	~97	Langmuir	[25]
HMO-biochar-supported hydrated	Pb(II) and Cd(II)	10–50	67.9 and 22.3	(3–53) and (3–33)	3–7	120	–	Freundlich	[92]
ZnO	Cu(II)	24.7	226	–	3–4	120	92.4–97.6	Freundlich	[70]
MgO	Cu(II)	70	593	–	3–4	120	93.7–98.2	Freundlich	[70]
ZnO-graphene	Ni(II)	–	66.7	–	8.2	–	–	Langmuir	[22]
Al_2O_3	As(III)	9–75	0.5	50–100	6.5	180	89.7	Langmuir	[68]
γ-Al_2O_3	As(III) and As(V)	2–10	–	10–40	6	–	–	–	[93]
γ-Al_2O_3	Pb(II) and Cd(II)	6–13	47.1 and 17.2	–	5	20 and 30	–	Langmuir and Freundlich	[94]

with multilayer adsorption. Having said that, other adsorption isotherms are now wildly implemented in the literature, including Sips, BET, Temkin, and Toth [95–97]. Some adsorption data follows a sigmoidal behavior that requires different models, such as the Klotz and the corresponding states models [98,99]. For a full discussion on adsorption isotherms, the reader is advised to review articles at the end of this chapter [95–99].

The adsorption efficiency of MNP can be improved by functionalizing the surface with organic molecules like polyamines, polyethylene glycol (PEG), polyacrylamide (PAM), and poly amidoamine (PAMAM) [87,100,101].This would not only increase the surface area but also involves changes in the surface functionalities and introduces other trapping mechanisms because of the ability of the functionalized polymer to interact through supramolecular chemistry [29]. This would involve the trapping of contaminants through noncovalent intermolecular forces (i.e., electrostatic interactions, hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, and pi-pi interactions) in addition to the host-guest interactions in the formed cavities within the polymer anchored on the nanoparticle surface [29].

In addition to the poor system stability mentioned earlier (due to the strong tendency to form agglomerates), the naked iron oxide nanoparticles (NFeOs) are easily oxidized in the air [102]. To obtain NFeOs that overcome these technical bottlenecks and have effective protection to the NFeOs, the coating is done with (into/onto) supports of larger size materials as illustrated in Fig. 2.6. Examples of these coatings include:

1. Hydrophobic polymers such as oleic acid, polyvinyl chloride (PVC), and polyvinylidene fluoride (PVDF).
2. Hydrophilic polymers such as cellulose, PEG, and ethylenediaminetetraacetic acid (EDTA).
3. Carbon-based materials such as AC, CNT, or graphene.
4. Natural products such as sawdust, clay, or chitosan.
5. Inorganic materials include silica, zeolites, LDH, or MXenes.

For instance, hydrophobic functionalized Fe_3O_4@oleic acid nanoparticles coated with graphene oxide have shown a remarkable result in the oil-polluted water field separation [103]. In another study, the superparamagnetic and hydrophilic Fe_3O_4@EDTA was shown to be an efficient, cost-effective, and reusable adsorbent for simultaneous removal of heavy metals from wastewater [87]. In terms of inorganic materials coatings, magnetic zeolite (Fe_3O_4@ZA) is an efficient adsorbent that is used to treat wastewater from organic dyes such as methylene blue [24]. Furthermore, the waste of pharmaceuticals such as promazine can be adsorbed from water by magnetic-activated carbon (Fe_3O_4@AC) with batch adsorption process [104].

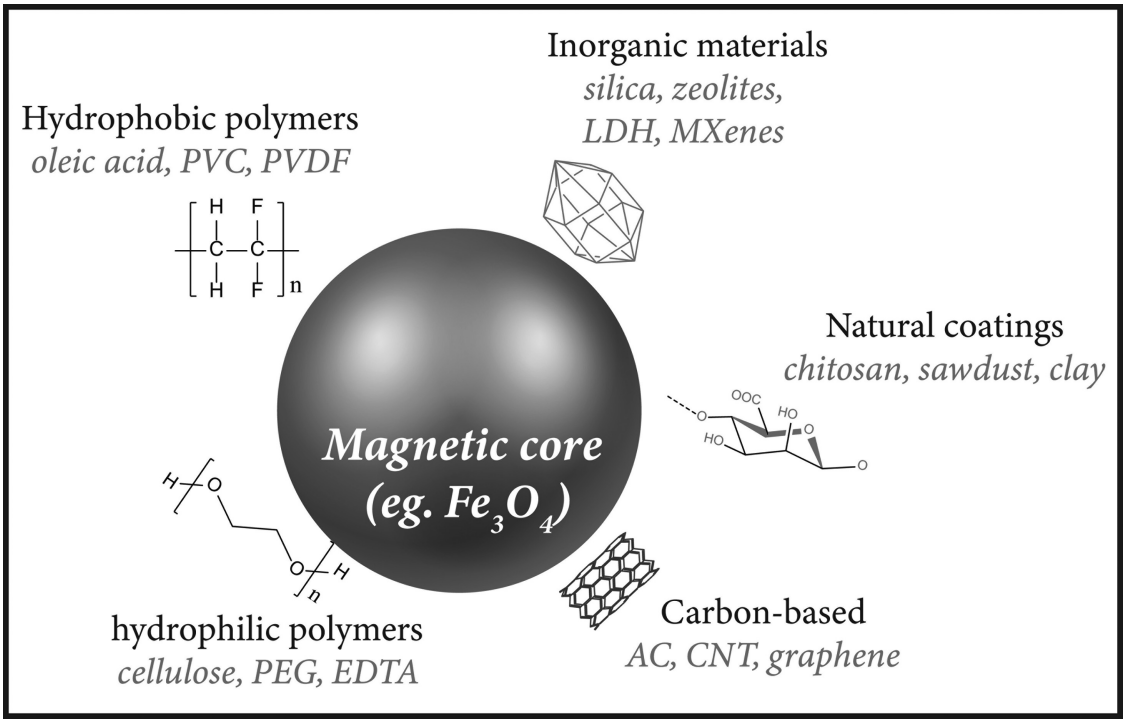

Fig. 2.6 Functionalization of naked iron oxide nanoparticles (NFeOs) with different types of materials. For abbreviations, see the corresponding text. Own source.

Once NFeOs are synthesized, they need to be characterized in situ to ensure its quality and uncover their properties. Scanning electron microscopy (SEM) images are usually recorded to examine the surface morphology of the nanoparticles [105]. N_2-BET (Brunauer-Emmett-Teller) physisorption tests are performed to measure the adsorption capacity and pore size of the prepared nanomaterials. Transmission electron microscopy (TEM) can elucidate information about the size and shape of NFeOs [106]. Furthermore, to investigate the crystal structure and phase of the magnetic core, X-ray diffraction (XRD) techniques can be applied. This technique scatters the angles of the X-ray that leave the sample by respecting the Bragg's law [107].

When it comes to the application of nanomaterial-based water treatment methods, it is crucial to evaluate the efficiency of the wastewater treatment system, by determining different parameters such as adsorption capacity, removal percentage, and adsorption rate [108]. Two of the most commonly employed evaluation systems are batch-type mode adsorption and fixed-bed-type mode processes. On a laboratory scale, batch-type contact process, a simple setup and easily operated method is usually

employed to evaluate the mechanism of the adsorption process and to compare the adsorption properties of various adsorbents [109]. In fixed-bed-type methods, on the other hand, the adsorbent is continuously in contact with fresh solutions, making it scalable and preferable on an industrial scale [109,110].

6. Carbon-based nanomaterials

Carbon-based nanomaterials have received tremendous attention in the field of wastewater treatment [111–114]. Fig. 2.7 shows some examples of different allotropes of carbon such as CNT, carbon nanodiamonds, fullerene, graphene, carbon nanocones, and carbon nanomembranes [111]. These materials have unique properties that paved their way onto several applications. These properties include:

- Small size ranging from few nanometers to tens of micrometers.
- High specific surface area.
- High thermal conductivity.
- High reactivity.
- High thermal and chemical stability.
- Catalytic potential at the nanoscale.
- Facile functionalization and modification.

These nanomaterials have been tested as adsorbents for the removal of several heavy metal ions, organic pollutants, as well as pharmaceutical compounds from water bodies. Recent applications that utilized carbon-based nanomaterials as adsorbents to treat the wastewater are tabulated in Table 2.3. As seen, these

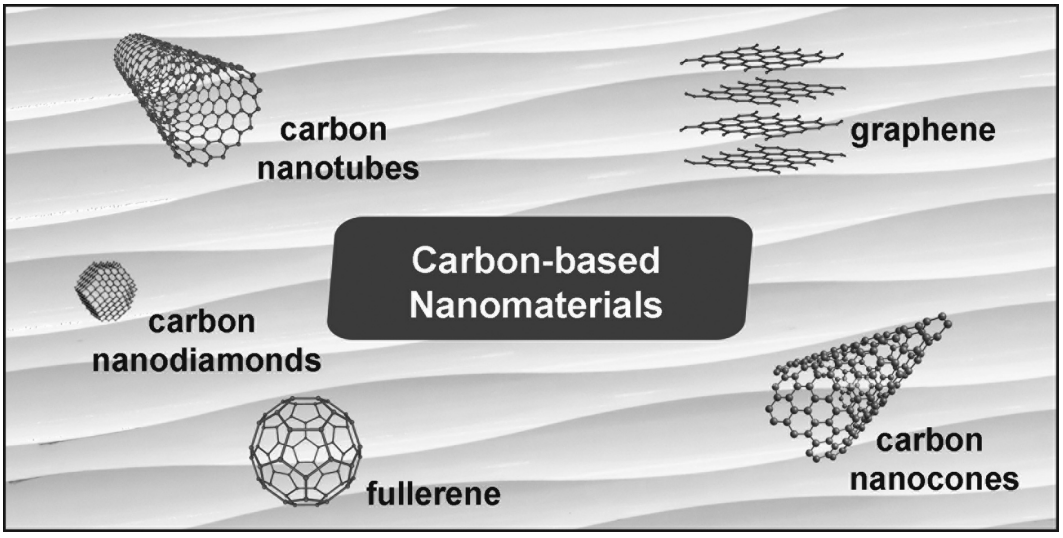

Fig. 2.7 Examples of carbon-based nanomaterials. Own source.

Table 2.3 Adsorption parameters for the removal of different pollutants by carbon-based nanomaterials.

Adsorbent	Adsorbate	Adsorbent particle size (nm)	Adsorption capacity (mg/g)	Concentration range (ppm)	Optimum pH	Equilibrium time (min)	Removal (%)	Isotherm model	Ref.
Graphene oxide-SiO_2-SWCNTs	Congo red (CR) dye	–	456.2	50–500	3	330	–	Langmuir	[63]
Polypyrrole–MWCNT	Potassium diclofenac (PD)	–	229.9	0.025–1.5	6	45	95	Dual-site Langmuir-Freundlich	[64]
Fe-SWCNTs	Arsenic ion (5+)	1.4–2.8	42.3	5–10	8	3	>98	Freundlich	[115]
Activated carbon-alginate	Methylene blue (MB)	1.4	230	20–100	9.5	1200	99	Freundlich	[116]
EDTA-graphene oxide	Pb(II)	–	479	5–300	6.8	24 h	–	Langmuir	[117]
Activated carbon	MB and Pb(II)	–	16.9 and 18	20–100 for Pb(II)	9	20	94.3 and 95.7	Freundlich	[118]
Activated carbon/cellulose film	MB	–	103.7	20–100	6.9	24 h	–	Langmuir	[119]
Cellulose-acetate-chitosan-SWCNT-Fe_3O_4-TiO_2	Cr(VI), As(V), MB, and CR	150–300	345.2, 285.6, 97.6, and 74.2	20–100	2–3	40, 60, 90, and 105	>95	Langmuir	[120]
MWCNT/alumina	MB and Cr(VI)	10–30	187.5 and 597	5–50	–	240	>85	Langmuir	[65]
MoS_2/SH-MWCNT	Pb(II) and Cd(II)	–	90 and 66	–	6	60	≥98 and 80	Freundlich	[121]
Graphene oxide	Diclofenac and sulfamethoxazole	<250	–	10–100	<7	6 h	35 and 12	Freundlich	[122]

nanomaterials vary in their adsorption capacities and other optimal experimental conditions. In general, most of the selected carbon-based nanomaterials show high removal efficiencies at pH around 6. However, some of the adsorbents are efficient at low pH values. The factors that influence the optimum pH of adsorption processes were discussed in Section 3. Table 2.3 shows that all carbon-based nanomaterials concur well with both models, Freundlich and Langmuir. The former poses the heterogeneous upload of the adsorbent's ions on the adsorbent's surface with multilayer adsorption, while the latter suggests homogenous monolayer coverage. Further, the table demonstrates that carbon-based nanomaterials establish relatively high removal efficiencies with ~99% due to their high surface area. The materials have been also studied for their potential use to treat oily water for oil recovery and oil spill applications cleanup [123–125]. In the context of this chapter, we will focus on graphene and CNT as they are the most common examples in this category.

Since its discovery in 2004, graphene is a monolayer 2D allotrope of carbon consisting of sp [2]-hybridized atoms arranged in a hexagonal crystalline structure [111]. In addition to the general properties associated with carbon-based nanomaterials listed before, graphene is characterized by its high specific surface area (~2630 m[2]/g) and high thermal conductivity (~5000 W/m K) [111]. It is also one of the strongest materials that have ever been made [111].

Graphene oxide (GO) and reduced graphene oxide (RGO) can be also prepared from graphene by simple chemical methods [111]. These two forms have been widely used to treat nonpolar and hydrophobic organic contaminants, and oil in particular. To achieve the best separation, surface modification of graphene oxides, and other carbon-based nanomaterials, can be made. The modifiers, in this case, can be classified into three categories [114]:

1. Hydrophobic and oleophilic, e.g.
   - Attapulgite
   - Zinc oxide
   - Polyaniline (PANI)
   - Polypyrrole (PPy)
2. Superhydrophobic and superoleophilic, e.g.
   - Polyvinylidene fluoride (PVDF)
   - Poly(vinyl chloride) (PVC)
   - Polystyrene
3. Hydrophilic and oleophobic properties, e.g.
   - Polyhedral oligomeric silsesquioxane (POSS)
   - Poly(ethylene glycol) diacrylate) (PEGDA)
   - Poly(diallyldimethylammonium chloride) (PDDA)

4. Superhydrophilic and superoleophobic properties, e.g.
   - Paraffin wax (PFW)
   - Poly(diallyldimethylammonium chloride) (PDDA)
   - polydopamine (PDA)

Therefore the surface of graphene, or any other nanomaterials, can be modified with one of the previously mentioned polymers to address specific application. In recent years, functionalization with oleophilic and superoleophilic materials gained high attention for oil/water separation, as a solution for oil ocean spills, oil recovery, and traffic accidents cleanup [123–125].

CNT are allotropes of carbon that are intermediate between fullerene and graphene. Fig. 2.8 (left) shows the structure of single-walled CNT. CNT is made up of rolls of long hexagonal lattice drawn on an infinite cylindrical surface, whose vertices are carbon atoms. CNT have remarkable properties that made them popular in several fields. They are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus [126,127]. CNT have high electrical and thermal conductivity due to their graphene-like sp^2 hybridization structures [16,128,129]. Because of their nanostructure and long chains, they can be chemically modified by different functional groups such as —OH and —COOH. This can be helpful to treat specific pollutants such as pharmaceutical drugs and dyes with electron-poor centers [16,128,129].

The most important feature of CNT is their high surface area which makes them excellent adsorbents. It is also found that CNT functions by adsorbing species on the outside surface as well as inside the tubes [15,130,131]. This feature maximizes the

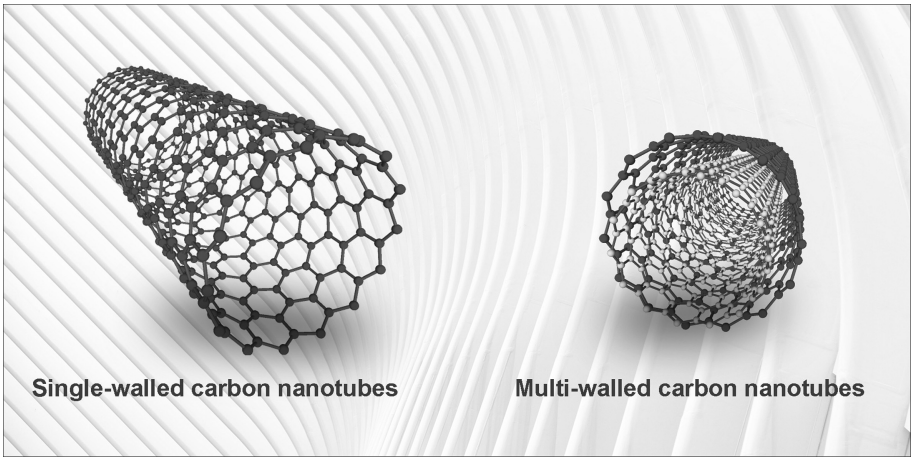

Fig. 2.8 Single- and multi-walled carbon nanotubes. Own source.

adsorption capacity of CNT and makes it one of the best adsorbents. However, the relatively high price of CNT and fears of their toxicity have limited their wide applications in water treatment. The cost is projected to decline under the high demand and the variety of production methods. It is estimated that the CNT market is valued at $1033 million and is expected to reach $3812 million by 2022 [132]. Also, composites of CNT and other materials such as magnetic iron oxides have been developed to reduce the cost.

Another common type of CNT is the MWCNT (Fig. 2.8, right). These are made up of rolled layers (concentric tubes) of SWCNT weakly bound together by van der Waals forces in a tree ring-like structure. MWCNT is commonly cheaper than SWCNT. Tests have shown that CNT is highly efficient in removing heavy metals [133]. For instance, using a column packed with CNT/magnesium oxide composite was found efficient to treat wastewater from lead (II). The optimum removal was observed when the pH optimized between 6 and 7 [134].

MWCNT are efficient adsorbents for organic pollutants as well as inorganic ones. The nanotubes can be used to remove pharmaceutical wastes from aqueous media. For instance, efficient removal of the antidiabetic drug glimepiride was achieved through MWCNT fixed-bed column supported on silica. As a result, the maximum adsorption capacity was found to be 275.3 mg/g with >98% removal efficiency. [15]

7. Ceramic and dendritic polymers

The word "ceramic" is derived from the Greek word "*keramikos*" which means burnt materials [135]. Ceramics are prepared from naturally occurring raw materials. They are composed of metallic and nonmetallic elements, which can be classified as oxides, carbides, borides, and silicides. Their bonds are either ionic or covalent. Due to their high electrical and thermal resistance, chemical stability, large surface area, and nontoxicity, ceramics have gained acceptance in many fields. In the context of environmental applications, ceramics are considered promising candidates for polluted water treatment. Ceramics can either be synthesized by heating or successive cooling [136].

Among the ceramics of interest, activated alumina (Al_2O_3) possesses mechanical strength, amphoteric properties, and high surface area [137,138]. Activated alumina is used to treat toxic heavy metal ions such as Cd(II), Pb(II), Ni(II), Zn(II), and Hg(II) with a percent removal exceeding 95% [137,138]. Generally, the adsorption of metal ions is more efficient at high pH. This is due to the competition of the H^+ ions with metal ions in an acidic medium. In addition,

nanostructure alumina can be also used to remove organic dyes, such as methylene blue (MB) from wastewaters. Nanoadsorbent of alumina functionalized by petroleum vacuum residue has great affinity toward nonpolar compounds. They have been recently tested for adsorptive removal of oil from oily freshwater [139].

Silica is one of the most researched nanomaterials as we observed in Fig. 2.1. It can be either used as support in fixed-bed columns, mixed with other composites, or by itself [15,140]. Hollow mesoporous silica (HMS) have unique morphology and nanostructure that allows different combinations of hollow patterns. The term mesoporous refers to materials containing pores with diameters between 2 and 50 nm. HMS has uniform and constant-sized pores, low density, high biocompatibility, active Si—OH bonds, large surface area, and internal hollow structure. Silica-based nanoparticles have shown good efficiency in removing pollutants from water. For instance, GO/HMS composite was prepared and used to treat methyl orange and methylene blue [140]. The adsorption capacities were 270.3 and 476.2 mg/g for the two dyes, respectively.

Dendritic polymers (Fig. 2.9) are macromolecules with intensively branched tree-like nanoarchitecture [136,141]. They can be classified into six main groups: dendritic-linear block

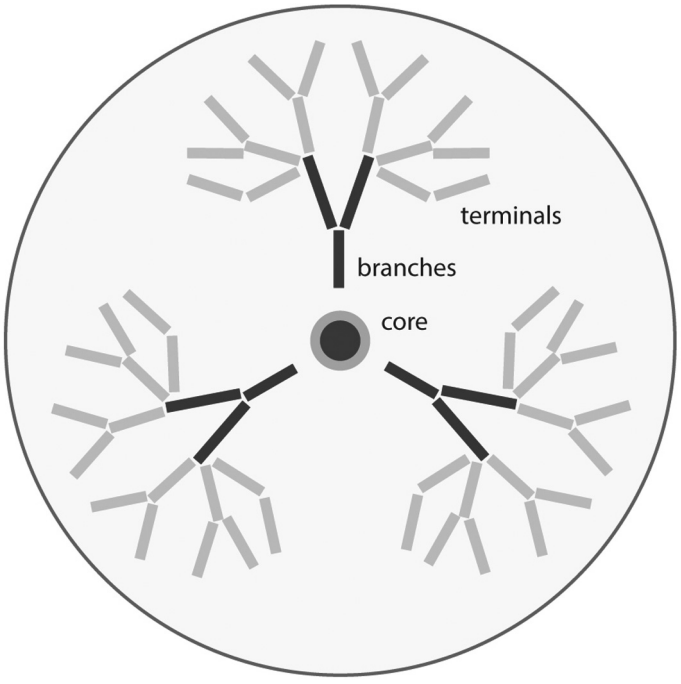

Fig. 2.9 General structure of dendritic polymers. Own source.

polymers, hypergrafted polymers, dendronized polymers, hyperbranched polymers, multiarm star polymers, and dendrimers. One of the widely used dendrimers is polyamidoamine (PAMAM). This is a family of highly branched and monodisperse synthetic macromolecules with well-defined structures and compositions [136,141]. PAMAM can be terminated by different functional groups including NH_2, OH, CHO, $COOCH_3$, COONa, and CH_3. PAMAM dendrimers immobilized onto the surface of silica have demonstrated high mechanical stability. However, the thermal stability of PAMAM is not as high as metal oxides [141,142]. Silica gel modified with PAMAM dendrimers was prepared and used to remove toxic Pb(II) and Hg(II) ions from aqueous media [141,142]. Salicylaldehyde was used as a linker to generate the PAMAM dendrimers. It was found that the adsorption depends on the medium, pH, the generation number of the dendrimers, contact time, and temperature.

We mentioned that MNPs can be coated or functionalized to form more stable and efficient materials. Composites of Fe_3O_4@SiO_2-X have been fabricated to target specific pollutants such as Pb(II) Hg(II) and organic dyes. X here might either be a hydrophobic or hydrophilic polymer that has a specific target. Hydrophobic polymers include oleic acid, stearic acid, and PVDF. These are efficient against nonpolar pollutants and therefore can be used for oil spills and oil-settling applications [123–125]. Hydrophilic polymers include EDTA, ethylene glycol (EG), tetraethylorthosilicate (TEOS), and aminopropyltriethoxysilane (APTES) [143].

8. Integrating nanoparticles with conventional treatment processes

Over the last few decades, there was extensive research on the use of nanomaterials as adsorbents for water treatment processes. The studies were mainly accomplished at a lab-scale level, either in batch or continuous mode. The studies have certainly provided a solid knowledge of the adsorption process and the parameters affecting its efficiency. However, fewer studies can be found for pilot- or full-scale implementations of the nanomaterials.

The most successful case of integrating nanomaterials in water treatment is the use of AC in commercial water and air filters. The next promising application is the deployment of nano ZVI in pilot tests in several places across the globe, including Europe, China, Canada, and the United States [144]. Recently, nanomaterials observed a milestone jump in a full-scale deployment in the Czech Republic. The Regional Centre of Advanced Technologies

and Materials at Palacký University has implemented a patented technology that used biotic and abiotic reductive species (i.e., zero-valent iron particles and lactate) to treat groundwater [145]. The process was good for the degradation of chlorinated organic pollutants such as dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE), as well as inorganic heavy metals such as Cr and Cu.

In the United States, a new center is currently aiming at developing nanoscale materials for use in water treatment that can completely replace metal-based catalysts within the next 10 years. The Nanotechnology-Enabled Water Treatment Centre (newtcenter.org) is a cluster formed by four US universities [146].

In China, a pilot program has been launched to purify drinking water from emerging micropollutants, such as pharmaceuticals, personal care products, and endocrine-disrupting compounds. The plant is built by GreenTech Environmental, a water treatment and recycling company based in Beijing. The company is using direct nanofiltration (dNF) membranes that are able to eliminate organic pollutants from water [145].

In addition, there are promising efforts of transforming nanomaterials into the industrial field by developing magnetic separation equipment that uses MNPs [147–149]. This equipment has a high-gradient magnetic separation system equipped with a superconducting magnet measuring few teslas in strength [150–152]. The basic concept of these systems is the use of MNPs and integration of magnetic separation in existing wastewater treatment plants. The principle is envisioned in three major phases [152]:

1. The effluent from the secondary treatment stage is treated with magnetic nanoadsorbent (advanced treatment).
2. The treated effluent from step 1 flows to the magnetic separation system.
3. The purified water and the magnetic adsorbent/adsorbate particles are separated to two different streams.
4. The magnetic particles are washed and reused.
5. The performance of these systems is promising as they can reduce the chemical oxygen demand (COD) to less than 40 ppm and can process water flows up to 2000 tons per day [152].

These industrial systems come with their own limitations. For example, using the zero-valent iron in groundwater treatment is costly. While the production is in the order of a few tons per year, millions of gallons of water need to be treated every day. Other drawbacks are as follows [147–149,152]:

1. Technological limitations, including limited migration in groundwater conditions.

2. The adsorption efficiency decreases because of a consistent loss of adsorbent particles.
3. The high-gradient magnetic separation was facing repeated shutdowns because of the need for regular flushing.
4. Blockage of the magnetic filter by the nanoparticles.
5. Limited regeneration cycles of the adsorbent materials.
6. High cost of building mega magnetic separation equipment.
7. Potential toxicity of the nanomaterials.
8. Social, jurisdictional, and economic issues, such as the use of nanomaterials for water purification, need lots of efforts to get the support of public and private decision-makers before adopting such new technology.

9. Challenges facing nanoparticles in real applications

Clearly, the use of nanomaterials as remediation tools is highly promising. However, the cost, potential toxicity, and the complication of integrating nanotechnology on-site call for continuous development in this field [12,144]. One of the most struggling challenges is their toxicity which deals with the possible implications on living beings and the environment. The success of nanomaterials is mainly attributed to their high adsorption capacity resulting from their small sizes. This is the same feature that raises concerns about their danger. Nanoparticles can easily enter the body through the skin or anhelation [12,153]. The size, shape, length, surface charge, and agglomeration can affect the toxicity of nanomaterials. The high chemical reactivity of these materials also leads to the production of reactive oxygen species (ROS) and free radicals, which are behind several health problems such as inflammation, oxidative stress, inflammation, and possible protein and nerves damage [12,154]. As an example, CNT exhibit different types of toxicity that affect human health in the long term [154]. This includes respiratory inflammations and possible accumulation in vital organs like the liver. Furthermore, CNT toxicity might also derive from the impurities, especially heavy metal contaminants, such as Fe, Y, Ni, Mo, and Co, that have been introduced during the synthesis of CNT [154].

The potential hazards of nanomaterials call for further research to assess their toxicity. It is important to provide a realistic assessment of their hazards rather than spreading fears. Also, a careful risk-benefit balance needs to be developed for better planning of their use in full scale [144]. This balance should be built on the following:

1. Accurate assessment of the risks and hazards of nanomaterials.
2. Enhance social awareness on the benefits and performance of nanomaterials.
3. Device jurisdictions that allow the use and control of nanomaterials.

The future use of nanomaterials in wastewater treatment requires substantial research beyond the field of chemical science. To transform the technology into a real application, there are needs to [153,155]:

1. Develop intelligent materials for adsorption systems that operate on a case-by-case basis.
2. Investigate the physical properties of such materials, for instance, their response to light.
3. Study their chemical stability, as for their influence by temperature, ionic strength, or pH.
4. Study their biological interactions with microorganisms, as this might cause microbial aggregates.
5. Investigate the geometry and configuration of the adsorption units, the dispersion of the magnetic nanoadsorbents, the spatial distribution of the nanoadsorbents within the adsorption flow, and study the effects of turbulences and shear forces.
6. Invest in fields of system modeling, numerical simulation, for better optimization of the process.
7. Device business plans and cost analysis for production of nanomaterials and the cost of integration with present treatment plants.
8. Partnership with policymakers.

Worth noting here is that the environmental hazards of nanomaterials are limited to some types, particularly those which are freely mobile and not incorporated into a material, such as support or solutions. Thus unlike free nanomaterials (like nanopowder), incorporating nanoparticles in a support or solutions or even in situ application of nanoparticles will minimize their contact with human during transportation or application.

10. Conclusions and future perspective

Nanomaterials have been proven to be excellent adsorbents for a variety of pollutants. The list involves metal oxides, magnetic materials, carbon-based nanomaterials, ceramic, and dendritic polymers. One of the most promising oxides is iron, which has a great potential in the field of wastewater treatment, mainly due to its low cost, low toxicity, magnetic properties, and high surface area. In this chapter, the adsorptive process was discussed

based on the recent advances in the field. The parameters affecting the adsorption, and insights into its mechanism and kinetics were discussed. The discussion was then focused on magnetic nanoparticles (MNPs) as they are the most promising nanomaterials in this sector, and also they can be easily separated and recycled at the end of the process. Such materials can also be modified by chemical methods. This enables different groups to functionalize the surface to aid in the removal of specific contaminants. The chapter also discussed the potential use of carbon-based materials in environmental remediation. Due to their superior physical and chemical properties, graphene, graphene oxide, and CNT have demonstrated excellent performance in removing both organic and inorganic pollutants. They also can be modified using hydrophobic polymers to be used in oil recovery or oil spill remediation.

The research in this field is numerous. But the future of using nanomaterials in real applications requires active contribution from several fields including chemistry, material science, chemical engineering, environmental science, control system, business, as well as policy making. Undoubtedly, the terms of the lab-scale proof-of-concept research are different than those in the field. Besides, a question on whether we need to integrate nanotechnology into existing treatment plants or build new ones needs to be answered based on feasibility studies. More importantly, the nanoparticles discussed in this context are geared to address modern environmental problems, such as emerging pollutants, and not to create new ones. Therefore the environmental impact, toxicity, and degradability of these materials need to be assessed in the short and long terms.

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