Nanomaterials for Environmental Applications

17

Yassine Slimani and Essia Hannachi

Abstract

The rapid growth in industrialization and population has resulted in the generation and permanence of a wide variety of inorganic and organic pollutants, posing potential risks to the environment and human health. The degradation (either removal or reduction) and sensing of these pollutants from various environmental media (e.g., air, water, and soil) are nowadays important problems worldwide. To address this issue, several nanotechnologies and numerous nanostructured materials and composites have been established for efficient environmental remediation applications. This is ascribed to their large surface area and improved characteristics and efficiency (like high reactive feature). The current chapter reports nanotechnologies such as filtration, photocatalysis, chemical reactions, absorption, adsorption, nanosensing, etc. It also offers an overview of the use of nanostructured materials and composites in the remediation of the environment. Novel nanostructured materials, involving inorganic-based nanomaterials (NMs) (e.g., zero-valent metal NMs, metal oxide-based NMs, silica-based NMs), carbon-based NMs, polymeric-based NMs, as well as their nanocomposites were extensively reported and discussed. These materials are efficiently employed for remediating various environmental pollutants such as halogenated herbicides, volatile organic compounds, chlorinated organic compounds, aromatic and aliphatic hydrocarbons, pharmaceuticals, dyes, heavy metals,

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biological substances (e.g., antibiotics, parasites, bacteria, and viruses), as well as gases (NO$_x$, CO, SO$_2$, etc.). Their efficiency, advantages, and limitations were compared and discussed. Moreover, some potential directions for future studies were proposed.

Keywords

Nanomaterials · Nanocomposites · Polymers · Carbonaceous-based materials · Nanotechnology · Pollutants · Environmental remediation

17.1   Introduction

Environmental contamination is without a doubt one of the most serious issues confronting civilization nowadays. Novel techniques for the remediation of pollutants in the environment (soil, water, and air) are continually being developed. Organic substances, wastewater, industrial waste, poisonous gases, spills of oil, fertilizers, herbicides, pesticides, heavy metals, and particulate matter are only a few of the numerous pollutants to be concerned about [1]. Because diverse substances could be used in remediating the environment, a broad range of methodologies are able to be used to accomplish this aim. Because of the complexities of the mixture of diverse substances, minimal reactivity, and significant volatility, capturing and degrading environmental contaminants might be difficult. Recently, scientists have concentrated on the utilization of nanostructured materials to establish novel environmental remediation technologies [1].

Because of the peculiar physical features of nanomaterials, nanotechnology has received a great deal of interest in recent years. Because of their larger surface-to-volume ratio, nanostructured materials have more potent reactivity and hence superior efficacy in comparison to their bulk equivalents. Furthermore, nanostructured materials have the ability to harness distinct surface chemical properties in comparison to standard techniques, allowing them to be coated or functionalized with functional groups that may target particular molecules of concern (contaminants) for effective remediation. Furthermore, purposeful tweaking of the physical features of nanoparticles (e.g., chemical composition, porosity, size, and shape) might bestow further favorable traits that could improve the material's efficacy for pollutant remediation. The complex surface modification chemistry of nanomaterials, together with their customizable physical properties, provides substantial benefits compared to current approaches dealing with environmental contaminants. Techniques designed as a mixture of multiple distinct materials (composites/hybrids), acquiring certain desirable features from each of their constituents, are possibly more stable, selective, and efficient over techniques founded on a single nano-platform. Once we compare the utilization of nanomaterials alone, gluing nanomaterials to a scaffold may be an alternate strategy to boost the material's

stability. The functionalization of a compound with specific substances accountable for addressing pollutant molecules of concern may boost the material's efficacy and selectivity [2–4].

The material used for remediating pollution should not necessarily be another pollutant itself after its use. So, for this application area, biodegradable materials are of particular interest [5]. In addition to increasing the trust and recognition by consumers of a specific technology, the use of biodegradable materials may also provide a more green and safe alternate route to remedy environmental contaminants, since there is no creation of product wastes to be discarded after use. In addition, there is a particularly strong appeal for new technologies that can leverage the targeted capture of contaminants to overcome low-efficiency results generated by direct targeting. Therefore, in order to obtain materials that can cope with a range of challenges related to the removal of contamination, several studies have been conducted, which focus on the use of nanotechnology principles and combine them with chemical/physical or mechanical modifications of material surfaces [4–6]. Some of the most significant challenges that should be considered while developing novel nanomaterials for the remediation of the environment include target selective capture, cost efficiency, easy preparation, green synthesis, nontoxicity, biodegradable feature, recycling, and possible recovery after utilization. Despite the promising benefits of nanostructured materials stated above, some nanomaterials are fundamentally nonstable in normal conditions and hence require specific procedures for the preparation of nanomaterials at the nanoscale. To avoid agglomerations and to improve monodispersity and stability it is necessary to carry out additional operations. Another factor that could limit their application is the feasible poisonousness of metal-based NPs included in remediation, together with their byproduct and recovery expenditures originating at the remediated location. Therefore, it is important to obtain a thorough knowledge of the nanomaterial features, their manufacturing processes, and performance improvement to identify excellent nanomaterials that are able to cope with environmental challenges.

This chapter aims to deliver an overall overview of the latest developments made in the design of nanostructured materials and/or composites employed for the treatment of the environment from different kinds of contaminants. Filtration, photocatalysis, chemical redox processes, adsorption, and absorption, as described in Fig. 17.1, are among a series of feasible routes that could remove contaminants [1, 3, 5]. For the methods mentioned in Fig. 17.1, some kinds of materials that could be utilized are also reported. For the case of distinct kinds of products that might be used for environmental remediation, it is to the best of our knowledge that no classification has been performed. Accordingly, the current chapter will focus on the different nanotechnologies as well as the diverse kinds of materials involved in environmental remediation applications. Particularly, it will focus on three major classes of nanomaterials reported in the literature: inorganic, polymer-based, and carbon-based nanomaterials and nanocomposites.
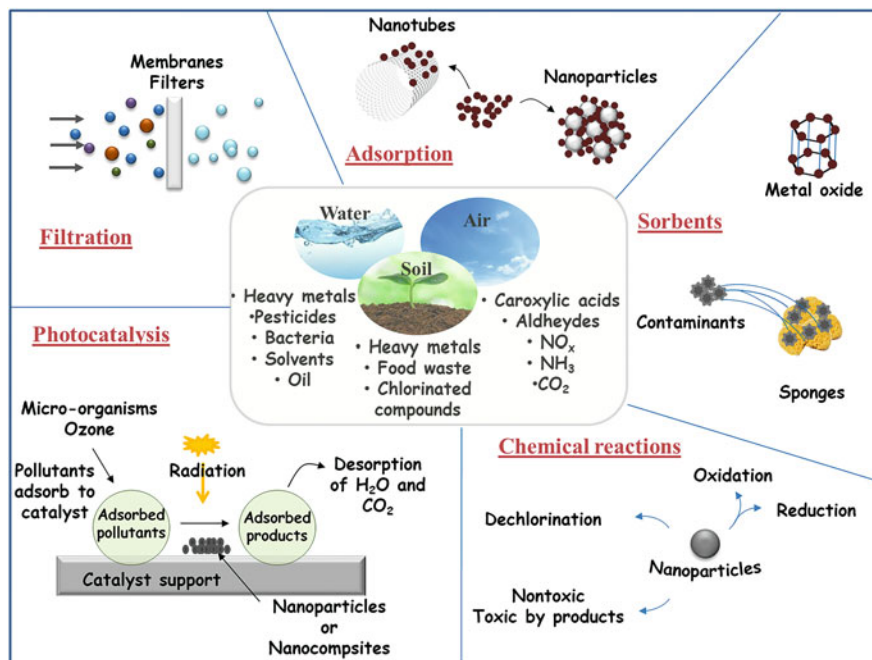
Fig. 17.1 Technologies used for environmental remediation

17.2   Nanotechnologies Used for Environmental Remediation

17.2.1 Photocatalysis

Advanced reduction processes (ARPs) and advanced oxidation processes (AOPs) are very potential environmental remediation alternatives, particularly for mediums that enable the transmission of light, such as water and atmosphere [7, 8]. The generation of highly reactive oxygen species (ROS), primarily superoxide radical anions ($O_2^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$), characterizes the above processes. In an aqueous medium, $HO^{\bullet}$ is the most powerful oxidant, $E_0\left(HO^{\bullet}, \frac{H^+}{H_2O}\right) = 2.73$ V vs.NHE [9]. Positive vacancies on the photocatalyst surface (usually designated as h^+) are likewise highly oxidant, $E_0 = 2.53$ V vs. SHE [10]. The occurrence of ROS assures an elevated reactivity (quick reactions) and poor selectivity (no differentiation among reducible and oxidizable molecules). Currently, AOPs are being widely utilized, more particularly for the remediation of our environment, and therefore our emphasis will be on them in upcoming sections. In AOPs, heterogeneous photocatalysis has been extensively utilized, with complete mineralization of both inorganic and organic contaminants being achieved in a number of cases [7, 8]. AOPs utilize various kinds of near-ultraviolet/visible
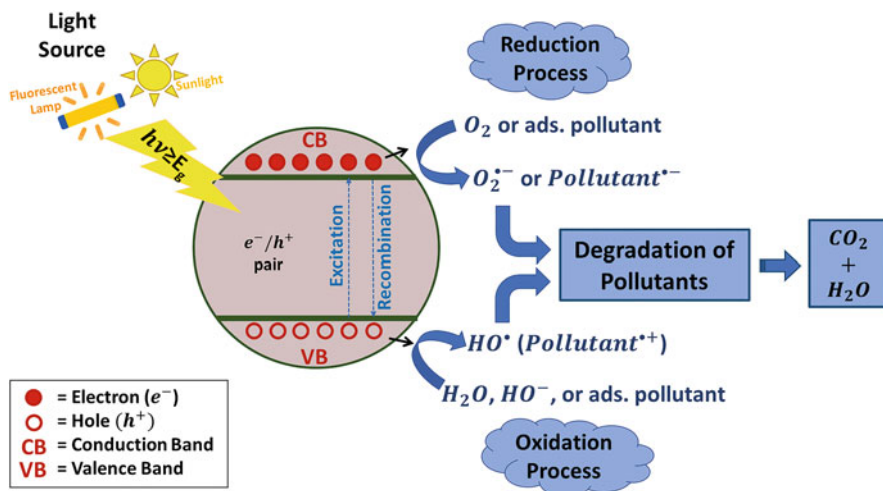
Fig. 17.2 Photocatalysis processes of a semiconducting photocatalyst in water containing pollutants

lamps (like LED) and, preferably, sunlight. The effectiveness of the photocatalytic processes is enhanced if there are sufficient overlaps among the photocatalyst absorption and the radiation spectrum of sunlight. Indeed, this is among the major defies in this area, and it has been addressed in a variety of ways, like altering the crystalline structure of the photocatalysts by doping and/or introducing defects.

The utilization of semiconducting materials, preferably in the form of nanoparticles or films placed on substrates, is relied upon for heterogeneous photocatalytic processes. Nanoparticles tend to be agglomerated when they are utilized, due to the decrease of some surfaces and thus their reactivity. The reactive surface of the hemi-sphere in contact with the surface will not exist once nanoparticles are made as films, considering that they display a sphere-like shape, due to a considerable deficit of the active surface in the product. The bandgap energy (E_g) separating the conduction band (CB) and the valence band (VB) should be identical to or smaller than the incident photon energy ($h\nu$), which means $E_g \leq h\nu$. As demonstrated in Fig. 17.2, the photons are adsorbed and the electrons (e^-) propagate from VB to CB, creating vacancies (holes, h^+) in VB and forming pairs of electron-hole ($e^- - h^+$).

Pairs of $e^- - h^+$ are extremely nonstable and typically annihilate in a few nanoseconds, going back to the starting state before the absorption of photons. A relatively small fraction of $e^- - h^+$ separates, which is governed by the experiment settings and, in particular, the material being studied. The magnitude of E_g is the essential parameter for the success of photocatalysts. To prevent undue energy consumption of irradiation lamps, a preference should be given to (nano)materials having E_g magnitudes within the energy spectrum of photons supplied by sunlight.

The main reactions that happen during the $e^- - h^+$ segregation in an aqueous media involve the oxidation of adsorbed H_2O to $HO^\bullet$ and the reduction of O_2 to $O_2^{\bullet-}$ (Fig. 17.2). The foregoing equations are the most significant reactions occurring [11, 12]:

$$H_2O + h^+ \rightarrow H^+ + HO^\bullet \tag{17.1}$$

$$HO^- + h^+ \rightarrow HO^\bullet \tag{17.2}$$

$$(O_2)_{ads} + e^- \rightarrow O_2^{\bullet-} \tag{17.3}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{17.4}$$

When other substances are adsorbed on the surface, they could likewise be reduced or oxidized:

$$Pollutant + h^+ \rightarrow Pollutant^{\bullet+} \tag{17.5}$$

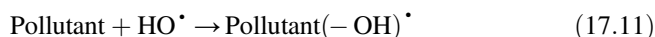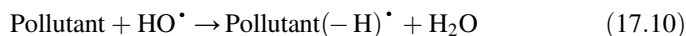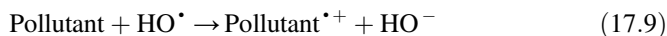$$Pollutant + e^- \rightarrow Pollutant^{\bullet-} \tag{17.6}$$
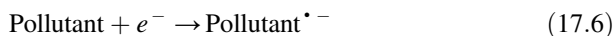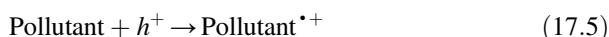
The reactions of adsorbed substances could enhance the effectiveness of a pollutant's removal, but they could open new pathways which result in products other than those resulting from ROS reactions and could also have different toxicities and stabilities.

During heterogeneous photocatalytic processes, additional ROS can also be produced. For instance, H_2O_2 is created by the dismutation of $HO_2^\bullet$ and $O_2^{\bullet-}$ and can then be reduced to $HO^\bullet$ as shown in the following equations [13, 14]:

$$O_2^{\bullet-} + HO_2^\bullet + H^+ \rightarrow H_2O_2 + O_2 \tag{17.7}$$

$$H_2O_2 + H^+ + e^- \rightarrow HO^\bullet + H_2O \tag{17.8}$$
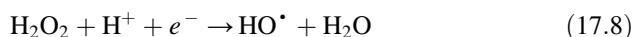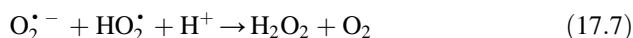
The findings from experiments on the great differences in reactivity dependences with $\left[O_2^{\bullet-}\right]$ and $[HO^\bullet]$ or other ROS support the view that $HO^\bullet$ is primarily accountable for degrading organic contaminants [11].

$HO^\bullet$ commonly combines with non-saturated functional groups to generate $HO^\bullet$ adducts, but it could alternatively interact with $H^\bullet$ abstraction to form radical entities with H-deficiency, or with an e^- oxidation to form a radical cation and HO^-:

$$Pollutant + HO^\bullet \rightarrow Pollutant^{\bullet+} + HO^- \tag{17.9}$$

$$Pollutant + HO^\bullet \rightarrow Pollutant(-H)^\bullet + H_2O \tag{17.10}$$

$$Pollutant + HO^\bullet \rightarrow Pollutant(-OH)^\bullet \tag{17.11}$$

The intermediates Pollutant$^{\bullet+}$, (Pollutant($-H$)$^\bullet$, and (Pollutant $- OH$)$^\bullet$ are of short life and would endure chemical reactions via distinct reaction routes, resulting in a

number of byproducts where the majority of them will hydroxylate and thus being soluble in water, greatly polar, and easily adsorbed on mineral surfaces like clays, potentially increasing their residence time in the environment. When a sufficient period is given for the reactions to occur, it may eventually result in mineralization, which means the conversion toward the most oxidized ionic substances (SO_4^{2-}, PO_4^{3-}, NO_3^-, CO_3^{2-}, and so on). Nevertheless, some kinds of refractory materials, like triazines, have been shown to create a stable intermediate that will not react anymore [15].

For different situations, $HO^{\bullet}$ reactions occur extremely quickly, with bimolecular rate constants of $k > 10^9$ $M^{-1}s^{-1}$ or more, which is near to or at the diffusion-controlled limit in water, and in a non-selective fashion. Throughout the oxidation of aromatics, h^+ and $HO^{\bullet}$ are shown to differ in regioselectivity and could provoke different materials [16]. Lately, it has been demonstrated that for similar processes, there are competing routes among the oxidation of chemisorbed species by h^+ and the reaction with $HO^{\bullet}$ [17, 18].

It is especially essential to note that the heterogeneous photocatalytic process is a superficial process, which means that the reactive substances must be diffused from the core of the solution to the surface, become adsorbed (perhaps with some changes in the structure), endure reactions, desorb, and diffuse back inside the solution [11]. The prospect of ROS being formed at the surface and migrating within the solution has been investigated, and it was demonstrated that $HO^{\bullet}$ is diffused just a few hundred Angstroms down from the surface inside the aqueous medium. ROS migrates just a couple of atomic lengths beyond the surface, according to ESR experiments. As a result, if the molecules are not adsorbed, they will not undergo reactions through heterogeneous photocatalysis. Since the adsorption/desorption equilibrium would be shifted as the reaction progresses, only a small amount of starting adsorption is required.

Titanium dioxide (TiO_2) is one of the widely utilized photocatalytic (nano)-materials for the remediation of the environment (water and atmosphere), both in suspensions and thin films [19]. It has good photochemical stability, less toxic, inexpensive, easily accessible, simple to recover, and so on. Its chief limitation is the limited level of spectrum overlapping with sunlight radiation, which is approximately 5% at ground level, reducing the degradation efficacy of TiO_2 photocatalysts under sunlight [19]. As a result, significant attempts are being made to enhance its photocatalytic efficacy by forming nanocomposites with other products [20–22], producing two-dimensional (thin films and nanosheets) [23] and three-dimensional (nanowires and nanotubes) nanostructures [24] and introducing imperfections into the crystalline system [25]. TiO_2 nanomaterials tend to agglomerate, resulting in a loss of photoactivity and active surface. Hence, sonication may be employed prior to or throughout the procedure to prevent agglomeration [26]. The resultant separation is not definite, since the equilibrium is favorable to reaggregate; however, the agglomeration process's kinetics could be sluggish. Prolonged ultrasound periods may not always aid deagglomeration. A significant issue regarding the utilization of nanoparticles, particularly in suspended form, was the ability to remove them out of the medium before discarding the photocatalysts [27]. Ultracentrifugation and

nanofiltration are frequent treatments for this; however, they require large energy costs, which need to be prevented.

Given that the reactions occur among entities that are adsorbed on the nano-photocatalyst's surface, the photocatalytic conversion of a contaminant could be appropriately characterized via an altered Langmuir-Hinshelwood kinetic model, as shown in the following expression [28]:

$$r = k_{\mathrm{LH}} \cdot \theta = k_{\mathrm{LH}} \cdot \frac{K_{LH} \cdot C}{(1 + K_{\mathrm{LH}} \cdot C)} \tag{17.12}$$

Here θ (cm^2) represents the material's surface coverage, k_{LH} (mol/s cm^2) is the kinetic rate constant per unit of surface area, and C is the contaminant concentration after the equilibrium of adsorption is achieved. When the Langmuir model was rigorously obeyed, the Langmuir-Hinshelwood adsorption constant (K_{LH}) will be equivalent to the Langmuir adsorption constant (K_{eq}, see Eq. 17.15). Typically, the amount of contaminants is very small, hence $K_{\mathrm{LH}} \cdot C \lll 1$, and the process rate subsequently falls to pseudo-first-order kinetics:

$$r = k_{\mathrm{LH}} \cdot K_{\mathrm{LH}} \cdot C = k_{\mathrm{app}} \cdot C \tag{17.13}$$

The mathematical model of first order typically fits the experimental kinetics very well. This could lead to estimating the rate constant and half-life duration of various processes and comparing rates of eliminating diverse contaminants. Generally, the size variations and the modification in the active surface display a significant impact on the rate as well as the degradation concentration. In this area, a large number of studies and techniques are under investigation to improve the photocatalytic performance of nanomaterials and nanocomposites under sunlight.

17.2.2 Adsorption

Adsorption represents a surface phenomenon wherein a material known as "adsorbate" which is submerged in an aqueous solution (it could even be a gas) diffuses in the direction of the adsorbent's surface and interacts with the adsorbent, causing it to be held (Fig. 17.3). This occurrence of interaction/retention is greatly determined by the physicochemical features of both adsorbate and adsorbent. They are of two natures: physical and chemical, which are known as physisorption and chemisorption, respectively. Physisorption corresponds to weak interactions which could be easily broken (for example, by low heating). Chemisorption corresponds to more strong interactions (but less strong than chemical bonds) which are hard to be broken. The adsorbate–adsorbent interactions have a significant impact on the former's electronic structure, which determine their interactions with the surface throughout the process of adsorption and could boost their reactivity in heterogeneously catalytic procedures [29]. As a result, the entire process of adsorption is dependent on the available surface and its porosity, two variables that grow
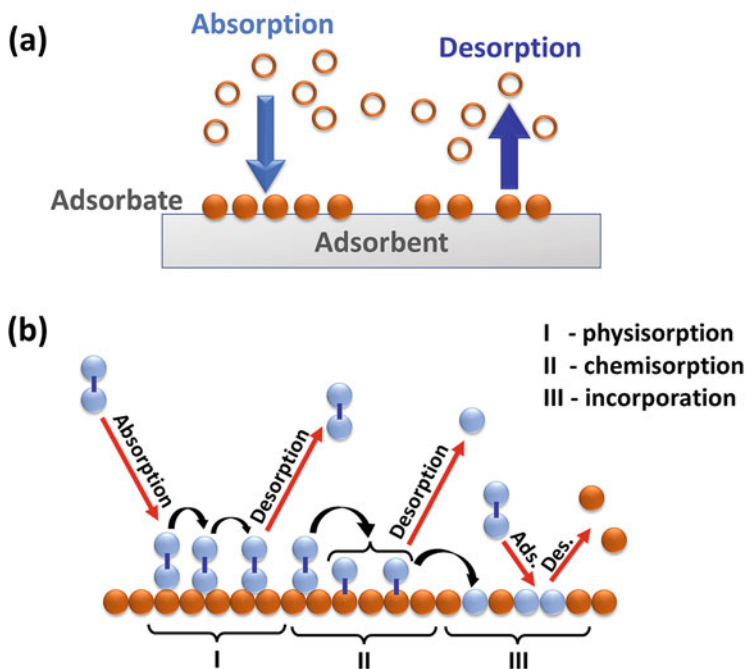
Fig. 17.3 Schematic illustrations of adsorption/desorption processes

dramatically at the nanoscale level. Not every place on the surface is accessible to interact with the adsorbate. Depending upon the chemical features of the adsorbate, the locations of interaction, or binding sites, should meet certain characteristics associated with the density of electrons, acidity, as well as shape. Accordingly, the most popular and most simple method of adsorption is Langmuir's model, which makes the following presumptions: (1) the adsorption–desorption procedure reaches equilibrium, (2) the catalyst's surface is homogeneous, (3) the various linking adsorption points on the surface have the same energy, (4) the adsorbent–adsorbate interactions occur via the same type of functional groups, (5) every single linking point connects with just one adsorbate species, (6) a single layer of adsorbate is created on the surface, and (7) there exists no adjacent interactions among adsorbed species when they are on the surface [15–17]. Even though these hypotheses oversimplify the issue, they result in the widely recognized Langmuir adsorption isotherm. Regardless of its clearness, the term "isotherm" relates to a specific temperature, thus each adsorption investigation should be conducted during temperature-controlled settings that are comparable with the ones that would be used in the environmental remediation processes.

When the equilibrium $A + S \rightleftarrows A_{ads}$ (where A_{ads} is the adsorbed species, S is the adsorbent, and A is the adsorbate) is reached, the rates of adsorption and desorption are equal:

$$r_{ads} = k_{ads} \cdot [A] \cdot [S] = k_{des} \cdot [A_{ads}] \qquad (17.14)$$

Here k_{des} and k_{ads} represent, respectively, the rate constants for desorption and adsorption. $[S]$ denotes the number of free binding points per unit of adsorbate surface. Hence:

$$K_{eq} = \frac{k_{ads}}{k_{des}} = \frac{[A_{ads}]}{[A] \cdot [S]} \qquad (17.15)$$

The Langmuir isotherm could be stated as mentioned in Eq. (17.16), by considering the overall number of binding locations (occupied and unoccupied) as $[S]_{tot} = [S] + [A_{ads}]$ and identifying the portion of populated binding locations as $\Theta = \frac{[A_{ads}]}{[S]_{tot}}$.

$$\Theta = \frac{K_{eq} \cdot [A]}{1 + K_{eq} \cdot [A]} \qquad (17.16)$$

This equation could be linearized by applying the reciprocal. Generally, a linear behavior occurs once $K_{eq} \ll 1$, while the system attains saturation once $K_{eq} \gg 1$ [30].

Considering that the various hypotheses (1)–(7) reported above fail, various models have been developed, which involve surface inhomogeneity, interactions among adsorbate molecules on the surface, the probability of multiple adsorptions, and the possibility of forming multilayers of adsorbate. Therefore, the Freundlich isotherm (Eq. 17.17) accounts for surface heterogeneity because the adsorption heat, ΔH_{ads}, varies with the number of occupied binding points (sites with the most favorable interactions being engaged first), whereas homogeneous surfaces with comparable active sites display an unchanged ΔH_{ads} [29, 30].

$$\frac{x}{m} = K \cdot C^{\frac{1}{n}} \qquad (17.17)$$

here, x represents the adsorbate mass, m denotes the adsorbent mass, and K and n are specific constants for each adsorbate and adsorbent at a certain temperature.

The Temkin adsorption isotherm accounts for adsorbate molecules' interactions when they are on the surface, arguing that these interactions decrease the adsorption heat and utilizing this method to adjust the Langmuir model's equilibrium rate constant [29, 30].

The Adsorbent's surface can include functional groups that are ionizable which can be either protonated or deprotonated based on the pH of the environment. The surface is neutral at a pH level that corresponds to the point of zero charge (pH_{PZC}). The surface is charged negatively if $pH > pH_{PZC}$ and charged positively if $pH < pH_{PZC}$. It can be feasible to predict if the interactions among the adsorbate and the binding locations would be favorable or unfavorable by looking at the pH of the environment and the pK_a values of various ionization sites on the molecule. Although it is sometimes overlooked, the research investigation of adsorption

process at regulated pH conditions is essential to the efficacy of adsorption as a remediation approach.

Nano-adsorbents, like other nanomaterials employed in environmental remediation, are supposed to be abundant, inexpensive, simple to utilize, highly stable (mechanically and chemically), safe for both human health and the environment, recyclable, and reusable. Most importantly, after they reach the end of their practical lifespan, the produced residues should be simply inertized or valorized to prevent residue accumulation. Nano-adsorbents should also be effective (possess elevated adsorption yields), enable simple on-demand adsorbates' desorption, possess high selectivity wherever feasible, and be easily separated from the environment. It is essential that nanomaterials employed in environmental treatment do not create additional forms of contamination, that is why biodegradable nanostructured materials are being extensively explored [31]. Nano-adsorbents are often hard to separate out except if nanofiltration is employed, which is a costly separation procedure. As a result, magnetic nanoparticles may be integrated with the nano-adsorbents to facilitate their separation using a magnetic field [26, 32].

Like other kinds of nanomaterials, nano-adsorbents could be also synthesized using the well-known top-down and bottom-up approaches [31]. Nevertheless, bottom-up synthesis of nanomaterials is preferable because it provides better control of the procedures as well as the shape, size, and characteristics of the final compounds. The emphasis is nowadays being directed to the biosynthesis of nanostructured materials, with the hope that they would display higher biodegradability or lesser toxicity [33].

Adsorption techniques are effective for removing a wide range of persistent and mobile organic substances from various kinds of liquid and gaseous discharges. The adsorption techniques are often simple and inexpensive to implement. Zeolites, polymers, activated carbons (ACs), and many other materials are presently employed as adsorbents, and many have been created by valorizing various kinds of wastes [34]. Nanomaterials' advancements have resulted in a significant rise in adsorbents' effectiveness and adsorption rate, owing primarily to the significant increase in active surface and porosity, as well as the existence of a much greater number of active sites. Nano-adsorbents are currently employed mostly for the removal/reduction of dyes, oil, and heavy metals from water. They have the potential as well to remediate the so-called toxic forever chemicals like perfluoroalkyl and polyfluoroalkyl substances (PFAS) [35].

Several publications have evaluated the adsorption potential in the remediation of the environment. Even though adsorption has been utilized for this task for a long time, its use in the form of nanomaterials is still in its early stages. There are many basic investigations that have to be conducted to effectively manage the procedure and its related factors. The potential changes in the surface (functionalization) for carrying out specific adsorption procedures, or the successful deposition as films for effective flow chemistry heterogeneously catalytic procedures, appear highly desirable.

17.2.3 Chemical Redox Processes

Chemical redox processes are a class of catalytic procedures that involve an exchange of electrons or ions with the medium to reach the reagents. Generally, a material, either at the nanoscale or not, emits ions inside the volume of the medium or undergoes oxidation to release electrons (e^-). As a result, for both situations, the process could be identified as a homogenous process, occurring inside the volume of the medium rather than on its surface. However, the use of nanomaterials aids since, as described previously in the above parts, the surface-to-volume ratio promotes the procedures occurring in comparison to the employment of aggregates of nanoparticles or macroparticles. The following subsections cover the two primary processes in this category.

17.2.3.1 Fenton and Photo-Fenton Processes

H_2O_2/Fe^{2+} combinations have particularly strong oxidation characteristics in acidic media, which is explained by a sequence of events known as Fenton reactions [36], wherein reactive oxygen species are created, mostly $HO^\bullet$ radicals (Eqs. (17.18) and (17.19)). Fe^{3+} regenerates at proper acidic circumstances (pH ~2.7–2.8) and various additional reactive oxygen species are created (Eqs. 17.20–17.23). $HO_2^\bullet$ may also regenerate Fe^{2+} as shown in Eq. (17.24). With the ex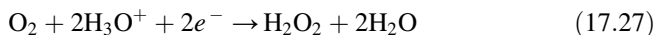istence of a Fe source and H_2O_2, sunlight or lamps simulating sunlight irradiation enable pollutant degradation. Such a process is referred to as the heterogeneous photo-Fenton process, and it has the potential to perform very well in the remediation of the environment. Fe^{3+} complexes could regenerate Fe^{2+} under irradiation ($\lambda \geq 300$ nm), as evident in Eq. (17.26). Lastly, throughout the electro-Fenton process, H_2O_2 is created in situ following Eq. (17.27). and Fe^{2+} is regenerated through Eqs. (17.21) and (17.22).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^- \tag{17.18}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{17.19}$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^- \tag{17.20}$$

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \tag{17.21}$$

$$FeOOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \tag{17.22}$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \tag{17.23}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{17.24}$$

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{17.25}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^\bullet \tag{17.26}$$

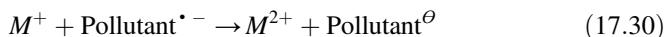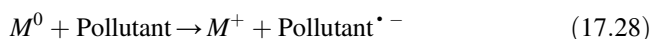$$O_2 + 2H_3O^+ + 2e^- \rightarrow H_2O_2 + 2H_2O \tag{17.27}$$
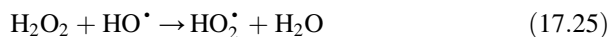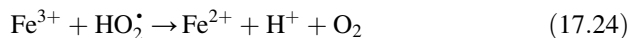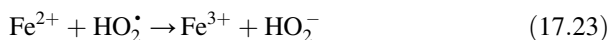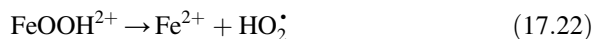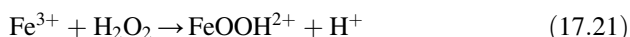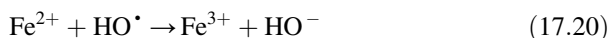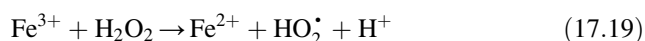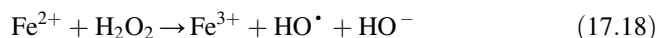
The various reactive oxygen species produced are extremely reactive and capable of effectively transforming contaminants existing in the media, eventually causing mineralization. Fenton processes offer many benefits such as iron being inexpensive, widely accessible, and non-hazardous, as well as H_2O_2 being simple to manage. Pharmaceuticals, phenols, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) have all been demonstrated to be degraded via Fenton processes [37]. One significant disadvantage is that Fe salts precipitate, and the inclusion of Fe^{2+} and H_2O_2 implies high economic costs. Consumption of energy also increases the expenses of electro-Fenton procedures. For that reason, photo-Fenton is widely employed utilizing sunlight, which significantly minimizes related expenses.

17.2.3.2 Metal-Based Processes

Nanoscale metal-based processes provide the advantage of using zero-valence features (Metal^0, M^0), assuming the metal's potential for reduction is adequate. The processes that occur are one-electron reduction or a sequence of sequential one-electron reductions:

$$M^0 + \text{Pollutant} \rightarrow M^+ + \text{Pollutant}^{\bullet-} \tag{17.28}$$

$$M^0 + \text{Pollutant}^{\bullet-} \rightarrow M^+ + \text{Pollutant}^{\Theta} \tag{17.29}$$

$$M^+ + \text{Pollutant}^{\bullet-} \rightarrow M^{2+} + \text{Pollutant}^{\Theta} \tag{17.30}$$

Here "$^{\bullet-}$" denotes a one-electron excess and "$^{\Theta}$" indicates a two electrons excess. The mechanisms described in Eqs. (17.28 and 17.29) often result in the breakdown of C–X bonds, wherein X is an atom that is electronegative with a large electron density charge, like halogen. After this process, the contaminant intermediate takes H^+ or $H^\bullet$ from the solvent (typically water) and generates reduced products:

$$H_2O + \text{Pollutant}^{\bullet-} \rightarrow \text{Reduction Products} \tag{17.31}$$

According to this approach, reactions with zero-valence nano-metals may be used to degrade halogenated solvents or halogenated aromatic compounds, which have extremely lengthy environmental lifetimes and are typically resistant to other remediation procedures. Due to Fe's excellent reduction potential, Fe^0 nanomaterials are commonly utilized for this intent [38, 39]. Nano-metals with zero-valence often undergo oxidation on the surface, permitting reactions with other substances that could exist with a larger reduction capability. This might be effective for heavy metals contamination removal. Certain nano-metals with zero-valence have also been demonstrated to exhibit antibacterial or antivirus capabilities, making them appropriate for disinfecting interior environments (such as inside buildings) and remediating microbe or virus-infested water bodies [40].

The usage of bimetallic nanomaterials has been investigated in order to benefit from the existence of metals that have various reduction potentials, which could boost contaminants' degradation [41–43]. This technique additionally contributes to addressing the earlier reported issues of nanomaterials' agglomeration and improving the stability of zero-valence nano-metals. Noble nano-metals have been also utilized to construct bimetallic nanomaterials, with improved rates of pollution reduction; however, this increases significantly the costs because of the cost of the utilized noble metals (Au, Pd, etc.) [41–43].

17.2.4 Nanofiltration

Filtration is a basic physical separation technique that separates objects from fluids (either liquid or liquid) with the help of a medium that serves as a filter having a particular structure that penetrates the fluids and maintains the objects of specific dimensions which depend on the pore size of this filter medium. Membrane filters incorporating material sheets, granular deep bed filters, or surface filters with sieves are some examples of useful filter media [44]. Pressure is applied to drive the process of filtering, either by applying it to the input side or by applying a vacuum to the filtrate side.

As shown in Fig. 17.4, the technologies of membrane filtration are categorized based on membrane selectivity (determined by membrane pore size and the associated size of particles excluded) and the needed applied pressure [46]. They could be classified as follows: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Here, MF uses the largest particle/pore sizes, while RO uses the smallest ones. The needed applied pressure varies with the filtering technique and rises as the size of membrane pores decreases as follows: MF > UF > NF > RO.

MF displays an exclusion size ranging between 0.1 and 10 μm and needs a driven pressure of roughly 0.2–5 bar. It is appropriate to eliminate most bacteria and cells, clays, Mycoplasma, *E. coli*, algae, etc. UF exhibits an exclusion size ranging between 0.01 and 0.1 μm and needs a driven pressure of about 1–10 bar. It is appropriate to eliminate some viruses, proteins, natural organic matter, humic acids, etc. MF shows an exclusion size ranging between 0.001 and 0.01 μm and needs a driven pressure of roughly 5–10 bar. It is appropriate to remove multivalent ions, heavy metals, synthetic dyes, carbohydrates, etc. MF presents a smaller exclusion size ranging between 0.0001 and 0.001 μm and needs a much higher driven pressure of about 10 up to 150 bar. It could eliminate practically the different objects other than water due to being built of semi-permeable membranes that only let water pass through.

Pretreatment of the input to the membrane filters is very important because it reduces fouling and enhances the functionality of membranes [47, 48]. For the pretreatment of the input in MF, traditional multimedia filtering processes and coagulation have been largely employed. Furthermore, considering the sequence of graduated size exclusion, each membrane stage could serve as a pretreatment for
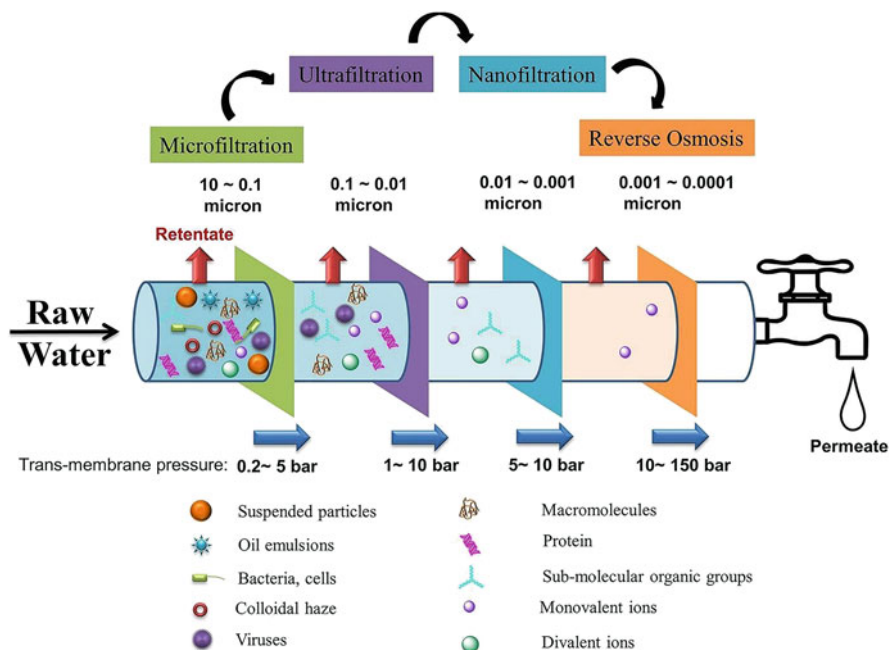
Fig. 17.4 Schematic illustration for water treatment using membrane filtration technologies. (Reproduced with permission from [45])

the succeeding one. Simply, microfiltration could be employed as a pretreatment for ultrafiltration, ultrafiltration as a pretreatment for nanofiltration, and ultrafiltration and nanofiltration as pretreatments for reverse osmosis.

17.2.5 Nano-Sensors

Continuously monitoring air pollution constitutes one of the vital and fundamental requirements in terms of controlling environmental pollution [49]. One of the risks of modern industrialization involves the release and spread of harmful and hazardous gasses (like H_2S, NH_3, NO_2, etc.). Inevitably, industry cautions are sometimes tardy to detect leakage of gasses. Furthermore, numerous issues, arising from the occurrence of heavy metal ions and other contaminants in water, air, and soil, emphasize the requirement to develop some technologies that are able to detect the contaminants earlier than that their amounts achieve dangerous levels in the environment. Once the technologies for pollution detection become more available and inexpensive, decision-making regarding the environment, monitoring of the ecosystem, and process management will be improved. Rapid and precise sensors capable of detecting contaminants at the molecular level will efficiently improve human capabilities to promote long-term human health and environmental sustainability.

Generally, sensors are basically a sort of energy converters, which are able to detect mechanical, chemical, and physical characteristics in their surroundings and show them as output signals (frequently optical or electrical signals). Consequently, numerous sensors have been designed and created for usage for diverse purposes. Interestingly, nano-sensors are one of the widely used sensors nowadays [50–52]. A nano-sensor is basically made up of nanostructured materials, accompanied by an identifying element and a signal transduction technique. Nano-sensors can be categorized into magnetic, optical, mechanical, and electrochemical nano-sensors depending on signal transduction processes. They are biological, physical, or chemical nanoscale sensors that could measure variations at the nanosized scale with extremely high precision and sensitivity, either quantitatively or qualitatively. The main essential features that contribute to the widespread trust in information provided by these nano-sensors are high detection power, high sensitivity, high accuracy, and the capacity to measure numerous kinds of species in the environment at the same time.

17.3 Examples of Nanomaterials Used for Environmental Remediation

17.3.1 Inorganic Nanomaterials

Various metal-based nanostructured materials have been reported for the remediation of a wide range of pollutants; however, most of these investigations have focused on the elimination of chlorinated organic compounds and heavy metals from water. Metal and metal oxide nanostructured materials are very effective nano-adsorbents possessing several advantages like excellent adsorption capacity and rapid kinetics. Some examples of metal-based nanomaterials examined for various environmental remediation applications are outlined in Table 17.1. Over the past years, effective physical and/or chemical synthesis approaches have been widely studied to obtain metal and metal oxide nanostructured materials with controlled shapes, high stability, and monodispersity. Hydrothermal, co-precipitation, sol-gel, etc., are some of the most extensively employed synthesis methods that provide large yields [54, 55].

Silver nanoparticles (Ag-NPs) have been used for disinfecting water due to their good antiviral, antifungal, and antibacterial activities [93–95]. Ag-NPs of very small size ($<$10 nm) were reported to be extremely toxic to *E. coli* and *P. aeruginosa*. They could additionally hinder viruses from attaching to host cells by attaching to the virus's glycoproteins preferentially. Slightly larger nanoparticles (~10 to 25 nm) showed lesser antibacterial activities [96]. Furthermore, Ag with nano-triangular shapes showed enhanced bactericidal activities in comparison to Ag nanospheres and Ag nanorods, highlighting the relevance of nanoparticle shapes in inducing their desirable effects [97, 98]. Ag-NPs have been combined with a variety of different materials, including polymers and metal oxides, in order to improve the global

Table 17.1 Some examples of metal-based nanomaterials applied for environmental remediation

Products	Applications	References
Silver nanoparticles	Water disinfection (antibacterial activities)	[53–57]
	Degradation of dyes (e.g., Congo red (CR), methylene blue (MB), methyl orange (MO), and rhodamine B (RhB))	
	Nano-sensors (Hg^{2+} and Fe^{3+} metal ions)	
Silver-based nanocomposites (e.g., combination with polymers or other oxide nanomaterials)	Water disinfection (antibacterial activities)	[58–62]
	Adsorption of dyes (like MB, acid red 37)	
	Removal of contaminants (like iodide I^-)	
	Filtration	
TiO_2 NMs	Dye degradation (MB, MO, and auramine O (AO))	[63–67]
	Remediation of eutrophic shallow freshwater systems	
	Antimicrobial and larvicidal activities	
Doped TiO_2 NMs	Dye degradation (MB, RhB, and basic yellow 28 (BY28))	[68–72]
	Degradation of heavy metal ions (like Cr^{6+})	
	Antimicrobial activity (*S. aureus* and *E. coli*)	
	Photocatalytic hydrogen production	
Titanate NMs	Catalytic reduction of gases—nitric oxide	[73–75]
Mixed oxide NMs	Degradation of dyes	[76–79]
Magnetic NMs	Elimination of various heavy metals	[80–85]
	Degradation of dyes	
Bimetallic NMs	Reduction of heavy metal ions (like Cr^{6+})	[86–92]
	Reduction of 4-nitrophenol to 4-aminophenol	
	Detection of Cr^{3+}	
	Degradation of dyes	

effectiveness of the resultant nanocomposites. This point will be further addressed in the upcoming subsections.

Titanium oxide nanomaterials (TiO_2 NMs) are another well-known explored metal-based product for environmental remediation applications. Because of their fascinating features such as energy-converting, gas sensing, electronic, photocatalytic, and semiconducting traits as well as their nontoxicity and lower cost, TiO_2 NMs have been widely investigated for wastewater treatment, surfaces'

self-cleaning, and air purification applications [99]. TiO_2 NMs could be activated by an illumination source and hence are considered as good photocatalysts to eliminate organic pollutants from diverse media. TiO_2 NMs can produce highly reactive oxidants such as hydroxyl radicals, which act in disinfecting microorganisms including algae, viruses, bacteria, and fungi. Generally, TiO_2 itself possesses a somehow low photocatalytic activity, hence, it is frequently doped with other transition metal ions to improve its efficiency. As a result, numerous investigations have been conducted on metal ions doped TiO_2 NMs. For instance, Ag-doped TiO_2 nanofibers (NFs) are prepared via a hydrothermal process and then tested as photocatalysts for degrading different dyes (crystal violet (CV), Congo red (CR), malachite green (MG), and Methylene blue (MB)) under direct sunlight irradiation [100] and 2-chlorophenol under UV light illumination [101]. As well their antibacterial activities are tested against *E. coli* and *S. aureus*. In comparison to control TiO_2 NFs, Ag-doped TiO_2 NFs demonstrated both good photodegradation and antibacterial efficiencies. This enhancement had been ascribed to the following possible variables: an appropriate content of silver on the surface that efficiently captures photo-induced holes and electrons, a rapid movement of photo-induced electrons to the adsorbed oxygen available on the surface of the NFs, an increase in the number of surface hydroxyl groups, and an expansion of the response interval to light to the visible spectrum. Recently, Y. Slimani et al. [69] prepared Ce-Sm co-doped TiO_2 NPs with various doping levels via a sol-gel auto-combustion process, which are then tested as photocatalysts for degrading MB dye. In comparison to control TiO_2 NPs, Ce-Sm co-doped TiO_2 NPs demonstrated better photodegradation efficiency. Indeed, excellent performances are obtained for NPs with a doping level of 0.5%, wherein the photodegradation efficiency achieved about 98% within 30 min and a reaction rate constant of 0.0616 min^{-1}. These performances are reported to be much better than many other oxide compositions. It was established that h^+ and $\bullet O^{2-}$ are the utmost important active species in the photocatalytic degradation process. In addition, the reported nanophotocatalysts revealed high stability and can be definitely recovered and reused easily, suggesting their capability for real applications in the future.

Inorganic titanium oxide-based materials, called titanates, have also been studied for removing pollutants. For example, neutral, acidic, and basic titanate nanotubes (NTBs) have been prepared via hydrothermal technique by Chen's group [74], which are tested as catalysts to reduce NO with ammonia. For neutral, acidic, and basic pH environments, manganese oxide was incorporated into different titanate NTBs formulations to produce Mn-doped titanate nanotubes, titanate nanorods, and titanate nanosheets, respectively. The neutral Mn-doped titanate NTBs showed the highest surface area, excellent active species' dispersion, and the greatest active redox performance. Hence, neutral Mn-doped titanate NTBs possessed excellent catalytic reduction efficiency, while those prepared under basic conditions revealed insignificant activity. Different kinds of titanates, $ATiO_3$ where A is a divalent ion like Ba, Ca, Sr, Na, Ni, Co, etc., as well as their composites are widely investigated and numerous of them revealed enhanced environmental remediation performances [75]. $ATiO_3$ NMs combine both piezocatalytic and photocatalytic behaviors,

suggesting them as promising multifunctional nanomaterials for practical applications in the environment and energy. To improve their efficiencies, numerous approaches have been performed to alter $ATiO_3$ NMs via doping or substitution, including hetero-cations, combining them with other semiconducting (nano)-materials or carbonaceous materials. Also, the preparation methods, preparation environments, crystalline phase, etc., greatly govern the activity of $ATiO_3$ nano-catalysts. Several studies reported that the cubic $BaTiO_3$ NMs display lesser piezocatalytic and photocatalytic performances under ultrasonication than tetragonal $BaTiO_3$ NMs. In-depth investigations must be performed to figure out the exact facts that lead to the piezocatalytic and photocatalytic activities in $ATiO_3$ NMs. Although numerous research articles investigated the piezoactivity and photoactivity of $ATiO_3$ NMs, the majority of them concentrated on the degradation of organic dyes, while fewer interest was devoted to other kinds of contaminants. Accordingly, the efficacy of $ATiO_3$ NMs for environmental remediation applications should be well verified regarding other inorganic and organic contaminants such as pathogenic species, NO_x, heavy metals, pharmaceutics, herbicides, pesticides, etc. Also, the evaluation of their toxicity in water should be studied.

Other metal oxide nanomaterials also demonstrated good photocatalytic activities for degrading dyes and removing heavy metal ions from polluted environments. For instance, E. Hannachi et al. [102, 103] synthesized a series of NMs made of ZnO NPs doped with rare earth elements like Y, Ce, Yb, etc. via a low-cost simple sol-gel synthesis approach. The findings revealed that an optimal concentration of co-dopants could significantly improve the degradation efficiency as well as accelerate the degradation rate. Numerous other metal oxide nanomaterials revealed enhanced photocatalytic activities [104–106].

Furthermore, mixed oxide nanomaterials have been studied. For instance, mixed TiO_2–SiO_2 oxide materials are synthesized using titanium isopropoxide or titanium butoxide and bamboo as sources of titanium and silica, respectively [76]. These binary materials were tested for their ability to degrade methylene blue (MB) dye photocatalytically. The degradation rate of MB at different treatment durations revealed substantial photoactivity. It has been speculated that these composites could find real use in industrial wastewater treatment systems on a small scale. Overall, although mixed oxide nanomaterials have higher photoactivity in comparison to pure TiO_2 nanomaterials in the majority of cases, their real use is restricted to the mineralization of specific contaminants. In the literature, numerous mixed oxide nanomaterials showed an improved ability to eliminate a broad range of contaminants [77–79].

Moreover, magnetic metal-based and metal oxide-based nanosized adsorbents have particular appeal due to their ease of retention and separation from the water that is treated. Iron and iron oxide-based nanomaterials (NMs) have been widely documented in previous studies for the elimination of various heavy metals (including Hg^{2+}, Cr^{6+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+}), as well as for the degradation of some dyes [80–85]. Recently, spinel ferrites, hexaferrites, and multiferroic materials received great interest for applications in environmental remediation [107–115]. Nevertheless, there are some limitations to utilizing such kinds of NMs for
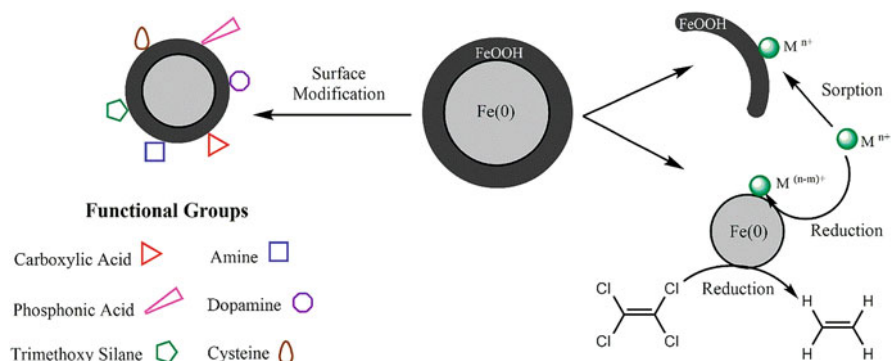
Fig. 17.5 Mechanism of degradation of heavy metals and chlorinated contaminants from aqueous systems utilizing core-shell iron nanoparticles. (Reproduced from [117])

environmental pollutants remediation. Agglomeration is one of the main concerns because it may drastically impact the reactivity of the product, reducing the benefit of employing nanomaterials to improve performance. Another issue to consider when dealing with metal and metal oxide NMs is the potential toxicity of the NMs utilized. Furthermore, the related costs and destiny of the remediation technologies are essential factors to think about when using NMs as remediation products.

Nanoparticles made of iron with a core-shell configuration could be as follows; the core consists of a zero-valent elemental iron (Fe^0) and the shell is comprised of mixed valent (Fe (III) and Fe (II)) oxides [116]. The mechanism whereby these core-shell nanoparticles could be employed to remediate environmental pollutants is depicted in Fig. 17.5 [117]. Electrons donated from the zero-valent Fe^0 core could be used for reducing both heavy metals and chlorinated compounds. Furthermore, the shell part of the nanoparticles may aid in remediating the pollutants, like heavy metals with a larger standard reduction potential (E^0) than the Fe^{2+}/Fe pair.

Some researchers investigated the utilization of sonication of magnetic nanoparticles (MNPs) solution in an attempt to prevent the agglomeration of NPs in order to improve their capacity to remove heavy metals [118]. When subjected to ultrasound treatment, nanoclusters may be dispersed; however, the released nanoparticles are susceptible to re-agglomeration if exposed to extended sonication durations. Hooshyar et al. [118] prepared 12 nm iron spherical NPs and found that sonication may improve the removal efficiency of heavy metals Co^{2+} and Ni^{2+}, with an ideal ultrasound period of around 30 min for the Co^{2+} case and 20 min for the Ni^{2+} case. The greatest removal efficiencies are about 60% and 39% for Co^{2+} and Ni^{2+}, respectively.

Numerous investigations examined the utilization of bimetallic nanoparticles to overcome some of the limitations related to mono-metallic nanoparticles, particularly agglomeration and poor stability. Various surfactants and stabilizers are usually used to boost the stability of NP solutions, but the incorporation of a second metal (or more) into the composition might improve the material's solution stability and eliminate the requirement for surfactants and stabilizers [86, 119]. Enhanced stability

may lead to higher capacity and efficiency, as well as a faster rate of pollutants' degradation. The inclusion of extra metals, like Co, Ni, Pt, Ag, or Pd as a way to improve the stability of Fe^0 nanoparticles, has been suggested in recent studies [86–91]. Some noble metals may be coupled with Fe^0 nanoparticles to catalyze hydrogenation and dichlorination reactions with pollutants, which leads to a more effective remediation process. Wang et al. [92] documented an increased rate of dehalogenation of chlorinated organic compounds by incorporating Pd into zero-valent iron nanoparticles, although the costs are being expensive owing to the price of elemental Pd. Additional strategies for improving NPs' stability involve the addition of supporting materials, like the examples provided below in the sub-section polymer-based (nano)materials.

An additional issue related to the utilization of metal-based nanomaterials is the potential toxicity of the chemicals employed to manufacture the nanomaterials as well as the byproducts released through pollutant degradation. In a previous study, Naz et al. [120] showed the effective application of zero-valent metal nanoparticles to remove Cu^{2+} and Ni^{2+} from aqueous mediums. They made up Mn, Fe, and Mn-Fe nanoparticles from using cannabis sativa leaf extract. This strong antioxidant extract includes substances that react with Fe (III) to create zero-valent Fe nanoparticles. Among the various prepared NPs, Mn-Fe NPs revealed increased photocatalytic activity toward MO and CR dyes in comparison to single Mn and Fe NPs. Hence, it is interesting to use natural products in the synthesis of nanomaterials for environmental remediation to alleviate worries about the potential toxicity of chemicals and byproducts when employing chemical production routes. Furthermore, the green synthesis of zero-valent Fe nanoparticles shown by this research group offers the benefits of adding value to natural resources that would otherwise be deemed garbage (like leaf extracts) and offering low-cost nano-catalysts for dye removal from water. In another study, Poguberović and collaborators [121] made bimetallic NPs using cherry, mulberry, and oak leaf extracts for the elimination of As^{3+} and Cr^{6+}. Their study showed rapid kinetics and adsorption rate of the zero-valent Fe NPs, where the highest capacity for Cu^{2+} is about 1047 mg Cu/g with the use of mulberry leaf extracts and the highest capacity for Ni^{2+} is about 777 mg Ni/g with the use of oak leaf extracts. The remarkable disparities in performance may result from the specific raw materials utilized in the synthesis of nano-adsorbents. The best removal capacity of Cu^{2+} was attained at pH = 7, whereas the best removal capacity of Ni^{2+} was attained at pH = 8. Although the results of this investigation appear encouraging, additional investigations are needed before these materials can be used on a large-scale basis in wastewater treatment. Moreover, pH-sensitive remediation systems could pose some limits in their application to in situ remediation since certain environmental situations might not provide suitable conditions for effective and efficient remediation. Therefore, the researchers were able to create a reasonably harmless and low-cost organic–inorganic combination product for targeting polychlorinated biphenyl pollutants.

The development of mixed magnetic nanomaterials can also lead to enhanced performance for environmental remediation [122–124]. For instance, nano-$NiFe_2O_4$–NiO composites are synthesized via a co-precipitation process and the

Table 17.2 Some studies on the use of silica NMs for environmental remediation of pollutants

Products	Applications	References
Amine-grafted silica materials	Removal of gases (CO_2, H_2S)	[125–132]
Carboxylic acid-functionalized silica	Wastewater treatment (heavy metals, dyes, radioactive ions)	[133–136]
Thiol-functionalized silica	Soil and wastewater treatment (removal of heavy metals)	[137–140]
Amino-functionalized silica	Soil and wastewater treatment (removal of heavy metals and dye degradation)	[127, 141–145]

results showed an optimal photocatalytic degradation of about 95.4% toward MB dye within 2 h for 50%$NiFe_2O_4$-50%NiO composition [122]. NiO–CuO and NiO–Co_3O_4 composite nanophotocatalysts are also prepared and revealed excellent degradation efficiency against cefixime antibiotic [123] and malachite green dye [124], respectively.

Conversely, mesoporous silica materials, because of their flexibility, have also acquired a great interest in numerous kinds of applications, including catalysis and adsorption. These materials provide many advantages for applications in environmental remediation, such as high surface area, controllable size of pores, ease of alteration of the surface, and a large volume of pores. A number of investigations have also documented the application of these kinds of materials in pollutant remediation in the gas phase because of their exceptional performance as adsorbents. Moreover, several papers have presented various surface modifications of mesoporous silica materials. Table 17.2 highlights some of the studies that examine the application of silica NMs in the environmental remediation of various pollutants.

The hydroxyl groups that exist on the surface of silica materials play a key role in gas adsorption, surface modification, and other surface-related phenomena like wetting. Putting functional groups onto the walls of the pores is another recognized method for developing novel catalysts and adsorbents [117]. For instance, A. Ayub et al. [125] used amine-surface-modified silica materials to selectively remove H_2S and CO_2. These materials attained rapid CO_2 uptake by achieving about 82% of their equilibrium CO_2 uptake in 1 min. The materials are able of completely removing H_2S and CO_2 by 100%. Additionally, the materials maintained about 99% of their initial CO_2 uptake during 100-cycle testing in hot air. Anyanwu et al. [126, 127] utilized amine-surface-modified mesoporous silica (SBA-15) grafted at different temperatures for capturing CO_2. The nano-adsorbents grafted at ambient temperature revealed outstanding stability even after ten adsorption–desorption cycling tests, which is comparable to the conventional process that implies grafting at much higher temperatures >75 °C. In another study, Anyanwu et al. [128] employed silica gels grafted with amine for CO_2 capture purposes. Materials with high amine loading and largest pores (1.12 cm^3/g pore volume, 14.9 pore diameter, and 309 m^2/g BET surface area) demonstrated excellent CO_2 adsorption performance, rapid CO_2 uptake rate, and excellent cycle stability. Unexpectedly, the performance of materials exceeded those of the excellent MCM and SBA-type sorbent materials. Bai et al.

[129] synthesized triamine-grafted MCF silica at room temperature. The findings indicated that these materials display excellent CO_2 adsorption capacity, rapid adsorption kinetics, and outstanding cyclic stability. Mesoporous silica SBA-15 materials are grafted by using different sterically hindered amines, which are assessed for removing H_2S [130]. Excellent adsorbance performance is achieved for materials with (*tert*-butylaminopropyl) trimethoxysilane grafting. The significant abundance of amine groups on the surface of silica materials was linked to the observed good efficiency in H_2S and CO_2 removal. Another research group (s) showed [131, 132] the effectiveness of amine-modified alumino-silicates for capturing CO_2 and other carbonyl substances such as ketones and aldehydes. CO_2 capture has been found to be achievable by reversible adsorption of the gaseous molecules into the amino-silica product. Likewise, the creation of hemiaminal or imine is necessary for capturing ketone and aldehyde. The reaction kinetics are very quick, attaining around 90% of the entire capacity of the material in a couple of minutes. As a result, the above-mentioned products offer a feasible replacement for the classical capture of carbon dioxide by aqueous amines and other silica-supported amines since they are simpler to prepare, less costly, and offer higher stability and performance. Nevertheless, this may restrict some of their applications to capture pollutants that do not react with amines. Amine-functionalized porous silica is employed as an aldehyde abatement product to trap aldehydes with low-molecular-weight (like formaldehyde). The obtained findings implied that primary and secondary amines, rather than tertiary amines, are more appropriate to capture aldehydes, which is in accordance with the covalent capturing of the desired pollutant through the creation of imine and hemiaminal intermediates.

An example of mesoporous silica materials and surface properties relevant to adsorption applications is depicted in Fig. 17.6.

In addition to the capture of gases, silica-based compounds are applied for the elimination of organic dyes from wastewater. Numerous research groups [133–136] successfully functionalized mesoporous silica with carboxylic acid groups (–COOH) because the latter may establish hydrogen bonds with a variety of substances, including contaminants, dyes, and metal ions. The best performance for the degradation of methylene blue was attained at a pH of 9. Although these products are good adsorbents under basic circumstances, the pH dependence probably limits their practical applicability. Moreover, other research groups examined the applications of thiol-functionalized silica materials [137–140] and aminopropyl or amino-functionalized silica materials [127, 141–145] in remediating numerous kinds of metal ions like U^{6+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Al^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, and Cd^{2+} as well as for degrading dyes.

17.3.2 Carbon-Based Nanomaterials

Carbon-based nanostructured materials are also utilized for the remediation of pollutants via photocatalysis and adsorption processes. Indeed, carbon-based nanostructured materials possess distinctive chemical, physical, and electronic
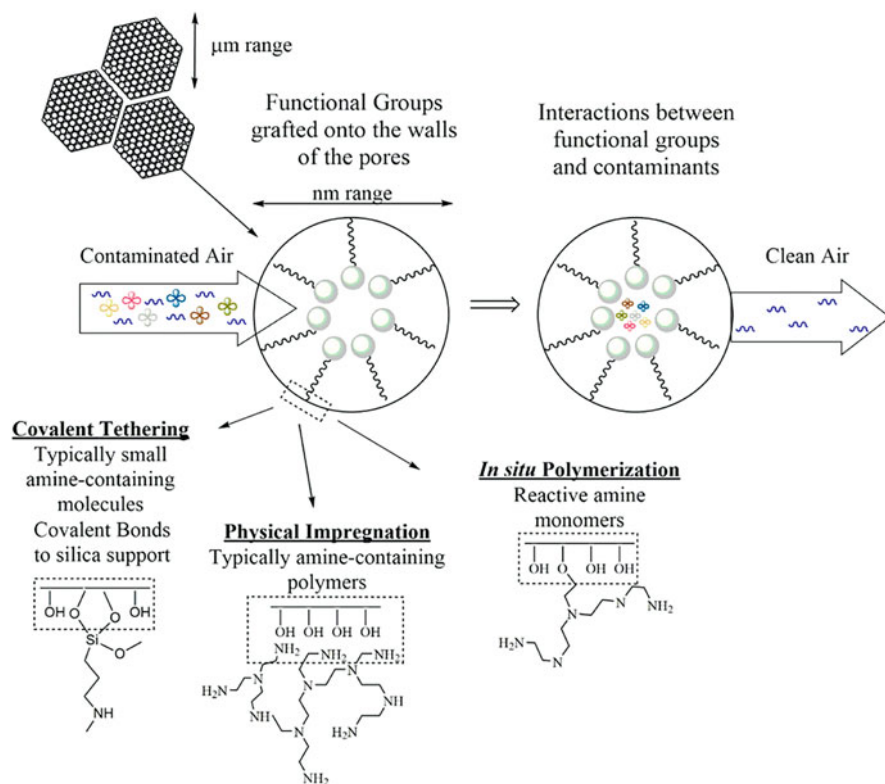
Fig. 17.6 A case of functionalized mesoporous silica materials applied in environmental remediation of pollutants. (Reproduced from [117])

features. Graphene, multi-walled carbon nanotubes (MW-CNTs), single-walled carbon nanotubes (SW-CNTs), and fullerenes C_{540} and C_{60} could all be formed through adjustable hybridization states [146–148]. Some studies reported that the surface modifications, functionalization, or activation of the virgin carbon material are initially needed for the feasibility of graphene and carbon nanotubes (CNTs) in environmental remediation applications. Many investigations have been conducted on MW-CNTs and SW-CNTs. The materials' adsorption capabilities render them especially suitable for removing inorganic and organic contaminants from large volumes of aqueous solutions and from the air.

Numerous papers have been published that detail the application of graphene to create nanocomposite photocatalysts. Pure graphene could be employed as an efficient adsorbent to remove contaminants from aqueous mediums like fluoride. At ambient temperature and pH of 7, graphene's monolayer adsorption capacity for fluoride is about 35.6 mg/g [149]. Although pure graphene could potentially be utilized for the remediation of the environment, a range of strategies depend on the usage of modified graphene to remediate various substances. Surface alterations

reduce graphene layers' aggregation and hence improve the effective surface area, rendering the modified graphene potentially better than pure graphene [150]. Graphene oxide (GO) is a kind of modified graphenes that has been reported for the remediation of the environment by the adsorption of a number of water and gaseous pollutants, like pharmaceuticals, heavy metal ions (like Pb^{2+}, Cd^{2+}, As^{3+}, and Cr^{6+}), organic (cationic and anionic) dyes, CO_2 separation, NO_2 detection, etc. [151–156]. On the surface of the carbon of graphene oxides, numerous functional groups that contain oxygen, like hydroxyls, epoxides, and carboxylic acids exist, which play a great role in adsorption. Several researchers demonstrated that nanocomposites comprising of graphene and semiconducting nanoparticles (TiO_2, ZnO, CeO_2, WO_3, etc.) revealed higher photocatalytic activities in comparison to pristine nanoparticles alone (TiO_2, ZnO, CeO_2, WO_3, etc.) [157–162]. These nanocomposites were examined, for example, for the reduction/removal of heavy metal ions (like Cr^{6+}), degradation of dyes (like MG, MB, RhB), antibacterial agents, as well as gas sensors. This could be ascribed to the rise in conductivity. Even magnetic iron oxide-based nanomaterials are combined with graphene oxide to form new potential nanocomposites for environmental remediation applications [163–165]. One should note here that the control of the composition ratio in the nanocomposites between the graphene and the nanoparticles is important to achieve optimal photocatalytic activity. Indeed, exceeding a certain graphene content, a reduction in photocatalytic activity could be noticed. Table 17.3 summarizes some examples of graphene-based nanocomposites used for environmental remediation applications.

Conversely, great efforts have been done to improve the adsorption capabilities of pure CNTs by opening the closed ends. Indeed, unaltered carbon-based nanostructured materials are frequently inert to environmental pollutants. To boost their performance, they are usually altered or coated by other reactive compounds that have the required functional groups or charges. As a result, these hybrid nanomaterials combine numerous properties within a single framework to achieve the required efficiency. SW-CNTs are often organized in a hexagonal pattern where each nanotube is encircled by six others, which results in packages of aligned tubes with a heterogeneous porous framework. Adsorption may occur in four distinct accessible sites for an ordinary open-ended CNT bundle, which are of two sorts: (1) those that have greater energy of adsorption, localized either among two adjacent nanotubes or inside an individual nanotube, and (2) those that possess lower energy of adsorption, localized on the outside surfaces of the external CNTs making up the bundle [179]. Because the exterior sites are directly exposed to the adsorbing substance, adsorption on outside surfaces approaches equilibrium considerably quicker than adsorption on internal sites. MW-CNTs are seldom found in bundles unless particular techniques of synthesis are applied to generate such arrangements. Via nitrogen adsorption–desorption isotherm measurements, Zhong et al. [180] proved that distinct kinds of pores (i.e., inner and aggregated) form a multi-stage process of adsorption. Aggregated pores have been found to be more substantially responsible for the adsorption capabilities of these products than the less available interior pores. Moreover, the oxygen concentration of CNTs might have an impact

Table 17.3 Graphene and CNT-based nanocomposites used for environmental remediation applications

Products	Applications	References
Pristine graphene	Treatment of aqueous solutions (like adsorption of fluoride)	[149]
Graphene oxide	Adsorption of a number of water and gaseous pollutants, like pharmaceuticals, heavy metal ions (like Pb^{2+}, Cd^{2+}, As^{3+}, and Cr^{6+}), organic (cationic and anionic) dyes	[151–156]
	CO_2 separation	
	NO_2 detection	
Semiconductor-graphene oxide nanocomposites (semiconductors like ZnO, TiO_2, WO_3, or CeO_2)	Gas sensing	[157–162]
	Removal of metal ions	
	Dye degradation (like MG, MB, RhB)	
	Water disinfection (antibacterial activity)	
Spinel ferrite-graphene oxide nanocomposites	Removal of heavy metal ions	[163–165]
	Degradation of synthetic dyes	
	Antibacterial applications	
Oxidized CNTs	Adsorption of metal ions	[166–170]
CNT-based nanocomposites:	Dye degradation	[171–178]
• Metal oxide semiconductor-CNTs nanocomposites	Metal ions removal	
• Non-oxide semiconductor-CNTs nanocomposites		
• Magnetic iron oxide-CNTs nanocomposites		
• Bimetallic NMs-CNTs nanocomposites		

on their adsorption ability. CNTs that possess –COOH, –C=O, and –OH groups might favorably influence adsorption capabilities. This could be done based on the particular synthesis techniques and the associated purifying operations. CNTs could be oxidized using a variety of chemicals, including NaOH, KOH, H_2SO_4, NaOCl, H_2O_2, $KMnO_4$, HNO_3, etc., which could significantly enhance the adsorption capacities of metal ions like Cu^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} [166–170].

Recently, several attempts are focused on the combination of CNTs with other kinds of photocatalysts/adsorbents to further enhance their performances, for example, metal oxide semiconductors like TiO_2, ZnO, and WO_3 [171–173], titanates [174, 175], non-oxide semiconductors like CdS [176], magnetic iron oxide-based NMs [177], bimetallic NMs [178], and so on. These nanocomposites demonstrated enhanced adsorption and photocatalytic performances in comparison to individual nanomaterials.

17.3.3 Polymer-Based Nanomaterials

Polymers are largely employed to detect and remove organic contaminants (such as volatile organic compounds, pharmaceuticals, and aromatic hydrocarbons), gases (such as NO_x, SO_2, and CO), pollutant chemicals (such as heavy metals, arsenic, iron, nitrate, and manganese), and a broad range of biologics (such as viruses, parasites, and bacteria). Polymeric hosts (such as surface functionalized ligands, stabilizing agents, emulsifiers, and surfactants) are often employed to enhance the stability and surpass certain limitations of pristine nanoparticles, and they also provide other beneficial characteristics like recyclability, durability, thermal stability, and boosted mechanical strength. Table 17.4 summarizes a few examples of polymer-based nanostructured materials employed for the treatment of environmental pollutants.

Amphiphilic polyurethane nanomaterials have been produced for the removal of polynuclear aromatic hydrocarbons (PAHs) from soils, proving that organic nanomaterials may be tailored to have desirable features [181]. Amphiphilic polyurethane nanomaterials recovered about 80% of the phenanthrene from polluted aquifer sand. An examination of diverse compositions revealed that the affinity of amphiphilic polyurethane nanomaterials for phenanthrene improved as the size of the hydrophobic core rose. In addition, rising the amount of ionic groups on the precursor chains reduced the agglomeration of amphiphilic polyurethane particles in the existence of polyvalent cations [181]. After that, numerous researchers developed diverse potential polyurethane-based nanocomposites for the removal of contaminants from water and soil, as well as for oil separation, by incorporating diverse kinds of oxide NMs like GO, ZnO, and SiO_2 [182–184]. Dendrimers, including, for example, poly(amidoamine) (PAMAM), have been employed in contaminated wastewater treatment [185–189]. These nano-dendritic polymers include functional groups like hydroxamates, carboxylates, and primary amines that may encapsulate a wide variety of solutes in water, such as cations (U^{6+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Au^+, Ag^+, and Cu^{2+}), as well as they effectively degrade

Table 17.4 Some examples of polymer-based nanomaterials employed for environmental remediation of pollutants

Products	Applications	References
Amphiphilic polyurethane NPs	Removal of polynuclear aromatic hydrocarbons from soils	[181]
Polyurethane-based nanocomposites	Oil adsorption and separation	[182–184]
	Dye degradation	
	Removal of metal ions	
Dendrimers	Wastewater treatment (degradation of dyes and removal of heavy metal ions)	[185–189]
Functionalized biodegradable polymeric nanomaterials	Removal of metal ions, dyes, and oils from water	[190–194]
Polymeric-based nanocomposites	Catalytic degradation of dyes	[195–202]
	Removal of heavy metals	
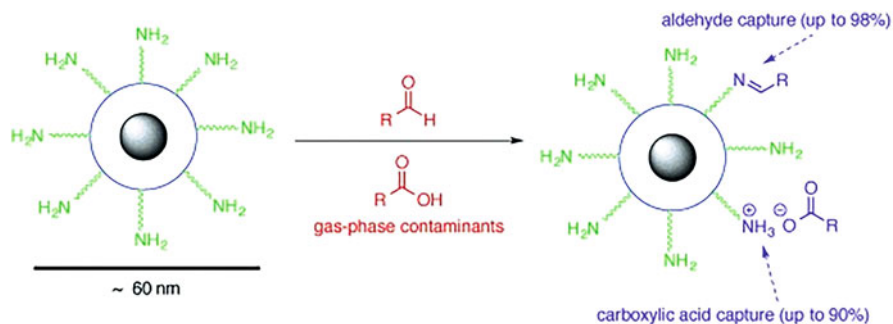
Fig. 17.7 Mechanism of PDLLA-PEG-PEI for aldehydes and carboxylic acid gaseous capturing. (Reproduced from [203])

the dyes. They could be employed as chelating agents and ultrafilters or microfilters that attach with metal ions, to facilitate the purification of water. Functionalized biodegradable and non-toxic polymeric nanomaterials, including cellulose, chitosan, polylactic acid (PLA), gelatin, etc., have been also utilized for specifically capturing volatile organic compounds and removing metal ions, dyes, and oils from water [190–194]. The modified target-specific reactivity of materials enabled the quick and selective capturing or removing of desirable pollutants. The development of ionic or covalent connections among the amine functional groups and the intended aldehydes and/or carboxylic groups is the basis for this technique, which could lead to a more selective and efficient capturing technology. As an example, Fig. 17.7 shows the mechanism of aldehydes and carboxylic acid gaseous captured by poly (D,L-lactic acid)-poly(ethylene glycol)-poly(ethyleneimine) (PDLLA-PEG-PEI) [203].

Polymer-supported nanocomposites (PNCs) are products that use a polymer as a base material and have nano-entities dispersed in or coated on it. These products combine the desired features of the nanomaterials (like high reactivity) and the base polymer (like exquisite mechanical strength). Biodegradability and biocompatibility are the two important factors in the utilization of polymer-supported nanocomposites. Numerous polymers have also been employed for environmental remediation applications by the construction of membranes that include metal and metal oxide nanomaterials [195–198]. Polymers are often utilized as base components in polymeric nanocomposites, while other elements of the nanocomposite, like nanomaterials, take the responsibility of remediating the pollutants. Nevertheless, in some studies, functionalized polymeric nanocomposites have been also identified to be the possible principal agent in the remediation process. Green hybrid polymeric-based nanocomposites, made of ZnO NPs loaded into a hydrogel, have been created by employing acrylamide-grafted on the polymeric chains of gelatin and chitosan [202]. These hydrogel nanocomposites showed a successful degradation of about 91% of Congo red dye in wastewater and under sunlight. Magnetic polymeric-based nanocomposites made of alginate and poly (vinyl alcohol) (PVA) hydrogels and Fe_3O_4 NPs have been prepared by Zhang et al. [204]. The prepared products demonstrated good catalytic performances for

the Fenton degradation of organic dyes. Remarkably, the double-cross-linked structure provides the iron oxide NPs much more stability and recyclability in comparison to the conventional Fenton catalytic process. The mass loss of these polymeric-based nanocomposites is about 10% after six cycles. This could prevent the creation of Fe sludge in Fenton-like reactions to the utmost level and offers widespread potential applications for the remediation of wastewater. In another study, biopolymeric hydrogel nanocomposites composed of gelatin-supported Sn-doped Gd_2O_3 have been prepared [199]. The existence of many functional groups on the gelatin's framework, like hydroxyl (–OH) and carboxylic acid (–COOH), facilitates the cross-linking with formaldehyde. These nanocomposites were employed for the catalytic degradation of different dyes (like 2-nitrophenol, 4-nitrophenol, CR, MO, and MB dyes) in aqueous medium $NaBH_4$ reducing agents. For instance, the catalytic degradation of CR dye was successfully performed with a reaction rate of about 0.915 min^{-1}. It has been also stated that these biopolymeric hydrogel nanocomposites can be recycled recovered by a simple discharge of the reduced dye and reutilized for another time. Ibeaho et al. [200] developed multifunctional magnetic hydrogels fabricated by Fe_3O_4 NPs-mediated radical polymerization of poly (ethylene glycol) diacrylate. The obtained products display multifunctional properties integrating photothermal response, superwettability, and magnetism, in addition to the rapid degradation of organic dyes with excelled recyclability. In another study, hydrogel nanocomposites of polyethyleneimine and magnetic NPs have been synthesized [201]. The resultant materials display a rough surface and high porosity, leading to a fast adsorption rate and great adsorption capacity of heavy metals like Pb^{2+}, Cd^{2+}, and Cu^{2+}, which could be further enhanced by raising the pH value of the initial solution.

17.4   Conclusions and Future Perspectives

Nowadays, our ecological equilibrium is being considerably disturbed by the rapid growth in population and in the amount of residues emitted by a large number of industries. The subject of environmental pollution and climate change is one of the dangerous issues of concern worldwide. The pollution of our environment is being a risk to our lives since it could be the main sources of a variety of undesirable diseases. Therefore, an immediate degradation (reduction or removal) of these contaminants is needed. Nevertheless, certain contaminants are extremely difficult to breakdown and require a long period of treatment. The unique function of nanotechnology could be employed for this purpose, and contaminants are able to be changed into safe ones or properly removed, which is attributed to their high surface area, adequate functional groups, and active sites. Additionally, nanotechnology can change strong surface complexes with many types of contaminants and so effectively remove the contaminants from the environment (like an aqueous solution). Accordingly, nanostructured materials and composites could be employed in the environmental remediation processes. For the remediation of environmental pollutants, many types of nanostructured materials and composites are utilized, such

as inorganic-based, carbon-based, and polymer-based nanomaterials. Contaminants such as halogenated herbicides, volatile organic compounds, organophosphorus compounds, chlorinated organic chemicals, dyes, heavy metals, pharmaceuticals, etc. could be effectively remediated by using these nanomaterials and nanocomposites. Moreover, processes such as photocatalytic reduction, catalysis, adsorption, (nano)filtration, nanosensing, etc., of pollutants are frequently identified as significant technologies for reducing or removing or capturing pollutants in the environment. In light of this, the current chapter will focus on the important nanotechnologies and nanomaterials employed in environmental remediation applications, as well as their advantages and limitations that must be overcome to achieve a clean and safe environment in the future.

The use of nanostructured materials and composites in the identification and elimination of diseases offers in-line and real-time detection, smaller sizes of samples, reduced costs, quicker treatment period, higher degradation yields, lesser toxicity (even nontoxicity), improved sensitivity and selectivity, and so on. Indeed, nanomaterials of metal and metal oxides have been widely utilized to eliminate heavy metals and organic contaminants by the oxidation or reduction of NMs. The level of degradation could be further improved by functionalizing these NMs with chemical groups capable of selectively capturing specific contaminants in the polluted medium. This technology is efficient and exciting, and it could potentially be employed in the treatment of air and water.

Nanomembranes have been used in the treatment of drinkable water, wastewater reclamation, and reuse, as well as the elimination of pesticides, natural organic matter, pharmaceuticals, dyes, and heavy metals from polluted water. Additional improvements should be done within environmental remediation applications to selectively eliminate the nanomaterials and nanocomposites after use, which should also possess stronger resistance to variations in pH values and concentrations of contaminants existing in polluted water, higher stability over very long durations, and lowest costs. Because of their low basic weight, small size of pores, and large permeability, nanofibrous media are also suitable for a broad variety of applications as filters. Furthermore, nanofibrous membranes exhibit distinctive characteristics including large specific surface area, strong connectivity between pores, and the ability to include active sites or functional groups at the nanoscale. Nanofiber filters could be utilized in a variety of applications, including the extraction of microparticles from wastewater. To extend the lifespan of the membranes, nanofiltration or ultrafiltration could be used. Some research activities are under examination to produce nanostructured materials with different fiber geometries and diameters in order to determine their influence on the efficiency of nano-fibers.

Polymer-supported nanocomposites have been also employed for environmental remediation applications, such as monitoring and detection (sensors) of pollutants, adsorption of contaminants, chemical catalysis degradation, and photocatalytic degradation, which provide a greener environment perspective. Nevertheless, an investigation of the relationship among the surrounding polymers and the encapsulated nanomaterials, as well as their dispersion in contaminated water and

air, should be conducted. Furthermore, the manufacture of polymeric-based nanomaterials for large-scale applications is still in progress.

The widespread use of sorbents in the remediation of the environment has revealed their potential to adsorb metals and organic contaminants from polluted air and water. High adsorption selectivity and capacity have been achieved by the use of nanostructured materials like titanate-based NMs, iron-based NMs, and polymeric nano-adsorbents. Sorbent surface modification is being investigated to improve process performances. Improving sorbent reusability and extending their lifetime should be also investigated in order to minimize their costs.

Nano-sensors that are able to detect and identify volatile organic compounds, contaminant chemicals, and toxic gases, as well as bacteria, have been created. Additional improvements in the multifunctional characteristics of nanostructured materials are needed to fulfill requirements for the detection and remediation of contaminants in air and water. Also, fundamental investigations are needed to understand well their capabilities.

Because of their fibrous body and large surface area, SW-CNTs and MW-CNTs have demonstrated outstanding adsorption capabilities to remove numerous chemical and biological pollutants. Tiny NMs made of carbon nanotubes are hard to be separated from aqueous solutions. To achieve this, an ultracentrifugation separation process would be preferably applied, nevertheless, such a procedure requires high energy. Filtration by membranes is an alternate and effective approach for separating carbon nanotubes from an aqueous solution. Nevertheless, these membranes could be easily plugged. Nanocomposites made of carbon nanotubes and magnetic NMs or metal oxide NMs are interesting products for large-scale environmental pollution control. Further attempts will be necessary to design and develop CNT-based nanocomposites for real applications. Nano-dendritic polymers have been created for use in filtering techniques that need low pressure to eliminate or recover contaminants from polluted water, wastewater, and soil, like metal ions, uranium, and perchlorate. The efficiency of composites based on nano-dendritic polymer has not been yet documented and needs to be studied in the future.

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