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Review

Nanomaterials for Water Remediation: An Efficient Strategy for Prevention of Metal(loid) Hazard

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Abstract: Different natural and anthropogenic global events and activities such as urban settlements and industrial development have led to a build-up of numerous pollutants in the environment, creating problems for nature and human health. Among the pollutants, metal(loid)s are persistent and ubiquitously present in the soil, water, and air. The presence of high concentrations of metal(loid)s in water is of serious concern, as water is a basic necessity of humans and plants. Through irrigation, metal(loid)s enter and accumulate in plants, and subsequently reach humans via food. There is demand for sustainable and practical technologies for tackling the challenge of metal(loid) pollution. Nanotechnology has found its place in diverse fields including cosmetics, sensors, remediation, and medicine. Nanoremediation is an effective, feasible, and sustainable technology for cleaning up water contaminated with metal(loid)s and other chemicals. The versatility of nanomaterials is huge due to their differences in size, shape, surface chemistry, and chemical composition. This review sheds light on different nanoparticles (NPs) used for water remediation and summarizes key recent findings. The successful application of NPs in laboratory studies warrants their potential use in water clean-up from a small to a large scale.

Keywords: metal(loid)s; nanoremediation; nanomaterials; pollution; water

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1. Introduction

Water is an important resource for the survival of life on Earth, and all living organisms, including humans, need water. In recent decades, excessive metal and metalloid contamination in water has become a serious concern all around the world. Metal(loid)s are defined as elements with a density of more than 4–5 g/cm^3 that are toxic to humans even at low levels [1]. Toxic metal(loid)s may harm the environment, plants, animals, and human health. The uncontrolled extraction and processing of metal(loid)s from natural geological sources owing to their demand by the rising population and numerous applications to support the modern living standards have resulted in increased metal(loid) contamination intensity and regarding area coverage. Simultaneously, agricultural operations have increased and resulted in the greater usage of soil and plant additives, fertilizers, and pesticides, which include metal(loid)s as impurities. Natural sources of metal(loid)s include the biogeochemical weathering of rocks and volcanic eruptions [1].

For biological systems, several metal(loid)s are essentially required from trace to large quantities. However, when present at higher concentrations than those optimally required, even the essential metal(loid)s induce toxicity. Metal(loid)s such as arsenic (As), copper (Cu), nickel (Ni), cadmium (Cd), mercury (Hg), chromium (Cr), and lead (Pb) are extremely detrimental to human health, and can enter the human body and cause various ailments. Arsenic can cause diseases such as skin lesions, and skin, bladder, and lung cancers [2]. Lead can cause various cardiovascular and neurological diseases due to accumulation in the human body if it is exposed to them for a long period of time [3]. The kidneys are an easy target for Hg toxicity. Mercury is easily spread through aquatic systems, and can cause renal dysfunction and proteinuria [4]. Chromium is a known human carcinogen that directly affects the nervous system, and can cause brain cancer and other motor neuron diseases [5]. Cadmium toxicity can cause various lung, kidney, and bone diseases, and affect the reproductive system [6]. The ill effects of Ni toxicity observed among workers in mining industries are lung cancer, skin allergies, and various cardiovascular diseases [7]. Considering the above-stated toxic side effects caused due to metal(loid) toxicity, it is important to alleviate this problem to prevent various harmful diseases in humans.

Contaminated drinking water acts as the major source of metal(loid)s for humans. Water is also used for irrigation purposes, and due to this, contaminated irrigation water can be a source of metal(loid)s for plants and grains, and subsequently for humans via food. The arsenic contamination of groundwater is a serious problem that has arisen due to natural and anthropogenic factors such as mining, overirrigation, and the natural presence of As in groundwater [2]. Mining and industrial activities discharge their wastewater in nearby streams, and this leads to the accumulation of metal(loid)s such as Cr, Cd, and Pb in water sources [3–6]. Mercury can volatilize in the air; thus, it can spread to longer distances from the original source via atmospheric deposition [4]. Contaminated water, wastewater, and drinking or irrigation water need to be remediated to render it suitable for discharge or other useful purposes. Metal(loid) resources are exhaustible. Hence, as much as possible, metal(loid)s must be extracted back from contaminated media for reuse.

A large number of physicochemical and biological methods are available for water clean-up. These include bioremediation, phytoremediation, chemical precipitation, membrane separation, adsorption, and ion exchange [8]. Adsorption-based methods are appropriate considering the possibility of removing adsorptive material and subsequent metal(loid) extraction. A number of materials such as microbial cells, crop residues, fly-ash, and red mud can be used for adsorption. Nanoremediation is the process of removing environmental toxins from polluted places by utilizing nanoparticles (NPs)/nanomaterials (NMs). These NPs/NMs can be generated either by chemical methods or biologically by plants, fungi, and bacteria [9]. Nanomaterials such as titanium oxide (TiO_2), silver (Ag), nano zero valent iron (nZVI), cerium oxide (CeO_2), zinc oxide (ZnO_2), nanohydroxyapatite (NHAP), and nano carbon black (NCB) were successful in eliminating metal(loid)s and other contaminants in several studies (Figure 1) [10,11]. Because of its enhanced properties, such as a high surface-area-to-volume ratio and high reactivity, nanotechnology has emerged as the most effective approach for remediation. The ultraminute size of NPs/NMs facilitates handling them for example via packing small filter cartridges. Further, even a small volume of NPs/NMs, can offer many-fold large surface area for interaction with metal(loid)s. Further, the surface of NPs/NMs can be modified by addition of other chemical ligands as per the requirement, and this can further enhance the reactivity, usability, and efficiency of NPs/NMs [12]. Nanotechnology can find application in remediation of metal(loid)s either alone or in conjunction with plants and other methods. The present review article discusses the application of various NPs in metal(loid) remediation.

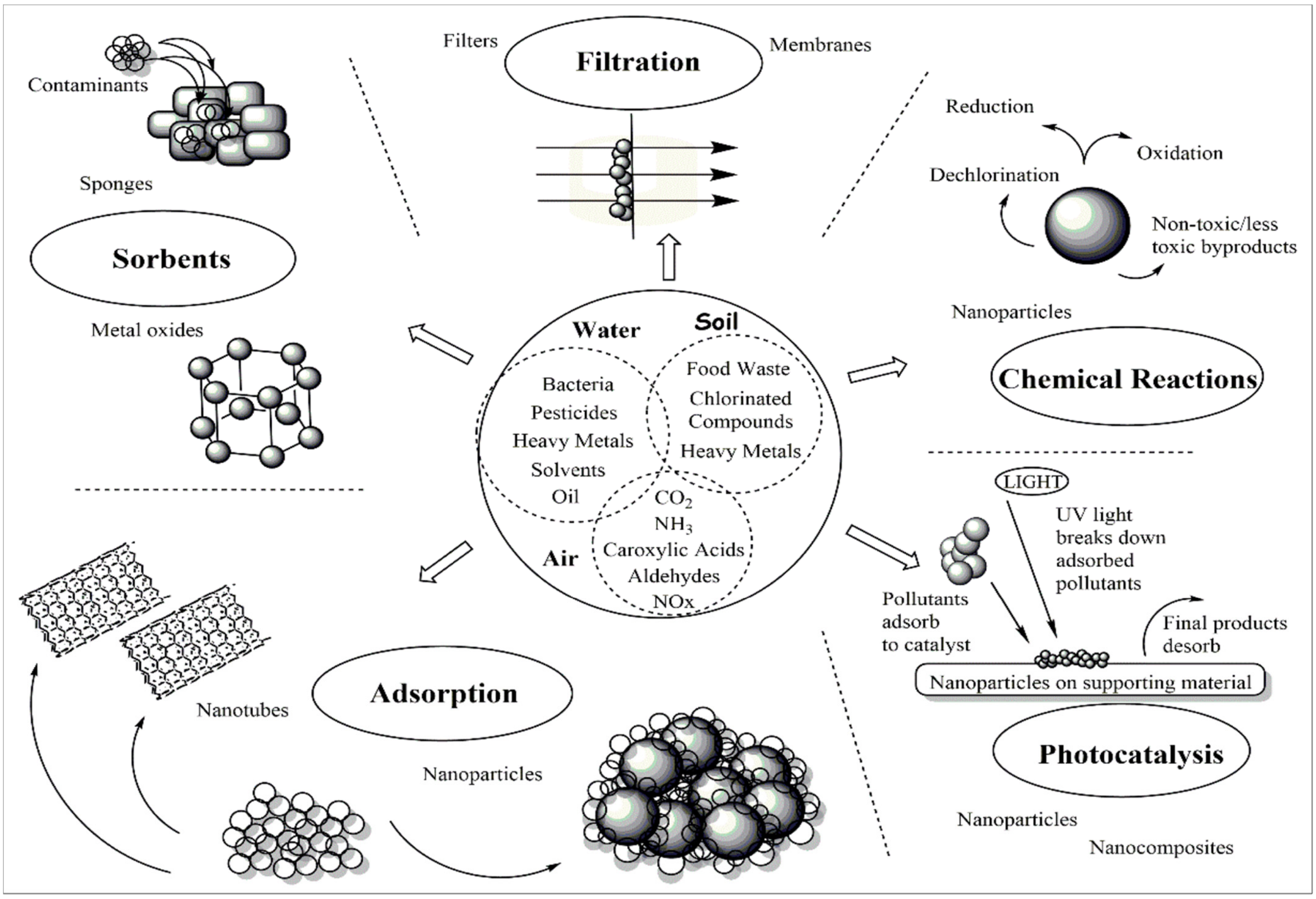

Figure 1. General overview of environmental remediation approaches with the use of nanotechnology.

Nanoremediation uses nanotubes, carbon and carbon-based NMs, NPs, nanofibers, nanoclusters, and nanocomposites to remove water pollutants. Due to their magnetic features, low toxicity, high chemical stability, ease of manufacture, and high recycling capacity, magnetic NPs are frequently utilized in remediation operations, particularly for the removal of pollutants from aqueous solutions. Carbon-based nanomaterials (CNMs) are effective adsorbents due to their unique morphological and structural features [13]. Despite the fact that their hydrophobic qualities and low solvent solubility set them apart from the competition in terms of cost, they have limited application in wastewater treatment. After functionalization, the problem of the hydrophobicity-related low solubility of CNMs can be tackled, and their selectivity for contaminants can be increased. Graphene is a single atomic sheet of graphite with remarkable mechanical, chemical, electrical, and physical characteristics, and low manufacturing cost. The graphene family has been applied as nanoadsorbents for remediation purposes [12]. Organic NMs prepared from synthetic polymers or natural compounds such as cellulose and chitosan are also often used, and they offer great metal(loid) removal due to presence of functional groups such as $–NH_2$, –COOH, and –OH [12]. Metal–organic frameworks (MOFs) are hybrid materials of organic and inorganic mixtures. These contain metals as an inorganic component, and zirconium (Zr)-based MOFs have gained interest for metal(loid) removal [14]. There are several other NPs of different metals and metal oxides whose application is continually increasing for the remediation of metal(loid)-contaminated media (Figure 2).

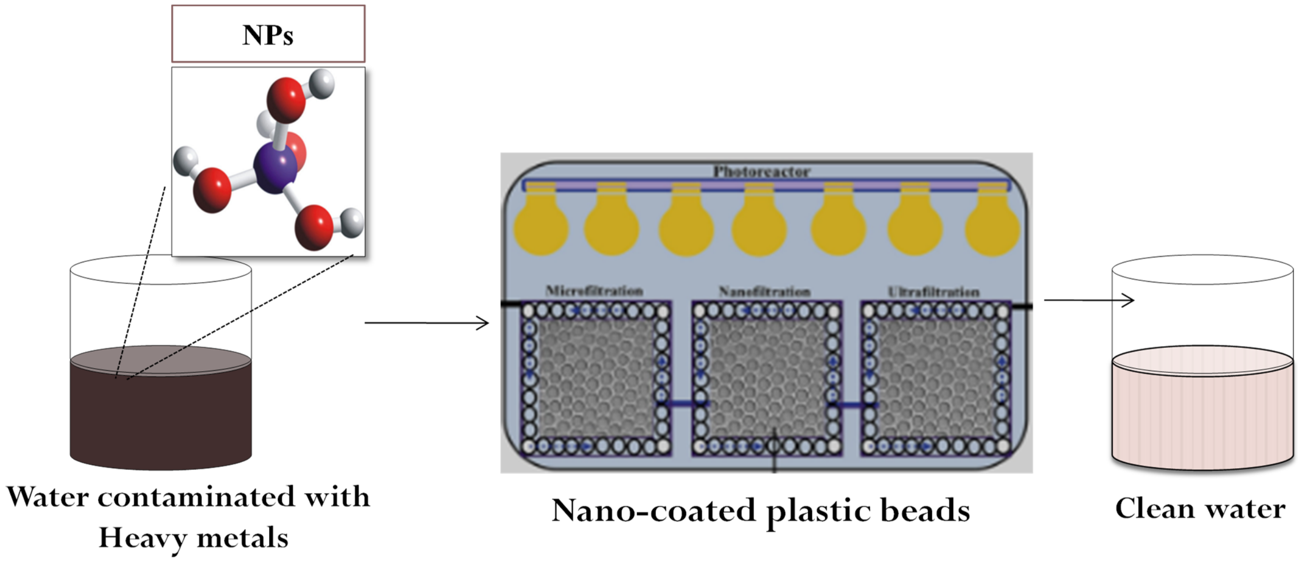

Figure 2. Nanoparticle-mediated water remediation.

The adsorption capabilities of adsorbents are analyzed using adsorption isotherms. There are various models that can be used to determine the adsorption isotherms. In the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbents, and there is no further adsorption behavior on these sites once the adsorbates have occupied them. The Freundlich model is used in the case of nonideal sorptions and is based on multilayer adsorption, which renders it different from Langmuir model where only a single adsorbate is bound to a site. The Sips model is a hybrid of the two above models that converts into a Freundlich isotherm at a low concentration, and a Langmuir isotherm at a high concentration of adsorbates [15]. So, on the basis of these isotherms, the adsorption capacities of various NPs are analyzed, and then these NPs are used for the removal of metal(loid)s from water. Table 1 summarizes the key findings of recent studies with respect to the NP-mediated remediation of metal(loid)s from water.

Table 1. Applications of nanomaterials in metal(loid) remediation from the environment.

Nanomaterial Types	Metal(loid)	Key Results	References
Fe_3O_4 magnetic nanoparticles (MNPs) coated with hyperbranched polyamidoamine (PAMAM) dendrimer, MNP-PAMAM; 0.1–0.2 g/L	Pb(II), Cd(II), Ni(II); 10–100 mg/L	The maximal adsorption capacities were 92.82, 80.10, and 57.72 mg/g in a single system, and 37.00, 31.91, and 24.94 mg/g in a ternary system for Pb(II), Ni(II) and Cd(II), respectively	[16]
FeONPs synthesized with *Rosa indica* flower petal extract	Cr(VI)	Cr(VI) (10–50 ppm) adsorption was good with 0.1 to 0.5 g/L NPs	[17]
Nanocomposite hydrogels of polyaniline–polypyrrole-modified graphene oxide in an alginate matrix (GO@PAN-PPy/SA)	Cr(VI) and Cu(II) (5–25 mg/L)	The maximal adsorption for Cr(VI) and Cu(II) was 133.7 and 87.2 mg/g at pH 3.0	[18]
Bilayer–oleic coated FeO NPs (bilayer–OA@FeO NPs) (0.1–3 g/L)	As(V) (0.01–0.15 mg/L)	High As(V) sorption (32.8 µg/g) occurred at pH 7.0 at 1 g/L dose	[19]
Calcium alginate entrapped in magnetic NPs and functionalized with methionine	As(III) (10–35 mg/L)	About 99.56% As(III) was removed from 10 mg/L solution at pH 7.0 with 1.6 g of adsorbent in less than 2 h	[20]
Aminopropyltrimethoxysilane (APTMs)-modified bamboo-derived TEMPO-oxidized nanofibrillated cellulose (TO-NFC) aerogels ((APTM-modified TO-NFC))	Cu(II), Cd(II), Hg(II) (0–200 mg/L)	Aerogel showed adsorption capacity of 99.0, 124.5, and 242.1 mg/g for Cu(II), Cd(II), and Hg(II), respectively; optimal adsorption efficiency at pH 3–7	[21]
Carboxymethyl cellulose (CMC) bridged chlorapatite (CMC-CAP) NPs	Cd(II) (5 mg/L) Zn(II) (7 mg/L)	Maximal sorption capacity of CMC-CAP was 141.1 and 150.2 mg/g, respectively, for Zn and Cd	[22]

Table 1. *Cont.*

Nanomaterial Types	Metal(loid)	Key Results	References
Fe_3O_4 NP-modified activated carbon prepared from biochar (FAC)	As(V) (15–600 mg/L)	The maximal adsorption of As(V) on FAC was 32.57 mg/g	[23]
Simarouba glauca leaf-extract-synthesized $CuFe_2O_4$ NPs; 0.025 to 0.1 g	Pb(II); 10–40 mg/L	Good Pb removal was achieved with NPs at pH 6 with 0.05 g adsorbent from Pb solution of 20 mg/L	[24]
Moringa oleifera activated carbon (AC) + chitosan (CS) and Fe_3O_4 NPs; 1 g/L	Cr(VI); 20 mg/L	Adsorption capacity of AC, CS/AC, AC/Fe_3O_4, and CS/AC/Fe_3O_4 adsorbers for Cr(VI) was 56.78, 114.80, 121.70, and 130.80 mg/g	[25]
Humic acid (HA)-coated hydrated ferric oxide (HFO)-porous resin D-201 nanocomposites (HA-HFO-D-201)	Cu(II), Cd(II) and Pb(II)	Excellent metal removal in pH range of 3–9, >90% metal removal achieved with nanocomposite	[26]
Biochar-loaded Ce^{3+}-enriched ceria NPs (Ce-BC) (20–50 mg/L)	As(V) (10 mg/L)	Up to 99.7–100% As was removed from 0.05 and 0.1 mg/L solution of As(V) by Ce-BC	[27]
SnO^2 nanoparticles (NPs) synthesized using Vitex agnus-castus fruit extract; 0.03–0.24 g/L	Co(II); 100 mg/L	The removal efficiency was higher than 94% at 298 K after 60 min at an adsorbent dosage of 0.12 g/L	[28]
Biochar fabricated with MgAl layered double hydroxide (MgAl-LDH) nanosheets; 0.2–1.0 g/L	Pb(II) and $CrO_4{}^{2-}$; 10–500 mg/L and 10–300 mg/L	The adsorption capacity for lead was 591.2 and 330.8 mg/g for $CrO_4{}^2$, which is 263% and 416% higher than the adsorption capacity of only the biochar	[29]
Superparamagnetic amino/thiol nanoparticle (Fe_3O_4@SiO_2@GLYMO(S)-en) (Glymo(S)-en; thio-(3-Glycidyloxopropyl)trimethoxysilane); 16 mg	Pb(II) and Cd(II); 50 mg/L	Adsorption capacity of 93.5 mg/g for lead and 89.64 mg/g for cadmium at pH 7 and contact time of 55 min	[30]
Ccarboxymethyl cellulose stabilized FeS NPs (CMC-FeS) (0.15 mg/L)	Hg (0.6 mg/L)	The maximal sorption of 3358.28 mg/g Hg by CMC-FeS	[31]
NiO-MgO-SBNs; 25 mg	Cu(II), Cr(III), and Zn(II); 50–400 mg/L	The adsorption capacity for Zn(II), Cu(II), and Cr(III) was 37.69, 69.68, and 209.5 mg/g, respectively, at pH 5.5	[32]
Fe and Cu oxide NPs stabilized by rice-husk biochar; 10 g	As(III) and As(V); 0.5–128 mg/L	The removal efficiency of As(III) + As(V) (70 mg/L) was 95.3% at pH 7 in 60 min of contact time	[33]
HTO NPs supported by rice straw (RS-HTO) via sol-gel method; 2 g/L	Cu(II); 10 mg/L	The adsorptive removal efficiency was more than 99% by RS-HTO at pH 7.5	[34]
Humic acid coated magnetic nanoadsorbent (HA/Fe_3O_4); 2–20 mg/ml	V(IV); 50 mg/L	With the Langmuir isotherm model, the maximal adsorption capacity for vanadium was 8.97 mg/g at pH 5	[35]
Polypyrrole functionalized magnetic Fe_3O_4 nanoparticle (Ppy@Fe_3O_4); 0.05 g/L	Ni(II) and Cr(VI); 10–40 mg/L	The maximal adsorption caapacity was 19.92 mg/g for Ni(II) at pH 6 in 150 min and 344.82 mg/g for Cr(VI) at pH 2 in 60 min of contact time	[36]
Fe_3O_4 sulfonated magnetic NP (Fe_3O_4-SO_3H MNP); 10 mg	Cd(II) and Pb(II) 10–200 mg/L	Fe_3O_4-SO_3H MNP showed maximal adsorption of 108. 93 and 80.9 mg/g for Pb and Cd, respectively	[37]
Lignin hydrogels loaded with nano-FeS with variable level of polymerization (LH1–LH6) and NPs concentration	Cd(II) (100 mg/L) and tetracycline	The removal capacity of hydrogels for both contaminants was increased initially (up to LH3/4) due to the increasing content and decreasing size of FeS NPs	[38]

2. Nanoparticle Mechanisms for the Removal of Metals

There are a number of methods that can be applied to treat wastewater and remove metals, such as chemical precipitation, oxidation reduction, ion exchange, and adsorption. An important and beneficial condition for the removal of metals is the availability of a large surface area for achieving greater metal removal in one cycle of operation, and this condition is well-satisfied by nanomaterials. Nanomaterial adsorbents have a nanoscale size providing larger surface area in a specific volume as compared to the bulk material. The larger surface area also provides more reactive surfaces in the case of chemically modified NPs. The interaction mechanisms that enable the removal of metal ions from aqueous solutions are still unknown [39]. The majority of remediation techniques used to remove these contaminants involve sorption, sorption reduction, photocatalysis, and precipitation (Figure 3) [40]. Due to the chemical interactions between nanomaterials and metal ions, sorption is one of the most basic methods for removing metal ions from contaminated water [41]. In the adsorption mechanism, nanomaterials such as mesoporous silica entrap metal ions with large adsorptive surfaces and via functional groups involving both physical and chemical interactions. Nanoadsorbents also offer the unique opportunity of regenerating them through chemical processes such as desorption and reusing for several cycles [42]. Similar to immobilization, sorption reduction is a technique for changing high-valent metal ions into low-valent ones. First, high-valent metal ions are reduced, resulting in denser particles or clusters that precipitate more easily. Similarly, in precipitation, various nanoparticles are used to modify metal ions to insoluble precipitates by converting them into hydroxides or carbonates etc. The solid precipitate can be separated later with filtration [43]. The conversions of Se^{4+} into Se^{2+} and Cr^{6+} into Cr^{3+} are two frequent instances of these sorption-reduction processes. The photocatalytic degradation process has been extensively used to remove low concentrations of metals [44,45] despite the fact that it is frequently used to remove various organic contaminants. This method is based on photocatalytic reactions that are greatly influenced by the catalyst's shape, the absorption of visible light, and active sites. Depending on the type of metal ions and light sources, the mechanisms for metal ions may change [46]. Moreover, the ion exchange mechanisms operate on the basis of the mutual exchange of cationic or anionic metal species with the ionic ligands attached to the nanomaterials [47].

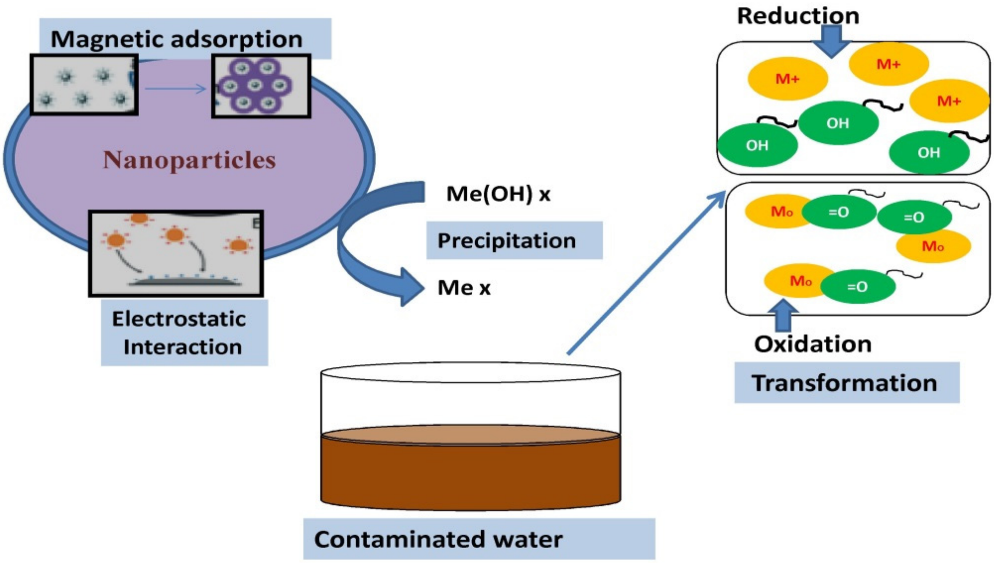

Figure 3. Key processes of the remediation of pollutants in contaminated water by nanoparticles.

3. Involvement of Nanomaterials in Metal(loid) Remediation

3.1. Role of Titanium Dioxide Nanoparticles (TiO_2 NPs)

Metal-oxide NPs such as TiO_2 are used to reduce the accumulation of toxic metal(loid)s such as As, Cd, and Cu. TiO_2 is the naturally occurring oxide of Ti and is typically found in crystalline polymorphs anatase, rutile, and brookite. Rutile and anatase generally exhibit similar qualities among the three polymorphic forms with the exception of rutile's lower weight and corrosion resistance. The fact that brookite is unstable at high temperatures and transforms into rutile also contributes to its rarity. It can be synthesized via microemulsion, hydrothermal, chemical vapor deposition, chemical precipitation, and sol-gel techniques. It can also be synthesized biologically with the help of plants, bacteria, fungi, and biological derivative compounds [48]. Nano-TiO_2 at a dose of 25 mg/L considerably lessened the negative impacts of wastewater on the growth characteristics of maize ($p < 0.05$) [49]. Qing et al. [50] reported that TiO_2 NPs had adsorption potentials of 22.63 and 14.06 mg/g for Au and Ag, respectively.

3.2. Role of Silica Nanomaterials

Mesoporous silica materials have been employed for a variety of applications, including adsorption and catalysis, due to their adaptability. Silica NPs are synthesized via several methods generating usually spherical and nonagglomerated Si NPs. The common precursors of Si NPs include tetraethyl orthsilicate (TEOS) and sodium silicate solution (SSS). Mesoporous silica materials aid in environmental cleanup methods due to their huge surface area, ease of surface modification, large pore volume, and capacity to modify pore size [51]. A number of studies have demonstrated the application of such materials for pollutant cleaning in the gas phase due to their outstanding performance as adsorbents. Furthermore, several investigations have discovered significant surface changes in mesoporous silica materials [52]. Silica NPs eliminated 70.3% (30 ppm) Ni and 60.1% (200 ppm) Ni in a batch adsorption experiment [53]. Sachan et al. [54] synthesized silica NPs by utilizing the leaves of *Saccharum officinarum* (SOL) *S. ravannae* (SRL), and *Oryza sativa* (OSL), and used these NPs for the removal of Pb(II) and Cu(II). The maximal adsorption capacity was 98.8 and 78.8 mg/g for SRL (5 mg), 99.5 and 97.52 mg/g for SOL (5–10 mg), and 99.75 and 97.99 mg/g for OSL SNPs (5–6 mg) for Pb(II) and Cu(II), respectively.

3.3. Role of Carbon Materials

A two-dimensional crystalline atomic structure of carbon is graphene. It is a feasible adsorbent for extracting dangerous inorganic compounds from wastewater because of its huge surface area, excellent chemical characteristics, and unique structure [55]. Because of hydrophobic contact, van der Waals forces, stacking, and hydrogen bonding, pollutants are easily drawn to the membrane. As a consequence, metal ion elimination becomes more efficient and versatile, and simpler. Graphene might be employed as a fluoride adsorbent due to its high adsorption capacity and efficiency. While pure graphene can be used to remove contaminants from the environment, other methods focus on the usage of modified graphene [56]. Modifications to graphene's surface diminish graphene-layer aggregation and hence increase effective surface area, rendering modified graphene more appealing. When a modified graphene oxide nanocomposite, graphene oxide-zirconium phosphate (GO-Zr-P, 150 mg), was used, ~99% of 50 ppm of (Pb(II), Cu(II), Cd(II) and Zn(II)) was removed in a time interval of 20 min, and ~98% of 50 ppb heavy metals was eliminated within 30 min when 50 mg of GO-Zr-P was used [57]. Moreover, carbon nanotubes have long been regarded as a paradigm shift in scientific breakthroughs due to their unique morphology and physical qualities, such as thermal, electrical, and mechanical conductivity. They have been a crucial instrument in the cleanup of metal(loid) contamination due to their extraordinary abilities [58]. These are divided into two types: single-walled carbon nanotubes (SWCNTs) and multiple-walled carbon nanotubes (MWCNTs). The way in which graphene is wrapped around the cylinder determines the zigzag, armchair, and chiral structural forms of SWCNTs. MWCNTs have a greater outside diameter than the inner nanotube diameter [59]. Inner and exterior grooves help with adsorption on the nanotube surface [60]. By changing the surface characteristics, oxidants such as $KMnO_4$, HNO_3, H_2SO_4, and NaOH can be used to promote adsorption. Carbon nanotube adsorption affinity to metal(loid)s is determined by their ionic radius, with higher electronegativity resulting in stronger adsorption. Contact, ion exchange, surface complexation, and electrostatic interaction all contribute to adsorption. It was attempted to open the closed end of pure carbon nanotubes in order to increase their adsorption capacities [61]. SWCNTs are frequently grouped hexagonally (one nanotube surrounded by six others), resulting in a bundle of coordinated tubes with a varied pore configuration [62]. SWCNT-based nanocomposites were created by using magnetite cobalt sulfide for fabrication. The nanocomposites were used to remove Hg, with findings demonstrating strong adsorption of more than 99.56% in under 7 min [63]. Alguacil and Lopez [64] reported the potential of MWCNTs in Au(I) and Au(III) removal. Further, CNTs with magnetic properties can be prepared by combining them with Fe_3O_4 NPs. Such materials can be used for metal(loid) removal and reused after metal(loid) extraction [65].

3.4. Role of Silver Nanoparticles (AgNPs)

Silver is the most widely used chemical, with well-reported antibacterial benefits, due to its low toxicity and destruction of microorganisms in water. Ag NPs, which are composed of silver salts such as silver nitrate and silver chloride, and are employed in a wide range of uses, have been discovered to be biocidal [66]. Ag NPs can be synthesized with chemical reduction (thermal, the oxidation of glucose, polyol process, Tollen, microemulsion), electrochemical (polyol process), physical synthesis, photochemical reduction (microwave radiation, pulse radiolysis, photoreduction, X-ray radiolysis) and biological synthesis (plants, bacteria and fungi) [67]. With efficiencies of 72.6%, 81.3%, and 88.1%, 0.75 g of walnut husk extract-silver nanoparticles (WHE-AgNPs) removed Pb, Cr, and Cd ions, respectively, from petroleum wastewater in 5 h at 25 °C. This was possible due to the WHE-AgNPs with metal ion physisorption on CN, NH, CO, CC, CO and OH sites [68]. AgNPs synthesized by using leaf extract of *Moringa stenopetala* successfully removed 97% of Cr(VI) from the solution as analyzed with the Freundlich isotherm [69].

3.5. Role of Gold Nanoparticles (AuNPs)

Gold NPs sizes range from 1 nm to 8 μm and can present different forms such as spherical, octahedral, tetrahedral, nanotriangular, nanorod, and nanoprismatic. Gold NPs can be coated with different biomolecules and polymers for distinct applications. Gold NPs are mostly utilized to remove mercury, resulting in amazing transformations into AuHg, $AuHg_3$, and Au_3Hg. Citrate-based Au NPs have been immobilized with Al_2O_3, and their behavior for mercuric ion removal was investigated. Other adsorbents, such as sodium borohydride, were also used to strengthen Au NPs, so that they could better remove mercuric ions [70]. When Hg(II) was reduced to Hg(0) using sodium borohydride, Hg(0) was removed with Au NPs supported on aluminum with a removal capacity of up to 4.065 mg/g, much more than the removal capacity in comparison to other adsorbents. Au NPs have a higher rate of Hg elimination than any other adsorptive substance. This type of Au NP supported on aluminum could be practically used to treat wastewater, as Au particles can be easily recovered, rendering it a cost-effective process as well.

3.6. Role of Zinc Oxide Nanoparticles (ZnO NPs)

ZnO NPs can be synthesized with chemical (precipitation, sol-gel, hydro/solvothermal, microemulsion, sonochemical, chemical vapor deposition (CVD), microwave-assisted method and electrochemical deposition), physical (pulsed laser deposition thermionic vacuum arc, thermal evaporation), and biological (plant extracts and microorganisms) methods [71]. ZnO NPs have a hard and rigid structure and low toxicity, and are biodegradable. The adsorption capacity of silica-based zinc oxide nanocomposites (nano-SZO) was 32.53, 32.10, and 30.98 mg/g for Cu(II), Ni(II) and Cd(II), respectively [72]. Casein-based ZnO NPs showed maximal adsorption capacities of 194.93, 67.92, and 156.74 mg/g for Pd(II), Co(II), and Cd(II), respectively [73]. The ZnO NP composite with clay, when used to remove Pb(II) ions, resulted in a maximal adsorption capacity of 14.54 mg/g for Pb(II) ions by using the Langmuir model [74]. The maximal removal efficiency of ZnO NPs, when used for the removal of Cu(II), was 98.4%, with a maximal adsorption capacity of 47.5 mg/g at pH. At pH 4, the maximal adsorption capacity was reached with an initial metal concentration equal to 8 mg/L [75].

3.7. Role of Iron Oxide Nanoparticles (Fe NPs)

Nanoscale zero-valent iron (nZVI) NPs are widely applied in the removal of metal ions from water. The synthesis of nZVI are divided into two types of methods, bottom–up (dissolved iron is transformed into nZVI with the use of reductants) and top–down (mechanical or chemical methods to convert large iron particles into minute nanoparticles). Toxic metal complexes such as Fe, Al, Ni, and Zn are treated using a variety of nZVI NPs. Because of their short half-life and strong reactivity to contaminants, they are good in disposing of a wide range of metal(loid)s. The use of an external magnetic field to remove contaminants is known as magnetic separation, and this strategy can be applied with nZVI. This nanomaterial exhibits a high level of reactivity in the presence of a range of contaminants and with different modifications. A few examples of modifications are surface-modified nZVI for improved dispersion, carbon-supported nZVI for better stability, and emulsified nZVI for better compatibility. The maximal adsorption capacity, according to the Langmuir isotherm, was found 16.56 mg/g for As(V) and 46.06 mg/g for As(III) when ascorbic acid coated iron oxide (Fe_3O_4) NPs were used for metal removal. When Fe_2O_3 nanoparticles were produced in a cellulose matrix, the maximal adsorption capacity was 23.16 and 32.11 mg/g for As(V) (Langmuir isotherm), and 9.64 and 3.25 mg/g for As(III) (Freundlich isotherm) [76]. The adsorption capacity for As removal was 216.9 mg/g when a Fe_3O_4/phenol–formaldehyde resin nanocomposite was produced via hydrothermal carbonization [77]. In the presence of high pH, the standard reduction potential of nZVI is less than the reduction potential of many metals such as Pb, Cd, Ni, and Cr, which helps in the binding of these metals to nZVI NPs. The removal efficiency of the nZVI adsorbent was 4.33–5.56, 5.40–6.94, and 5.41–6.95 mg/g for Cd, Cu, and Pb, respectively [78]. The adsorption capacity was 93% for Cd (6 ppm) after an interval of 5 h when nZVI was used for its removal [79]. The maximal adsorption capacity of Cr(VI) was 244.07 mg/g with a contact period of 2 h, and 221.84 mg/g with a contact period of 0.25 h [80]. However, the successful application of nZVI may be hampered due to their formation of agglomerates or due to (oxy)hydroxide corrosion. In the presence of other contaminants such as microplastics, the efficiency of nZVI may be affected. Luo et al. [81] showed that the metal removal potential of nZVI for Cu, Cr, Pb, and Zn was reduced when microplastics were also present. nZVI NPs could retain their metal removal potential even after storage for long duration. In a study, nZVI NPs were used fresh and after 10 months of storage, and the two potentials of nZVI for Pb(II) removal (98%) were almost the same [82].

3.8. Role of Aluminum Nanoparticles (Al_2O_3 NPs)

Aluminum is among the most abundant elements on Earth. The physical and chemical properties of Al NPs are good for a variety of applications, and their reactivity varies with size. Al_2O_3 NP production can be divided into three phases, solid (mechanical ball milling and mechanochemical), liquid, and gas [83]. About 87% As and 98% Pb were efficiently removed with the use of Zn-doped Al_2O_3 NPs with a high surface area and hydrophilicity [84]. In another study, 97% Pb(II) and 87% Cd(II) were efficiently removed with adsorption capacities of 47.08 and 17.22 mg/g on γ-Al_2O_3 NPs according to the Freundlich isotherm. When aluminum hydroxide NPs were applied for the removal of Cr(VI) and Pb(II), the removal efficiencies were 97% (pH 5) and 95% (pH 5.5), respectively, where the concentration of the metal ions was 10 mg/L, and of the adsorbent, it was 1 g/L [85].

4. Disadvantages of Using NPs for Water Remediation

The major disadvantages of using NPs for preventing metal hazards in water consists of the difficulty in collection of these NPs after the treatment process, the need for high mechanical strength for the separation of NPs from metals, preventing the accumulation of NPs in the water, and the leaching of new potential contaminants from NP complexes into wastewater. The other drawbacks of using these NPs include lesser reliability, high maintenance costs, and declining operating efficiency. The advancement in technology with the use of NPs for water remediation also comes with toxic effects that can be harmful for humans and the environment. Metal ions that are initially inert in bulk form can be highly toxic at the nanoscale. The small size of NPs is one of the major factors due to which they can easily access the internal organs and tissues, and can subsequently accumulate in humans and animals. CuNPs are deposited in gills and can induce oxidative stress in crayfish when they are exposed to them for a long time [86]. Other factors that contribute to the toxicity of NPs are their shape, crystallinity, surface charge and reactivity, large surface area, and solubilizing and agglomerating properties [87]. There are globally no specific laws for the regulation of nanomaterials, to the best of our knowledge. Although NPs are propagated as cost-effective, the cost of NPs such as Au and Ag can be too high for wide-scale application in water treatment, particularly for low-income countries [88].

5. Conclusions

Herein, we reviewed the various types of nanomaterials that can be used in removing toxic metal(loid)s from water. NPs such as titanium dioxide, silica, graphene, carbon nanotubes, silver, gold, zinc oxide, iron oxide, aluminum, and nano zero valent iron are excellent adsorbents of metal(loid) ions due to their large surface are, small size, and high stability. Nanotechnology opens up new possibilities for producing low-cost, environmentally friendly items. They have a wide range of physical and chemical characteristics rendering them a great waste treatment option. We now have a viable alternative to conventional adsorbents for metal(loid) extraction because of the progress of nanotechnology. It has the ability to provide ecologically friendly and green cleaning and management solutions that do not harm the environment. The field's expanding relevance is due to the range of expected possibilities, cross-disciplinary character, potential for innovation, and the influence of nanotechnology's potential advantages. Nanotechnologies have the potential to both improve and empower existing technologies while also enabling the development of new ones.

Nanotechnology's use in environmental cleanup might provide promising outcomes in the future. Environmental conservation necessitates the quest for new and better materials. In recent years, nanostructured materials have received much press as adsorbents or catalysts for removing toxic and destructive substances from the environment, such as wastewater, soil, and air. Due to the nanoscale of these materials, the long-term ill effects that can affect the environment and human beings should also be considered while using these nanoparticles in heavy-metal remediation and wastewater treatment, thereby creating the need for further research with respect to the toxicity of nanomaterials, as not enough material is available in this regard.

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