Chapter 9
Nanoparticles-Based Adsorbents for Water Pollutants Removal

Ayushi Jain, Shweta Wadhawan, and S. K. Mehta

Abstract Water pollution can cause severe health hazards in living organisms since most of the contaminants are toxic, mutagenic, and carcinogenic. There is a critical need to decontaminate the water from industrial effluents preceding their discharge into water bodies. The current chapter explores the potential of various nanoparticle-based adsorbents with special reference to nano zero-valent iron (NZVI), iron oxide, titanium, alumina, and silica in the field of adsorptive hosting of inorganic and organic pollutants from aqueous solutions. The nano adsorbents exhibit greater adsorption capacity, rapid adsorption rate, and competence to host various pollutants, recyclability, and reusability when compared to conventional adsorbents. These properties emphasize the relevance of nano adsorbents for the remediation of water contaminated with heavy metal ions, dyes, and chlorinated organic compounds. This chapter gives an overview of the progress and application of bare and functionalized metal and metal oxide nanoparticles for this purpose. Moreover, the mechanism of heavy metal ions, dyes, and organic chlorinated compounds removal by nanoparticles has also been discussed. The present chapter offers advanced information about the imperative characteristics of some metal and metal oxide-based nanoparticles and demonstrates their advantages as adsorbents in water remediation.

Keywords Degradation · Functionalization · Nano adsorbents · Water remediation

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9.1 Introduction

Extensive growth in the population of the world, along with urbanization, has lead to the rising demand for fresh water [1]. About 1.2 billion people in the world do not have access to hygienic and safe drinking water, and this issue is anticipated to augment in the years to come [2]. In addition, contamination of water with a variety of pollutants such as heavy metal ions, dyes, chlorinated organic compounds, pharmaceuticals, sediments, and radioactive contaminants has intensified the problem [3]. Among these contaminants, heavy metal ions, even in relatively small quantities, cause severe health vulnerability to human beings since they are poisonous, persistent, and non-biodegradable in nature. The effluence of heavy metal ions into water bodies caused by widespread industrialization and unsystematic removal results in contamination of aquatic ecosystems [4]. For instance, Pb^{2+} is employed in various industrial products, i.e., battery, pigments, printing, explosive, and fuel manufacturing. The Environmental Protection Agency (EPA) has recommended that the maximum Pb^{2+} contamination level in drinking water is 15 l $\mu g\ L^{-1}$. The toxic effects of Pb^{2+} ions in human beings include inhibition of hemopoiesis, germinal cell dysfunction, hypertension, cognitive deformities, miscarriages, renal dysfunctions, and nervous disorders. Therefore, the elimination of Pb^{2+} from water is necessary to save living organisms [5]. Another heavy metal ion, Hg^{2+} is the common inorganic form of Hg, which can be transformed into more poisonous organic forms through biological methylation [6]. Undesirable effects of Cu^{2+} in human beings encompass an accumulation of this ion in the liver leading to Wilson's disease, which further causes psycho-neurotic defects [7, 8]. The intake of Cu for humans should be below 5.0 mg d^{-1}, as recommended by the European Commission [9] and made mandatory in the WHO guidelines. As a result, the concentration of Cu in drinking water has been stipulated to below 2.0 mg L^{-1} [10]. Similar to Cu^{2+}, the devastating effects of numerous other heavy metal ions on the human body have been discussed by different scientists from time to time. In this regard, Cd leads to multiple chronic organ damage [11, 12], and Mn affects the CNS and respiratory system. Some of the ions like Ag^{+} and Zn^{2+} are important trace elements but turn toxic when taken in higher amounts. The removal of Ag could protect the resources and benefit human beings' sustainable development [13]. Zn^{2+} in high doses can be toxic and cause detrimental health hazards to many biological and biochemical processes [14, 15].

Organic dyes constitute another category of pollutants that are released from several industries such as paint, cosmetics, textile, leather, pigment, paper, etc. [16]. Dyeing runoff has a dangerous impact on the environment since its presence in water causes carcinogenic effects. Moreover, colored effluents can decrease the level of O_2 in water by affecting the photosynthesis of aquatic plants, and in extreme cases, leading to the suffocation of aquatic plants and animals [17]. Amongst the diverse kinds of dyes, Methylene blue (MB) and Rhodamine B (RhB) are mainly used in textile manufacture. These dyes may lead to eye burns and, in extreme cases, result in permanent damage to the vision of humans and animals [18]. Literature studies reveal that inhalation or ingestion of RhB may cause harm to the liver and thyroid [19].

The stability and persistence of the dyes in the water increase if not treated properly. Consequently, it is essential to eliminate the perilous dyes from wastewater before disposing of these into the aquatic ecosystem with an appropriate treatment process [20]. Malachite green (MG), a triphenylmethane cationic water-soluble dye [21], has carcinogenic, mutagenic, and teratogenic effects on humans. Noxious substances are produced on MG degradation that causes damage to the liver, lungs, and bones [22–24]. For that reason, it is obligatory to eliminate these contaminants from effluents prior to their discharge into water bodies.

With the increasing water pollution resulting from various kinds of pollutants, it becomes of utmost importance to develop and apply water remediation techniques to diminish the effects of contaminants. Significant efforts have been dedicated to developing effective physical and chemical treatment processes for removing inorganic and organic pollutants from contaminated water [25]. The methods such as adsorption, ion exchange, ozonation, precipitation, membrane separation, etc., are being employed (Fig. 9.1) to eliminate pollutants from aqueous runoffs [26]. However, some of these techniques have limitations, such as high processing cost, sludge formation, and inappropriateness at a large scale (Fig. 9.1) [27].

Amongst different methods, huge consideration has been gained by the adsorption phenomenon because of its benefits such as simplicity, easy operation, recyclability, uncomplicated removal, and reusability [28]. The characteristics of a particular adsorbent depend on its specific surface area, composition, and accessibility of various functional groups; therefore, the effectiveness of an adsorption process

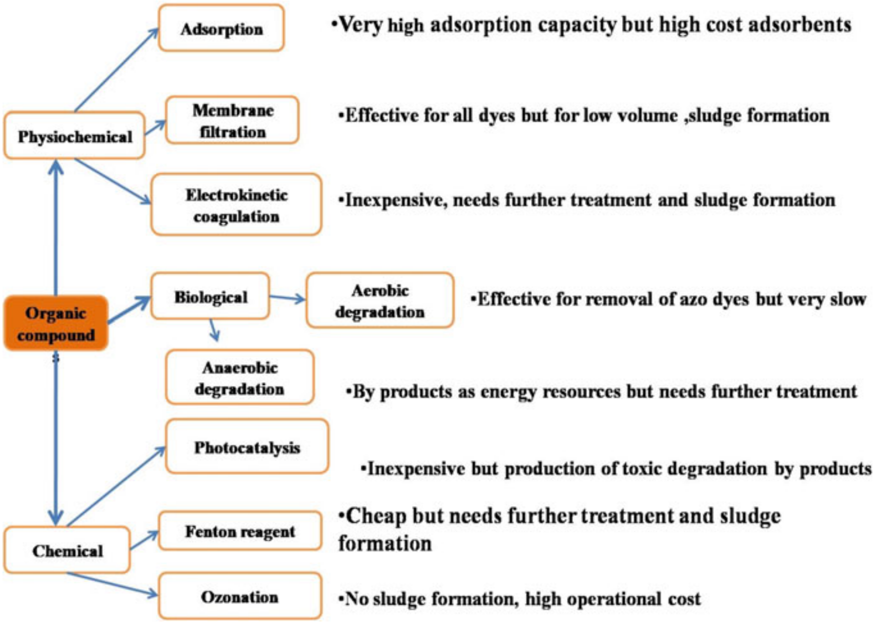

Fig. 9.1 Different techniques for the removal of dyes with positive and negative points

is controlled by these factors. Numerous adsorbents like ion-exchange resins, activated carbons [29–32], natural zeolites [33], chitosan [34], bio sorbents [35–37], and chelating materials [38, 39] have been investigated by the researchers for the elimination of pollutants from aqueous solutions. The ability of adsorbents depends on the presence of functional groups on their surfaces. For instance, an adsorbent with nitrogen-containing ligands (amino, amidoxime, hydrazine, and imidazole) are efficient in complexing metal ions [40–46].

In recent times, the production of nanomaterials with greater surface area, improved absorption capacity, and superior regeneration performance has exhibited immense potential in eliminating a wide range of pollutants [47]. For example, manganese oxides have been found to be excellent nano adsorbents for the uptake of heavy metal ions due to their greater adsorption ability, enhanced stability, and low price [48–50]. Also, the rational design and adsorbents possessing outstanding adsorption ability and easy separation are of paramount importance [51]. Compared with traditional adsorbents, magnetic nanoparticles have attracted intensive attention of many researchers and been widely used for the removal of heavy metals in wastewater treatment due to their excellent physical and chemical properties, such as super paramagnetism, high surface area, easy separation under external magnetic field and strong adsorption [52–55]. Based on these advantages, Fe_3O_4 nanoparticles were exploited to remove heavy metals from water by strong adsorption [56–60]. Not only heavy metal ions, metal oxide nano adsorbents also were extensively used for the hosting of dye pollutants owing to their enhanced surface area, improved photocatalytic properties, and reusability. The nanoparticle-based adsorbent can be recycled, thus leading to the production of very small volumes of sludge. A variety of metal and metal oxide nanoparticles like Fe/Ni [61], Ni [62], TiO_2 [63–66], ZnO [67–70], Fe_3O_4, Fe_2O_3 [71–74], SnO_2 [75, 76] ZnS [77], CdS [78], WO_3 [79, 80] etc. have been utilized for hosting of both cationic and anionic dyes.

In addition to heavy metal ions and dyes, chlorinated organic compounds have also been effectively hosted mainly by metallic and bimetallic nanoparticles. Yet, there are fewer reports available on the use of metal oxide nanoparticles for the hosting of organo chlorines. The successful use of NZVI and Fe-based bimetallic in the hosting of organo chlorines has been demonstrated both in situ and ex situ, attributing to their high active surface area and higher number of adsorption sites. NZVI has been used for the effective hosting of heptachlor, lindane, pentachlorobenzene, and hexachlorobenzene [81].

The aim of this chapter is to explore the use of various types of metal and metal oxide-based nanomaterials for the adsorptive hosting of different water pollutants, particularly organo chlorinated compounds, dyes, and heavy metal ions, along with their mechanism of hosting. Further, the role and need for functionalization of these nanomaterials for the improved pollutant hosting performance has also been discussed in detail. The last section depicts the future perspective and research gaps regarding the use of these nanomaterials in the hosting of water pollutants.

9.2 Metal and Metal Oxide Nanoparticles

The hosting of water pollutants using metal and metal oxide-based nano adsorbents has emerged as the most promising approach for researchers. Many metal and metal oxide nanoparticles have been synthesized and employed for the removal of both organic (dyes and pesticides) and inorganic (heavy metal ions) pollutants present in the waste water. Among the metal nanoparticles, nanoscale zero-valent iron (NZVI) has emerged as the most successful nano adsorbent for hosting water pollutants, whereas a variety of metal oxide nanoparticles viz TiO_2, iron oxides (Fe_2O_3 and Fe_3O_4), silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), etc. have also been fabricated for adsorptive removal of water pollutants (Fig. 9.2). The role of these nano adsorbents in the removal of pollutants from water has been proved very significant.

9.2.1 Nanoscale Zero-Valent Iron (NZVI)

Zero valent iron has been widely used for the breakdown of chlorinated organic compounds and inorganic pollutants for water remediation. Iron in zero oxidation state (Fe^0) is known as zero-valent iron. Bulk zero-valent iron is a strong reducing agent that gets oxidized to Fe^{2+} upon reduction of pollutant molecules. Further, the properties of ZVI are improved when it is converted into nano-sized zero-valent iron. NZVI is of utmost importance owing to its improved properties like high surface area, greater thermal stability, less toxicity, better adsorption efficiency, and reducing properties as compared to bulk zero-valent iron. NZVI is obtained by both top-down and bottom-up approaches. Various studies describe the successful utilization of NZVI in the treatment of water containing pollutants viz heavy metals, dyes, and pesticides. An investigation [82] illustrated the use of NZVI for the complete removal of multiple heavy metal ions like Ni^{2+}, Hg^{2+}, and As^{5+} from water. In another study, the complete removal of As^{5+} from ground water was demonstrated [83] using NZVI,

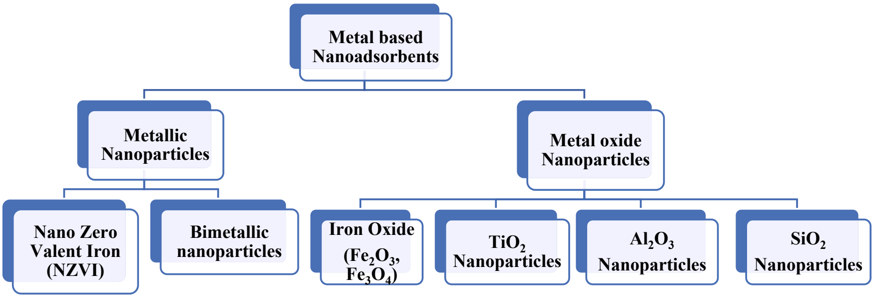

Fig. 9.2 Different types of metal-based nano adsorbents for hosting of water pollutants

where adsorption of As^{5+} was followed by precipitation. NZVI was found to be more effective as compared to ZVI in terms of efficiency and time duration.

Most of the studies demonstrate that when bare NZVI is exposed to an aquatic system containing dissolved oxygen, an oxide layer is formed on its surface, which provides core–shell nature to NZVI, where the shell forms the oxidized layer that protects the Fe^0 state in the core. Consequently, the direct implication of using bare NZVI for hosting the pollutants leads to iron pollution as well as deactivation of NZVI. This issue can be resolved by functionalizing and entrapping the NZVI with some stabilizing agents, which not only prevents the quick oxidation of NZVI to magnetite but also provides functional groups for better hosting of contaminants. For example, NZVI can be entrapped into some non-toxic biomolecules like chitosan, cyclodextrins, cellulose, etc. One of the research studies demonstrated the use of functionalized NZVI, where it was entrapped into a complex of chitosan and cyclodextrin for the complete adsorptive hosting of Cr^{6+} and Cu^{2+} ions. The mechanism of metal ions hosting was supposed to be physisorption for both metal ions followed by their reduction i.e., Cr^{6+} and Cu^{2+} to Cr^{3+} and Cu^0, respectively, by NZVI. In this case, NZVI itself gets oxidized from Fe^0 to Fe^{3+} [84].

NZVI has also found a promising use in the hosting of organic pollutants, i.e., organochlorinated pesticides and dyes, followed by their degradation in the waste water. NZVI has been employed for more than 97% removal of many pesticides, including lindane, hexachlorobenzene, pentachlorobenzene, and hexachlorobutadiene [81]. Similarly, some experimental studies describe that bare and functionalized NZVI can act as effective adsorbents for remediation of water contaminated by colored pollutants, i.e., dyes. The studies for the removal of various dyes viz. Basic Blue-3 [85], MB [86], AB24 [87], Reactive Red [88] etc. have been reported from time to time.

The possible mechanism of removal of heavy metal ions is based upon adsorption followed by reduction, precipitation, and co-precipitation depending upon the standard electrode potential of heavy metal ions (Fig. 9.3). The heavy metal ions like Pb^{2+}, Ni^{2+} and Cd^{2+} which possess reduction potential slightly higher than Fe^{2+} are reduced by Fe^0 core which is followed by their sorption on ferric hydroxide (FeOOH) shell (Eqs. 9.1 and 9.2)

$$\mathrm{Fe^0(Core)} + \mathrm{M^{n+}} \xrightarrow{\text{Reduction}} \mathrm{Fe^{2+}} + \mathrm{M^0} \tag{9.1}$$

$$\mathrm{FeOOH(Shell)} + \mathrm{M^{n+}} \xrightarrow{\text{Sorption}} \mathrm{FeOOM} + \mathrm{H^+} \tag{9.2}$$

On the other hand, for the heavy metal ions such as Cr^{6+}, Se^{2+}, Cu^{2+} and Hg^{2+} whose electrode potential is significantly higher than Fe^{2+} ions, the mechanism involves reduction by Fe^0 core followed by precipitation or co-precipitation by ferric hydroxide (FeOOH) shell (Eqs. 9.3–9.5).

$$\mathrm{Fe^0} + \mathrm{M^{n+}} \xrightarrow{\text{Reduction}} \mathrm{Fe^{2+}} + \mathrm{M^0} \tag{9.3}$$

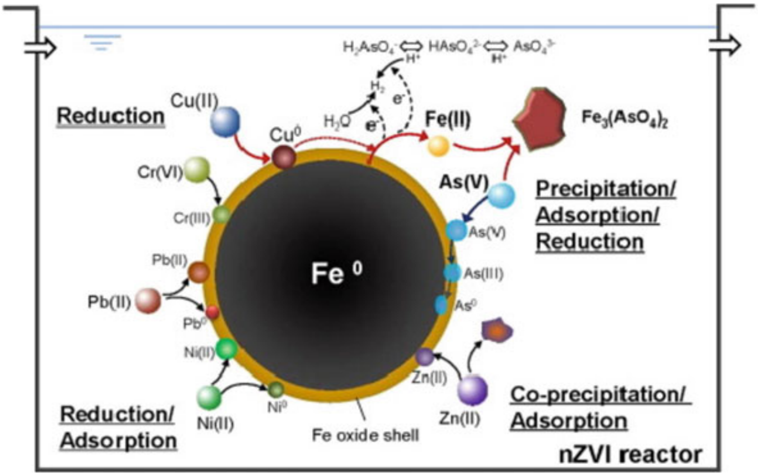

Fig. 9.3 Different possible mechanisms of heavy metal ions removal in NZVI reactor (adapted from 89 with permission)

$$M^0 + Fe(OH)_2 \xrightarrow{\text{Precipitation}} M(OH)_x \tag{9.4}$$

$$M^0 + FeOOH \xrightarrow{\text{Co-precipitation}} M - Fe - OOH \tag{9.5}$$

Further, the metal ions such as Ba^{2+} and Zn^{2+}, whose standard electrode potential is lower than iron, get oxidized on the iron hydroxide shell (Eq. 9.6).

$$M^{n+} + Fe^{2+} \xrightarrow{\text{Oxidation}} M^{(n+z)+} + Fe^0 \tag{9.6}$$

The mechanism of hosting of chlorinated pesticides and dyes generally comprises physisorption followed by reduction (Eq. 9.7)

$$\text{R-Cl}\ ,\ \text{Dyes} + Fe^0 \xrightarrow{\text{Reductive degradation}} \text{R-H} + Fe^{2+} \tag{9.7}$$

The literature illustrates a variety of studies describing the use of bare as well as functionalized NZVI for the hosting of organic and inorganic water pollutants. In one of the reports [90], NZVI obtained from a plant extract of *Syzygium jambos* (Malabar plum) was employed for the effective hosting of Cr^{6+} with an adsorption capacity of 983.2 mg g^{-1}. In another study [91], 99% of As^{5+} was also removed using NZVI. Even though the use of NZVI for waste water treatment has many advantages still there are certain shortcomings with their use. NZVI gets easily agglomerated, resulting in reduced surface area for adsorption. Also, their oxidation in water hinders the reduction process leading to their deactivation. In order to overcome these limitations, various functionalization strategies like a surface modification or doping (discussed in Sect. 9.2.5) have been developed. In a study, NZVI was surface functionalized by chitosan and employed for the removal of Cr^{6+} ions [92]. Also, the chitosan carboxymethyl β-cyclodextrin NZVI complex was fabricated for the effective removal of Cr^{6+} and Cu^{2+} ions [93]. The chitosan functionalized NZVI nanostructure possessed higher removal efficiency towards Cr^{6+} ions as compared to bare NZVI.

In addition to this, the use of NZVI for the decontamination of dyes and chlorinated organic compounds (R–Cl) from water has also been investigated. The hosting of these organic pollutants is based upon adsorption of pollutants on NZVI surface followed by their reductive degradation (Fig. 9.4). For example, an azo dye, i.e., Reactive Red A, was effectively removed using NZVI in the presence of hydrogen peroxide within 40 min [88]. The mechanism was based on the Fenton process where –OH free radicals are formed in two steps which lead to enhanced efficiency.

Adsorptive removal of a cationic dye, i.e., methylene blue with 100% efficiency using NZVI with adsorption capacity of 208.33 mg g^{-1} was reported [94], where the mechanism of removal was physisorption of dye onto the surface of NZVI via electrostatic interactions. Also, the NZVI supported on the surface of pillared clay for the effective hosting of Acid Red 315 dye where the removal efficiency of clay supported NZVI was found to be higher (100%) as compared to alone NZVI (80%), attributing to the enhanced surface area and higher number of functional groups [95].

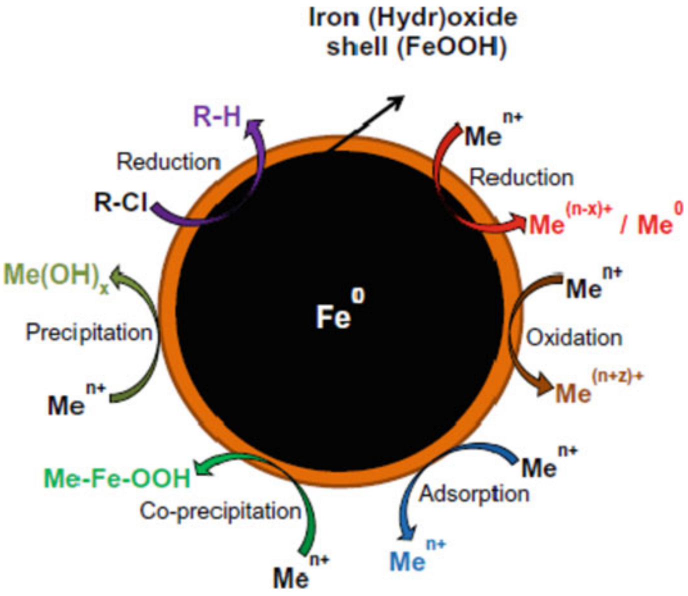

Fig. 9.4 Mechanisms of hosting of different water pollutants by NZVI (adapted with permission from [3])

NZVI alone or in combination with hydrogen peroxide has also been found effective in the hosting of chlorinated organic compounds from waste water in a Fenton-like process. The Fenton process using NZVI showed higher efficiency for hosting of pollutants attributing to the double formation of –OH radicals in contrast to conventional process which involves the use of bulk iron (Eqs. 9.8–9.10). This is the most important process for the removal of organic pollutants like dyes and organo chlorines.

$$\mathrm{Fe^0 + H_2O_2 \rightarrow Fe^{2+} + OH^- + OH} \tag{9.8}$$

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH} \tag{9.9}$$

$$\mathrm{OH^{\cdot} + Organic\ compounds \rightarrow H_2O + oxidized\ products} \tag{9.10}$$

9.2.2 Nano Titanium Dioxide (TiO_2)

Nano TiO_2 generally exists in three forms; two of them are active crystalline phases, i.e., anatase and rutile, and the third is an amorphous phase, i.e., brookite. The anatase phase is distinguished for its photo catalytic behavior and used in sunscreen for protection to the skin against UV rays. In contrast, the rutile phase of TiO_2 is a stable phase. Photocatalytic behavior of nano TiO_2 (anatase) depends upon the band gap of the material, which in turn is dependent upon the size and mode of synthesis. Nano titanium oxide has been comprehensively used for hosting various organic and inorganic contaminants via both adsorption and photocatalytic degradation. This can be attributed to its excellent stability, less toxicity, biocompatibility, and strong oxidizing nature. Bare nano-TiO_2 has been employed for more than 95% removal of various organic dyes like Eriochrome Black T [96], Indigo Carmine [97], Methyl Orange [98], and Malachite Green [78]. The commercial use of bare TiO_2 nanoparticles is limited because these can be activated only through UV radiation due to the high energy band gap of 3.2 eV. Moreover, their separation from the dispersion solution is very complicated. These limitations can be overcome by the functionalization of nano TiO_2. For this, TiO_2 NPs can be entrapped into a polymer matrix which not only increases the volume to surface area ratio of the polymer but also enhances the number of adsorption sites. A study illustrates the complete adsorptive removal of MB dye by employing a nanocomposite where TiO_2 nanoparticles were filled into polyacrylamide-based hydrogel [99]. Here, the mechanism of adsorption was mainly based upon the ion exchange process accompanying the adsorption of dye molecules on the surface of the adsorbent.

In addition to the fact that nano TiO_2 has been extensively employed for hosting of organic pollutants, it also found its use in the adsorptive removal of heavy metal ions. Many reports have described the use of mesoporous nano titania for the effective removal of Cr^{6+} [100], Pb^{2+}, Cu^{2+}, Fe^{3+}, Cd^{2+}, Zn^{2+} [101], Fe^{3+} and As^{5+} [102]. The functionalized nano titania has proved to be a superior adsorbent as compared to bare TiO_2 NPs due to their greater surface area and easy separation. In addition, TiO_2 embedded in the polymer matrix has also been employed for the hosting of heavy metal ions via adsorption. For example, in a study, polyvinyl alcohol (PVA) coated TiO_2 was employed to host Cd^{2+}, Ni^{2+}, U^{6+}, and Th^{4+} ions [103–105] from an aqueous solution.

The mechanism of removal of heavy metal ions by TiO_2 usually consists of physical or chemical adsorption, whereas for organic dye pollutants, the adsorption process is followed by photocatalytic degradation (Eqs. 9.11–9.19).

$$\text{(Waste water)Dyes, } M^{n+} + TiO_2 \overset{\text{Adsorption}}{\longrightarrow} \text{Clean Water} + TiO_2\left(\text{Adsorbed Dyes, } M^{n+}\right) \tag{9.11}$$

$$TiO_2 + hv\,(UV) \rightarrow TiO_2\left(eCB^- + hVB^+\right) \tag{9.12}$$

$$TiO_2\left(hVB^+\right) + H_2O \rightarrow TiO_2 + H^+ + OH\cdot \tag{9.13}$$

$$TiO_2\left(hVB^+\right) + OH^- \rightarrow TiO_2 + OH\cdot \tag{9.14}$$

$$TiO_2\left(eCB^-\right) + O_2 \rightarrow TiO_2 + O_2^{-\cdot} \tag{9.15}$$

$$O_2^{-\cdot} + H^+ \rightarrow HO_2^{\cdot} \tag{9.16}$$

$$\text{Dye} + OH^{\cdot} \rightarrow \text{degradation products} \tag{9.17}$$

$$\text{Dye} + hVB^+ \rightarrow \text{oxidation products} \tag{9.18}$$

$$\text{Dye} + eCB^- \rightarrow \text{reduction products} \tag{9.19}$$

Irradiation with UV light leads to the generation of electron–hole (hVB^+–eCB^-) pair in TiO_2. The positively charged hole interacts with water to produce ·OH and H^+ ions, whereas electrons interact with dissolved O_2 to give superoxide ions ($O_2^{-\cdot}$) which further reacts with water to give rise to hydroxide (OH^-) ions and (·OOH) peroxide radicals. Further, OH is formed by the combination of H^+ with ·OOH and hole with OH^-. These ·OH free radicals, holes, and electrons are responsible for the degradation of organic pollutants.

Researchers have illustrated the enormous use of bare and modified TiO_2 NPs and nanocomposites for the efficient hosting of heavy metal ions and organic dye pollutants. In this context, the mesoporous TiO_2 nanoparticles were fabricated with the highest Cr^{6+} ion uptake capacity of 26.1 mg g^{-1} than ever reported [100]. Not

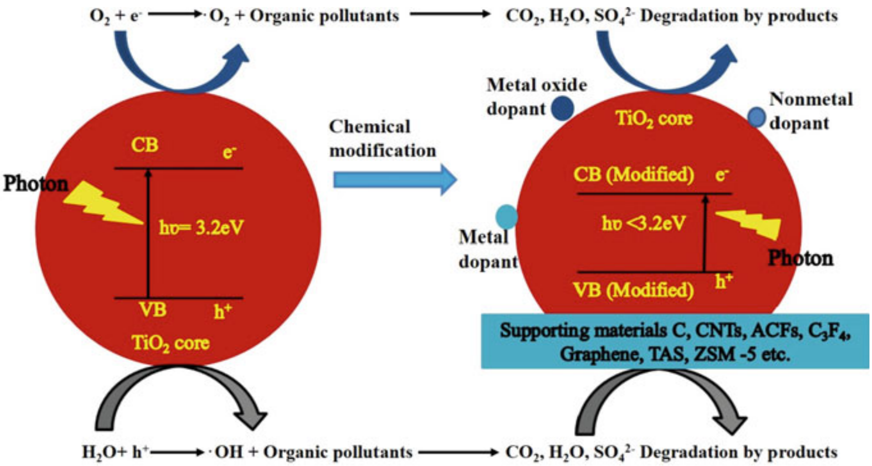

Fig. 9.5 Mechanism of hosting of organic pollutant by pure and modified nano titania (adapted with permission from [106])

only the nanoparticles, but nanowires of TiO_2 having a diameter of 30–50 nm were also established for the adsorptive hosting of different heavy metal ions viz Pb^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} ions. The TiO_2 nanowires were found to be selectively effective for the maximum uptake, i.e., 97 and 80% towards Pb^{2+} and Fe^{3+} ions, respectively [101].

In addition to bare TiO_2, functionalized and doped TiO_2 nanocomposites have also been investigated for the adsorptive uptake of metal ion pollutants. The addition of metal and non-metal dopant or different supporting materials results in enhanced removal efficiency of TiO_2 by reducing the band gap (Fig. 9.5). Razzaz et al. developed a nano fibrous nanocomposite of TiO_2 with chitosan for the adsorptive hosting of Pb^{2+} and Cu^{2+} ions [107]. Another nanocomposite, i.e., TiO_2– chitosan fabricated using microwave synthesis technique were used for the 88, and 72.56% adsorption of Cu^{2+} and Cd^{2+} ions, respectively, and maximum adsorption capacity was obtained to be 1,800 mol g^{-1} [92]. Also, the nano TiO_2 coated with a biomolecule, i.e., starch, was also investigated for the hosting of Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} ions with 90% removal efficiency [108]. Besides this, doped nano TiO_2 has also been employed in heavy metal ions remediation, e.g., Fe-doped nano titania was used for the higher uptake of As^{5+} ions where the adsorption efficiency of doped nano titania was found to be higher than that of pure TiO_2 attributing to the enhanced surface area by grain growth termination and photo catalytic response [102]. Further, pure and modified nano TiO_2 can also be employed for the removal of organic dyes. The mechanism of removal of dyes is based on adsorption followed by photo catalytic degradation. In a batch adsorption experiment, Malachite Green dye was hosted by nano TiO_2 with 85% removal efficiency [77]. Sood et al. and Yang et al. investigated the use of nano TiO_2 for the 95% photo catalytic removal of Indigo Carmine dye [97] and 98.6% removal of Methyl Orange dyes [98]. Not only bare nano titania, functionalized or doped nano TiO_2 have also been utilized for the removal of dyes. In a report, nano TiO_2 doped with Niobium (Nb), i.e., TiO_2: (Nb, N-x), were fabricated for the photocatalytic hosting of Methylene Blue dye (MB). The effect of doping was investigated on the removal efficiency, indicating the sixfold increased adsorption performance in doped NPs compared to bare ones [109], attributing to decreased band gap from 2.7 to 2.3 eV. In a batch experiment, TiO_2 nanoparticles doped with 0.5–2.5% Bi^{3+} were employed for the removal of Alizarin Red S dye, where removal efficiency was found to be as high as 80% [110]. Similarly, Pd and N co-doped nano TiO_2 were tested for the effective removal of Eosin Yellow dye [111]. Also, Ag^+ doped $TiO_2$was reported for 99% degradation of MB dye [112].

9.2.3 Nano Iron Oxide

Iron is the fourth most abundant element found in Earth's crust. It exists in divalent and trivalent oxidation states. There are three types of iron oxides, i.e., hematite (α-Fe_2O_3), maghemite (y-Fe_2O_3), and magnetite (Fe_3O_4) whereas Fe exists in trivalent oxidation state in α-Fe_2O_3 and y-Fe_2O_3, while in Fe_3O_4, both divalent and trivalent states exist. Nano iron oxide has received the great attention of researchers for hosting both organic and inorganic water pollutants through adsorption due to its abundance and simplicity of fabrication.

Both hematite (α-Fe_2O_3) and maghemite (y-Fe_2O_3) nanoparticles possess great potential for the adsorptive removal of heavy metal ions from waste water. For this application, both have their own advantages. α-Fe_2O_3 is one of the most stable forms of nano iron oxide and exhibits corrosion resistant nature, whereas maghemite possesses a large surface area and is magnetically separable. Bare nano iron oxide (both α-Fe_2O_3 and y-Fe_2O_3) have been employed for the removal of heavy metal ions like Cr^{6+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Ni^{2+} and Mn^{2+}ions [113, 114] from the waste water. The mechanism of removal of heavy metal ions was based on electrostatic interactions, which were responsible for the adsorption of these metal ions. The surface of nano iron oxide is covered with FeOH due to water which forms either Fe^{-+} OH_2 or FeO^- depending upon the pH of the solution. The increased number of FeO^- sites leads to increased adsorption of positively charged heavy metal ions and vice versa. Another simple, low cost and eco-friendly iron oxide, i.e., magnetite (Fe_3O_4), is also widely used as a nano adsorbent for hosting heavy metal ions. Magnetite also exhibits the property of magnetism which enables its easy separation from the solution after adsorption. Magnetite has also been used for the removal of Cr^{6+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+} [115–117] etc. Different values of adsorption capacities were obtained for diverse heavy metal ions using different iron oxide-based nano adsorbents. This can be accredited to the fact that various metal ions have different hydrated ionic radii in the aqueous solutions, which interact differently with dissimilar negatively charged adsorption sites. Metal ions with higher hydrated ionic radii adsorb weakly as compared to metal ions with lower hydrated ionic radii [118]. Scientific reports illustrate the extensive use of magnetic and non-magnetic nano iron oxide for the hosting of organic and inorganic pollutants. In a study carried out by Iconaru et al., magnetite, i.e., nano Fe_3O_4, was utilized for the removal of As^{5+} and Cu^{2+} ions where better efficiency of nano-magnetite was observed as compared to commercial magnetite [119]. In a batch adsorption experiment, nano-magnetite were demonstrated for the removal of Cu^{2+}, Pb^{2+}, Mn^{2+} and Zn^{2+} ions where highest and lowest adsorption capacities were observed towards Pb^{2+} and Mn^{2+}, respectively [120]. This is attributed to the difference in hydrated ionic radii of metal ions resulting in different electrostatic interactions of metal ions on the surface of the nanoparticle. Similarly, non-magnetic haematite, i.e., nano $\alpha\text{-}Fe_2O_3$, was investigated for the effective adsorption of Cd^{2+} and Cr^{6+} with the adsorption capacities of 146.41 and 16.17 mg g^{-1}, respectively [121, 122].

Nevertheless, the use of bare iron oxide nanoparticles suffers from the limitation of their easy oxidation in water due to the presence of Fe^{2+} ions, the tendency to agglomerate, and corrosion by acids and bases as well. These limitations can be overcome by the functionalization of nanoparticles with organic and inorganic shell materials, which not only prevent their oxidation but also provide sites for enhanced metal ion adsorption. Functionalization not merely improves the adsorption efficiency of the adsorbent but also provides chemical binding to the pollutant via electrostatic and Van der Waals interactions for the adsorptive hosting of pollutants on the surface of the adsorbent [123, 124]. Enhanced adsorption capacities have been reported with polymer functionalized iron oxide nanoparticles. The surface modification of these nanoparticles combines the advantage of a magnetic core with organic and inorganic shell. Many materials like polypyrrole, polyaniline, polyvinyl imidazole, silica, polyethylene glycol, chitosan, tannin and surfactants have been used for the functionalization which improved the adsorption capacity and stability of nano iron oxide [125–133]. A variety of studies demonstrated the use of functionalized nano iron oxide for the improved adsorption efficiency towards heavy metal ions. In a scientific investigation, improvement in stability, mechanical strength, and removal performance was observed where nano Fe_3O_4 were functionalized with a polymer, i.e., polymeric mercaptoethylamino [134] for the removal of Ag^+, Hg^{2+}, Pb^{2+}, and Cd^{2+} ions and with polyacrylic acid and diethylenetriamine for the uptake of Cu^{2+} and Cr^{6+} with higher removal efficiency towards Cu^{2+} as compared to Cr^{6+} [135]. The higher adsorption capacity was calculated for Cu^{2+} ions as compared to Cr^{6+} ions. Furthermore, the toxicity of nano iron oxide was minimized along with improved metal ion uptake capacity by functionalization with some biomolecules like glycine [136] and carboxy methyl cellulose [137] for improved hosting of Pb^{2+} ions. The incorporation of amino functional groups in the former and chelation in the latter was responsible for the enhanced removal performance. Also, some organic molecules have been used as chelating ligands to increase the adsorption capacity and selectivity of nano iron oxide. In a scientific investigation, nano Fe_3O_4 were amino-functionalized with a chelating ligand, i.e., triethylenetetramine [138] for the 85% removal of Cu^{2+} ions and with humic acid [139] for the removal of Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} ions where the adsorption capacity was found higher than bare nano-Fe_3O_4.

In addition, nano iron oxides have also found their application in the removal of dyes. Both bare and coated iron oxide nanoparticles have been investigated for dye adsorption. In a report, Reactive Red 2/A [140] was 95% removed adsorptively using nano-magnetite within 10 min. Another magnetite adsorbent functionalized by 3-aminopropyltriethoxysilane (APTES) was illustrated for the 96% adsorptive hosting of Sunset Yellow [141]. Similarly, surfactant i.e. sodium dodecyl sulphate (SDS) and hyperbranched polyglycerol modified Fe_3O_4 based nano adsorbent, were successfully demonstrated for the efficient removal of Crystal Violet [72] and MB [142] dyes, respectively. Scientists have also employed amino acids, i.e., L-arginine coated magnetite nano adsorbent for the elimination of Reactive Blue 19 dye [143] through adsorption. Not only bare and modified, but nano-magnetite supported on activated carbon surface have also proved as an efficient candidate for the dye pollutant hosting, attributing to the highly enhanced surface area of nano adsorbent. Magnetite mounted on activated carbon and Mn-doped magnetite doped on activated carbon have shown their implication in the elimination of MB [144] and MG [145] dyes with adsorption capacities of 117 and 87.5 mg g^{-1}, respectively.

9.2.4 Nano Silicon Dioxide

Silicon dioxide i.e., silica is a known inorganic material due to its applications in chromatographic columns. It is a porous material with high specific surface area of 700 m^2 g^{-1} which makes it suitable for the adsorptive removal of water pollutants. Nano silica exhibits great potential in adsorptive removal of organic and inorganic pollutants owing to its unique properties i.e. increased surface area, tailorable surface properties, and well-defined pore size. Further, the adsorption capacity and selectivity can be enhanced by modification of nano silica with different organic functional groups like $–NH_2$, –SH, –OH, etc., or by using as support for other NPs and nanocomposites. Biofunctionalized silica nanospheres were fabricated and were modified with 3-aminopropyl and phenyl groups for the hosting of Cu^{2+} ions and a cationic dye, i.e., MB [146]. The adsorption capacity was increased towards Cu^{2+} ions and MB upon increasing the number of amino groups, which may be due to the rise in the number of binding sites on the surface of silica nanospheres. To enhance the adsorption capacity of nano silica, a nanocomposite of nano polyaniline and nano silica, as well as a crosslinked nano polyaniline immobilized on the surface of nano silica, was developed for the removal of different ions like Cu^{2+}, Hg^{2+}, Cd^{2+}, and Pb^{2+}. Higher adsorption capacities were noticed towards each metal ion in the case of crosslinked nanocomposite [147]. Not only the surface-modified but magnetic nano silica also gained considerable interest for hosting different pollutants from waste water. In this perspective, nano magnetite coated with silica showed their ability in this application at an industrial scale. In addition, core–shell nanoparticles of $Ni@SiO_2$ were fabricated where magnetic properties of Ni were combined with porous silica for the enhanced and cost-effective removal of different dyes containing –OH group, i.e., Rhodamine B and Orange II and dye without –OH groups, i.e., Methylene Blue and Methyl Orange. Here, the effect of functional groups and charge on dye structures on the removal performance of nano adsorbent was examined, indicating higher adsorption capacity towards negatively charged dyes with –OH group with respect to the positively charged without –OH groups [148].

9.2.5 Nano Aluminum Oxide

Nano aluminum oxide is another low-cost and effective adsorbent for hosting waste water contaminants with efficient decontamination ability [149, 150]. Aluminium oxide possesses different crystalline structures like α, y, η, and θ where y-alumina (y-Al_2O_3) is most widely used. The bulk y-Al_2O_3 has been utilized as a conventional natural adsorbent for the elimination of water pollutants due to its interesting properties viz high compressive strength, resistance to corrosion, good thermal conductivity, and high electrical insulation [151]. The use of Al_2O_3 in the form of nano significantly enhances the capability as compared to bulk alumina. This can be accredited to the increased specific surface area, which leads to outstanding adsorption capacity and mechanical strength, low-temperature modification process [152]. The nano alumina has been used for hosting a number of organic and inorganic water pollutants. Tabesh et al. fabricated nano Al_2O_3 for the 97 and 87% adsorptive removal [153] of Pb^{2+} and Cd^{2+} ions, respectively. The maximum adsorption capacities of 47.08 and 17.22 mg g^{-1} were obtained for Pb^{2+} and Cd^{2+}, respectively. The adsorption potential of nano alumina was also investigated for the removal of Zn^{2+}, Cr^{6+}, Ni^{2+}, Cu^{2+}, As^{2+}, and Hg^{2+} [154–158] ions. Excellent adsorption capacities were observed for these metal ions. Further, the removal capacity of nano alumina can be enhanced by their surface modification with surfactants. The modification process not only improves the adsorption efficiency but also enhances their stability by preventing them from agglomeration. The surface of nano Al_2O_3 was modified with two different surfactants, i.e., SDS and Sodium tetra decyl sulphate (STS), for the enhanced removal of NH_4^+ and Cd^{2+} ions, respectively [159–161]. It was proposed that surface coating of anionic surfactant leads to alteration in surface charge which was responsible for the improvement in adsorption capacity. Nano alumina has also been found effective in boosting the adsorption performance of polyethersulfone (PES) membrane matrix towards Cu^{2+} ions [162].

Along with the hosting of heavy metal ions, nano-alumina has also found applications in the removal of organic pollutant dyes from the waste water. The high specific surface area and charged surface enable them to be effective in the adsorptive elimination of dyes. A number of scientific studies report the exclusion of different cationic and anionic dyes from the waste water. Scientists employed bare nano y-Al_2O_3, and SDS modified nano y-Al_2O_3 for the removal of a cationic dye i.e., Rhodamine B. The adsorption performance of SDS modified nano y-Al_2O_3 (97.7%) was found to be better as compared to bare y-Al_2O_3 (40%) [163]. This was due to the higher negative charge on the surface of SDS modified nano y-Al_2O_3 providing enhanced interaction towards cationic dye. Another cationic dye i.e., MB was also removed using nano y-Al_2O_3 with adsorption capacity of 1000 mg g^{-1} [164]. Electrostatic interactions between y-Al_2O_3 and MB were responsible for high adsorption capacity. In addition to cationic dyes, nano y-Al_2O_3 have also been found effective in the hosting of anionic dye i.e. Orange G where adsorption occurred via physisorption with 100% removal efficiency [165].

9.2.6 *Bimetallic Nanoparticles*

The name bimetallic nanoparticles indicate the blend of two different metals providing an assortment of new, different, and improved properties. Bimetallic nanoparticles are obtained in different forms like alloys, core–shell, and contact aggregate. In alloyed structure, two different metals are present homogeneously, whereas in core–shell type arrangement, one of the metals usually the inexpensive one is made core and the other acts as a shell. Bimetallic nanoparticles are fabricated by co-reduction or successive reduction of two metals. The properties of bimetallic nanoparticles depend upon the metals combined, mode of combination, size, and difference in reduction rates of two different metals. The process of bi-metallization results into improved and flexible electronic, structural, catalytic and surface properties. These bimetallic nanoparticles have received great attention among industrial and scientific areas owing to their novel properties. In the field of catalysis, bimetallic nanoparticles have demonstrated improved performance as compared to their monometallic counterparts. The mono metal and metal oxide nanoparticles exhibit the limitation of easy deactivation [166–170] and are easily affected by pH [171, 172] of the solution, which can be conquered by coating a small amount of noble metals on the surface of other active metals. Till date, a variety of bimetallic nanoparticles have been explored for the hosting of various organic compounds like chlorinated organic compounds, dyes, and inorganic metal ions from waste water. Fe-based bimetallic nanoparticles containing Ni, Cu, Al, and Pd as second metals have been investigated for the hydro dechlorination of polychlorine organic pollutants (Table 9.1).

Table 9.1 Removal of various chlorinated water pollutants using bimetallic nanoparticles

Sl. no	Chlorinated pollutant	Bimetallic NPs	% Removal	Refs
1	2,4-Dichlorophenol	Pd–Fe	99.0	[174]
2	Hexachlorobenzene	Cu–Fe	99.4	[175]
3	2,4,6-Trichlorophenol	Pd–Zn	100.0	[176]
4	3-Chlorophenol	Pd–Al	99.7	[177]
5	Pentachlorophenol	Ni–Fe	100.0	[178]
6	γ-Hexachlorocyclohexane	Pd–Fe	100.0	[179]
7	Dichloromethane	Cu–Al	98.0	[180]

The use of Fe-based bimetallic nanoparticles suffers from the certain limitations of spontaneous corrosion of Fe surface, which causes easy deactivation of nanoparticles system. This issue can be addressed by loading of bimetallic nanoparticles on carbon microspheres, or by adsorption of surfactants or polymers on the nanoparticles surface for prevention of agglomeration and corrosion [179] which can lead to increased cost-effectiveness of the process. Therefore, substantial attempts are being made to replace Fe with other active metals Al, Pd, Zn, Mg, etc. [180, 181]. Scientists have also synthesized Pd–Mg [182] and Pd–Al [183] bimetallic nanoparticles for the dechlorination of 2-chlorobiphenyl.

In addition to the hosting of chlorinated organic compounds, bimetallic nanoparticles have also emerged as a promising candidate for heavy metal removal. Bimetallic nanoparticles pose higher redox activity and adsorption capacity as compared to their mono metallic counterparts. Again, the Fe-based bimetallic nanoparticles containing other metals have achieved great success for the reductive hosting of Cu^{2+}, Cd^{2+} and Cr^{6+} ions [184–186]. Further, the removal performance of bimetallic nanoparticles can be ameliorated by supporting them on polymeric surface. Enhanced removal capacity of Fe-nanoparticles supported on montmorillonite clay towards Cr^{6+} was observed because of the combined adsorption tendency of montmorillonite clay and reduction capacity of nanoparticles [187]. Other toxic metals like As^{5+} and Se^{4+} have also been successfully removed using bimetallic nanoparticles. Fe–Mn nanoparticles were synthesized [188] for the oxidation of As^{3+} to As^{5+} followed by complete removal of both ions owing to the oxidation capacity of Mn and adsorption efficiency of iron oxide. Similarly, Fe–Al nanoparticles (Fig. 9.6) were also employed for the complete elimination of As^{3+} to As^{5+} ions via simultaneous oxidation and reduction

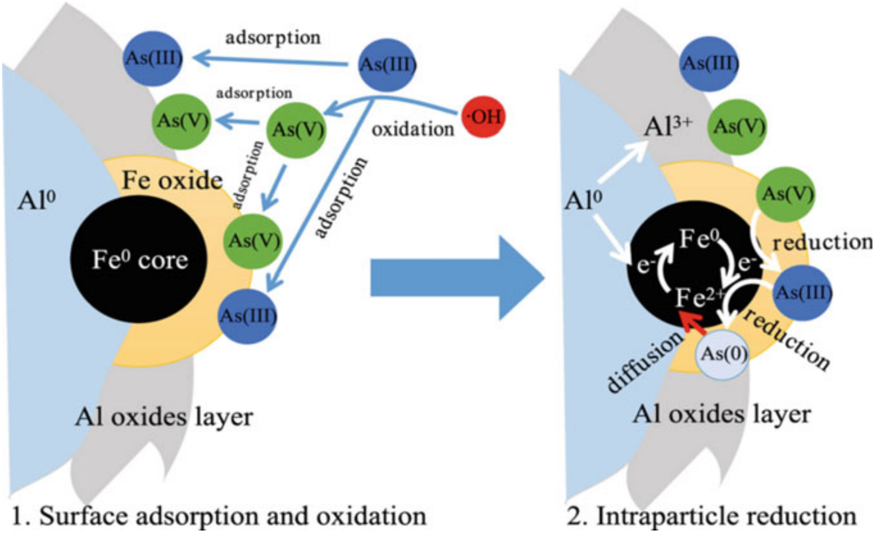

Fig. 9.6 Possible mechanism of As ions hosting by Fe–Al bimetallic nanoparticles (adapted with permission from [188])

followed by adsorptive hosting [188]. The As^{5+} ions adsorbed on the Fe oxide layer get diffused to Al part where these get reduced to As^{3+} which further reduced to As^0 via oxidation of Al and Fe into Al^{3+} and Fe^{2+} ions.

Bimetallic NPs have also gained a lot of attention from researchers for the removal of other organic and colored pollutants, i.e., dyes from the waste water. The scientific literature describes the outstanding behavior of bimetallic nanoparticles for the effective removal of dyes containing azo (–N = N–) functional groups, i.e., azo dyes. Scientists utilized Fe–Ni NPs for the effective hosting of Orange G in the waste water. The complete reductive degradation of dyes into by-products like aniline and naphthol was observed, which was followed by adsorption of byproducts [189]. Similarly, Fe–Cu [190] nanoparticles were developed for the complete decolorization of MB dye. Fe–Zn nanoparticles [191] were also exploited for the effective removal of Congo Red and MG dyes.

Further, to reduce the toxicity and threats caused by the leaching of toxic metal from bimetallic metals, these nanoparticles can be immobilized on many versatile catalytic supports. These nanoparticles supported on catalytic surfaces considerably enhance the removal performance and eco-friendliness of the system. Fe–Cu and Fe–Pd supported on agar gel were employed for the removal of Methylene Blue and Rhodamine B dyes with 90 and 80% efficiency, respectively [20].

9.3 Research Gaps

Although these nano adsorbents have emerged as the most promising candidates for effective hosting of contaminants from waste water, however, there are some issues in the bottleneck which are required to overcome for making them a superior host of water pollutants. Most metal oxide nanoparticles exhibit the limitation of instability, dispensability, and agglomeration, which lessens their removal performance. Also, their nano scale size makes separation from the waste water difficult. The use of modified and doped nano composites can provide the solution to these problems as it not only enhances the removal capacity but also provides stability and selectivity to the nano adsorbents. These metal oxide nanomaterials have been modified with a variety of polymeric, organic, and inorganic compounds to increase their removal capacity and selectivity towards the target contaminant. However, their synthesis and long-term performance is an issue. Similarly, bare NZVI and bimetallic nanoparticles containing iron suffer from the disadvantage of loss of activity due to corrosion and agglomeration. This problem has been solved by supporting nanomaterials on the surface of polymeric or surfactant support which combines the advantage of the high surface area of support with the removal activity of bimetallic nanoparticles by preventing them from agglomeration and corrosion. Although functionalized, doped, and supported metal-based nanoadsorbents have emerged as a promising solution. However, their synthesis and long-term performance are still an issue.

The commercial availability and use of nanoparticle-based adsorbents used for the hosting of water pollutants are rare; therefore, it is required to fabricate these nano adsorbents at an industrial scale. Also, from the economic point of view, the development and production cost of nano adsorbents should be optimized. Further, the application of nano adsorbents for onsite treatment is simple, more effective, and also reduces the operational cost of waste water treatment. Therefore, there is a strong need to develop the nano adsorbents which can be utilized and recycled for the onsite treatment of waste water.

Last but one, the escalated use of nano adsorbents at an industrial scale could impart toxicity to fauna and flora persistent in the environment. Therefore, the toxicity evaluation and biocompatibility of developed nano adsorbents towards the environment and human beings should be investigated prior to their implication in the field of hosting of water pollutants. The synthetic procedure for the development of nano adsorbents should meet the requirements of green chemistry. However, the reports on the toxicity evaluation of synthesized nano adsorbents are fewer.

9.4 Conclusions

The metal oxide-based nanostructures have been extensively utilized for the complete removal of inorganic and organic water pollutants owing to their excellent properties. The current chapter describes the extensive applicability of different metal, metal oxide-based nanomaterials, viz. NZVI, nano iron oxide nano alumina, nanosilica, nanotitania, and bimetallic nanomaterials for the removal of heavy metal ions, dyes, and chlorinated organic compounds from waste water. The mechanism of hosting of water pollutants using NZVI and bimetallic nanoparticles is usually based upon the adsorption followed by oxidative or reductive degradation of contaminants. Therefore, these have found great success in the complete removal of organic compounds, i.e., dyes and chlorinated organic compounds. The hosting of heavy metal ions using NZVI depends upon the standard reduction potential of heavy metal ions being hosted. Fewer reports on the reductive removal of metal ions, specially As^{5+}, Cu^{2+}, Cd^{2+}, and Cr^{6+} involving the use of bimetallic nanoparticles are available. Among all the metal oxides, oxides of iron, i.e., Fe_2O_3 and Fe_3O_4 have been exploited the most for the adsorptive hosting of heavy metal ions owing to their magnetic properties. Further, ceramic-based nano adsorbents like nano silica and nano alumina have also established their higher applicability on the hosting of heavy metal ions as compared to organic contaminants. Nevertheless, the commercial availability of such nanomaterials and their toxicity imparted on fauna and flora are also the issue of concern. To minimize the harmful effects of nano adsorbents, regulatory measures on their use are also recommended. So, nano adsorbents have emerged as an excellent alternative to conventional adsorbents due to their unique and remarkable properties. Still, there is a long way to go to use nano adsorbents in practical applications of the hosting of waste water pollutants.

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