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Review

Sustainable Use of Nano-Assisted Remediation for Mitigation of Heavy Metals and Mine Spills

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Abstract: Increasing globalization in the last two decades has transformed the environment; hence, the demand for sustainable remediation approaches has also recorded an increasing trend. The varied sources of soil pollution include the application of chemical fertilizers and pesticides, industrial discharge, and transformed products of these accumulated chemical residues. These processes may hamper the composition and soil ecosystem. Different types of methodologies ranging from physical, chemical, and biological approaches have been exploited to tackle of this challenge. The last decade has observed a significant application of nanotechnology for the treatment and removal of contaminants. Nanomaterial (NMs) research has contributed to a new dimension for the remediation of polluted soils. The use of engineered NMs has not only carried out the remediation of contaminated sites but also has proven useful in combatting the release of soil pollutants. They have paved the way for eco-friendly approaches for the detection of pollutants along with the restoration of polluted sites to their nascent stages, which will also help in increasing soil fertility. Nano-enabled remediation mechanisms require extensive field and target-specific research to deliver the required output. This review focused on recent trends, emphasized the areas for further improvement, and intended to understand the requirement of an interdisciplinary approach to utilize nanotechnology for multitasking remediation approaches comprising different contaminants.

Keywords: remediation; sustainable; microbe; metal; nanoparticles

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1. Introduction

The increasing accumulation of heavy metals (HMs) in the food and water supply chain is a major cause of public health concern. Their high density and non-biodegradable nature make HMs such as Hg(II), Cr(VI),Pb(II), and Cd(II), the potent and most challenging environmental contaminants [1,2]. Soil acts as an important sink for supporting various lifeforms on earth, ranging from organisms as small as microbes to the most complex ones, i.e., animals and humans. The invasion of natural flora by various anthropogenic sources has resulted in the disruption of the natural cycling of nutrients and the accumulation of many undesired components such as HMs in the soil. The concept of sustainable development is not attainable pertaining to the present scenario of soil pollution. Due to rising populations, soil conservation should be a top priority in today's society, which is facing a challenging situation of diminishing land area and scarcity of food and shelter. The various approaches employed to tackle this situation involve thermal treatment, filtration, adsorption, chemical abstraction, membrane bound separation, microbial degradation, etc. Heavy metal removal can also be efficiently accomplished by employing methylene phosphonic acid (DTPMP) phosphonate intercalated with layered double hydroxide [3]. In another study, lysine intercalated with montmorillonite was reported to remove Pb (II) from wastewater via an adsorption mechanism [4].

The processes documented above consist of a single approach to treatment. It is true that these treatments have been successful, however, they also have certain drawbacks such as inefficiency, high costs, and failure at scale-up [5,6]. Acid mine drainage (AMD) is a form of pollution caused by drainage water flowing from sulfur-bearing sites into water bodies [7]. The mining of sulfide minerals exposes them to the environment, causing excessive amounts of acid to be produced, which can cause both immediate and long-term environmental harm. Some of the adverse effects of AMD include the corrosion of mining machinery and equipment, degradation of soil quality, and groundwater contamination due to the leaching of HMs present in mine and drainage water [8].

Air or water exposed to iron disulfide or iron pyrite produces acid mine drainage by oxidizing mineral sulfides. Oxygen and water react with metal sulfides to produce metal sulfates and sulfuric acid. Subsequent oxidation of the metals results in increased acidity [9]. In one such example, ferrous sulfide (pyrite) undergoes oxidation on reacting with water and oxygen to form ferrous sulfate and sulfuric acid. Ferrous sulfate oxidizes further to form ferric sulfate, and the rate of this reaction can further be enhanced by the action of certain bacteria such as *Acidithiobacillus ferroxidans*. Further, ferric sulfate reacts with water to form ferric hydroxide releasing hydrogen ions, which subsequently enhance the acidity of water. The resulting ferric hydroxide formed further reacts with pyrite and produces more acid. The amount of acid produced depends on the amount of iron getting oxidized [10].

$$FeS_2 + H_2O + 3\ 1/2\ O_2 \rightarrow FeSO_4 + H_2SO_4$$

$$FeSO_4 \rightarrow Fe_2(SO_4)_3 \rightarrow 2Fe^{3+} + 3SO_4{}^{-2}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Rainwater or water used in mining operations for dust control, drilling, or other purposes enters the mine as fresh water. Fissures and cracks in underground mines can allow ground water to seep into the mines. Sulfide minerals yield oxidized products that are transported to nearby rivers and other water bodies by flowing into the surrounding aqueous environment [11]. As pyritic sulfur reacts with water and oxygen, sulfuric acid is produced, and iron sulfate is formed. As a result, certain acidophilic bacteria such as *Acidithiobacillus ferroxidans* thrive and grow in this type of acidic environment created by coal mines. As a result, the acid production reaction is catalyzed by the bacteria and occurs more quickly than chemical oxidation [12]. The acidity in mine drainage water is primarily due to the production of sulfuric acid and hydrolysis of oxidized pyrite products [11].

The selection of any remediation technique employed for the removal of HMs is governed by several factors including the type and nature of the contaminant, its concentration, its form (simpler or complex form), the objective and time frame for treatment, the cost involved, and the environmental impact. Furthermore, treatment techniques are categorized into in situ and ex situ types depending on the nature and location of the site, the degree of contamination, and the treatment strategy to be employed (Figure 1). The former category is the most preferred as it employs the treatment of soil at its natural site by utilizing air, water, microbes, and plants. On the other hand, the latter is based on the excavation of contaminated soil to a point where it can be treated, i.e., into a fermenter, which makes it more complex and ultimately leads to a higher cost. All the conventional methods being employed today have several drawbacks including cost, time frame, and the release of by products, which result in post-treatment challenges involving environmental contamination.

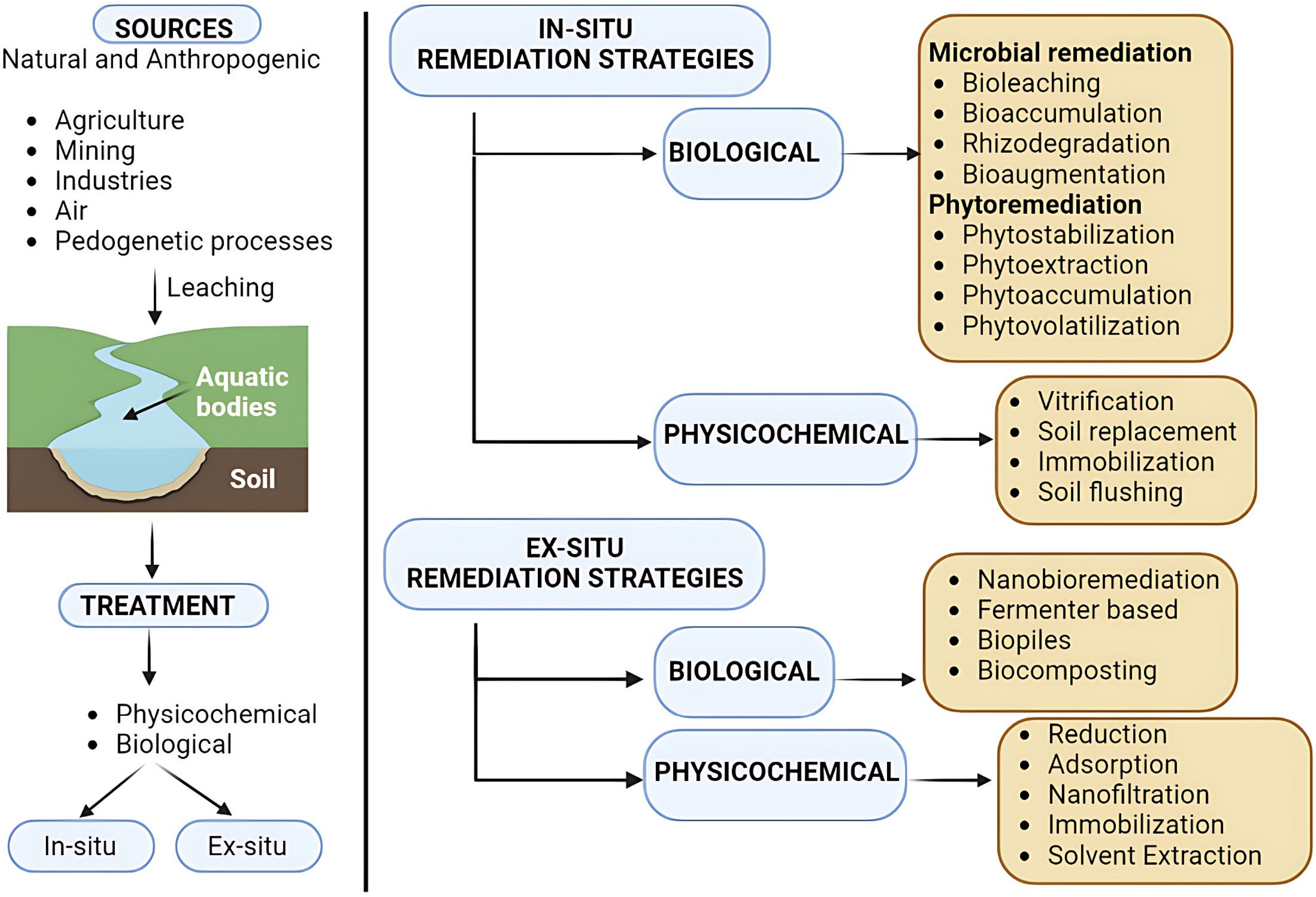

Figure 1. Sources and remediation strategies of water and soil contaminated with heavy metals.

The last two decades have documented a considerable rise in the synthesis and application of NMs in several fields, and bioremediation is one of the important areas of their application. Nanoparticles are known to exhibit multiple unique properties owing to their optimum size range and increased surface area making them a preferred choice as environmental remediation agents, which can be employed in various forms such as nanoadsorbents, nanocatalysts, nanofilters, etc., [13]. These novel candidates still pose a risk to the environment due to their unnecessary build up in the environment and then causing toxicity to plants and other living systems in the ecosystem. In view of their technological importance, there is a need to understand their post-treatment behavior and the movement of nanoparticles in soil or aquatic ecosystems. An emphasis must be placed on their design during the developmental phase, their effective management during application, and the disposal pathways post application in the environment in order to avoid and overcome the risks posed by them and ensure environmental safety. Another option is to utilize plant systems for tackling the issues by exploiting their hyperaccumulator potential for the removal of nanoparticle residues and thus attributing beneficial aspects to the use of nanoparticles [14]. Additionally, NMs provide a means of detecting contaminants in addition to removing them. NMs have been found to have a wide range of applications, which have been the subject of extensive research. The present review addresses the mechanisms for the removal of HMs from contaminated soils and mine spills by using various facets of nanotechnology and the challenges they present.

2. Mechanism of Action of Nanoparticles

To work as bioremediation agents, NMs should possess the following characteristics: (1) be deliverable to the target site and (2) be confined to the site without getting aggregated [15]. These challenges can be overcome by employing organic stabilizers such as collagen, starch, etc., [16]. The conventional methods employed for the removal of HMs suffer from a variety of drawbacks, hence the consortia of nanotechnology along with the available methods can offer a solution to the existing associated challenges [17]. Various NMs have been explored for the removal of a wide variety of contaminants including HMs via various modes such as precipitation, catalysis, conjugation, adsorption, and redox properties [18]. They can be further employed in a variety of forms, i.e., based on sensors, nanotubes, oxides, catalysts, and membranes, and the most commonly used NMs are magnetic-based NMs, which can be easily recovered and reused [19].

The enormous specific surface area of NMs makes them ideal for removing contaminants through several physicochemical and biological methods based on redox reactions, precipitation, co-precipitation, adsorption, ion-exchange, bioremediation, and phytoremediation [18].

Following the entry of NMs into the system, pollutants are subjected to a variety of physicochemical processes and alterations representing abiotic mechanisms, which include absorption, dissolution, adsorption, and photocatalysis [20]. In the next phase, biotic processes are used to remove the pollutants, including biocides, biostimulation, bioaccumulation, and biotransformation [21,22].

2.1. Remediation Techniques

There are numerous processes such as clarification, de-aeration, de-carbonation, sludge densification, or the high-density sludge (HDS) process being extensively employed to treat acid mine drainage water, but most of them are not sustainable and lead to the production of secondary waste in the form of end-products such as methane (CH_4) and non-soluble metal oxides or hydroxides, which need to be treated further and hence may not be cost-effective [23]. Acid mine drainage must therefore be properly remedied by integrating novel emerging techniques. Phytoremediation and nanoremediation are two of the most promising techniques for the remediation of acid mine drainage water (Figure 2). The former involves using plants to decontaminate mine drainage water infested with various toxic metals and pollutants. In contrast, the latter reduces the load of pollutants in such water by using NMs with diameters below 100 nm [10]. Both these techniques are effective in revegetating soils contaminated with heavy metals and have gained a high degree of public acceptance as sustainable alternatives to eliminate emerging pollutants such as heavy metals, chlorinated solvents, halogenated chemicals, or pesticides. Furthermore, the synergistic application of these techniques can result in improved heavy metal removal, reducing environmental stress as a result of the application of nanomaterials in low concentrations due to the inculcation of plants as additional remediation agents [24].

2.2. Reduction

A reduction reaction using nano-zero valent iron (nZVI) NMs can effectively remove both HMs and organic compounds from contaminated soils as well as from polluted groundwater and water [25]. There has been a wide application of nZVI NMs in wide fields. Their large surface area and small size facilitate the direct contact of nZVI particles with contaminants for an improved remediation efficiency. In addition to having a strong reduction capacity and superior adsorption ability, nZVI particles are competent in transforming toxic contaminants into less noxious compounds such as transforming chromium(VI) into chromium(III) and forming ferrous chromite [26]. Moreover, it has been demonstrated that biochar added to nano-zero valent iron nanoparticles (nZVI NPs) enhances the reduction reaction capacity of nZVI and increases its removal efficiency as well as reducing the movement of mixture in the soil by strengthening the disparity of iron particles. For instance, combining nZVI NMs with biochar has been found to remove 66% of the chromium (VI) content in soil [25]. It has been found that one gram of nZVI injection into contaminated soil reduces 28% of the mass of 1 kg chromium(VI). Additionally, in a treatment condition with a pH level of 5, 98% of the chromium(VI) was removed within 24 h [27]. Another study reported the successful application of biochar and NPs for the restoration of soils contaminated with potentially toxic elements [28]. Biochar prepared using low-cost raw materials such as rice husk, water hyacinth, and black tea waste showed the removal of copper, nickel, cadmium, and zinc from affected soils [29–31]. Burachevskaya et al. [32] documented the decreased absorption of highly concentrated copper and zinc in *Hordeum sativum* upon augmentation with biochar and granular activated carbon.

Moreover, it has also been shown that combining carboxymethyl cellulose (CMC) stabilizer and nZVI significantly reduces the amount of chromium(VI) contaminants that can be converted into carbonates as well as iron-manganese oxides, which will increase chromium bioavailability and leachability by 50% when 1 g to 10 mL of soil is added [33]. It has also been reported that nZVI combined with a carboxymethyl cellulose stabilizer removes organic contaminants from soil columns such as trichloroethylene (TCE), dichlorodiphenyltrichloroethane (DDT), and pesticides. For example, an injection of nZVI stabilized with CMC into potting soil containing 9.2% organic matter dechlorinated 44% of the TCE in the soil within 30 h of treatment. One kg of soil containing 24 mg of DDT was effectively treated with 20% aqueous nZVI within 72 h, thereby removing 25% of the DDT. To remediate soils that have been contaminated for prolonged periods, a higher concentration of nZVI was required to enhance its reaction activity [34].

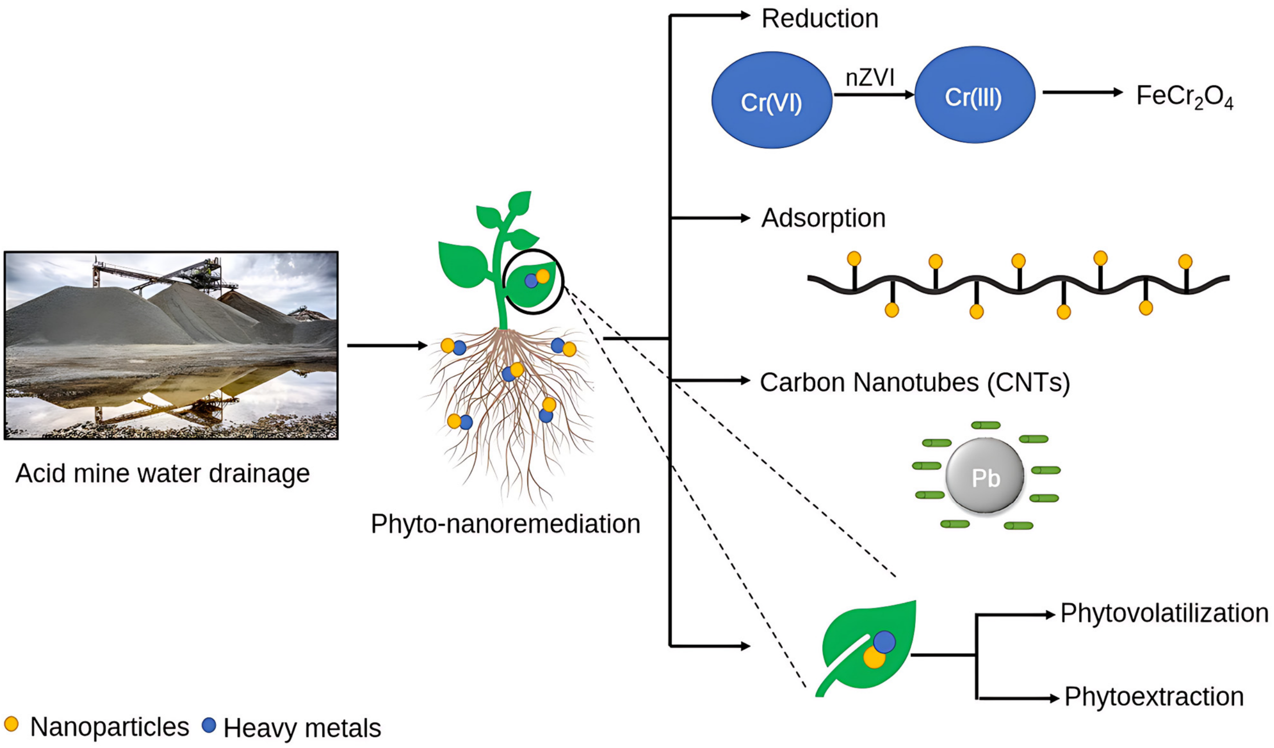

Figure 2. Remediation strategy for acid mine drainage (AMD).

2.3. Phytoremediation

Rhizofiltration and avoidance mechanisms for HM uptake have enabled a few plants to survive at an optimal level of HMs, including *Amaranthus spinosus*, *Pedioplanis burchelli*, and *Alternanthera pungens* [35]. Plant growth and human health are adversely impacted by HMs at concentrations above the optimum [36]. Despite this, metals are ingested in high concentrations by hyperaccumulating plant species and are then transported and accumulated in different parts at much higher concentrations than non-hyperaccumulators without showing apparent phytotoxicity [37,38].

The mechanism of phytostabilization and phytoextraction can account for HMs with a bioconcentration factor (BCF) more than one [39]. A TF (translocation factor) and BCF of more than one demonstrates phytostabilization traits [40]. A similar study by Kisku et al. [41] found that *Sacrum munja*, *Parthenium hysterophorus*, and *Ipomoea carnea* had both phytostabilization and phytoextraction activities, and the authors found that Cr, Ni, Cd, and Pb had at least one BCF and TF, indicating a phytostabilization mechanism, while Zn and Mn had more than one BCF and less than one TF, indicating a phytoextraction mechanism. On the other hand, there is a need to understand the exact mechanism of the interaction of NPs with plants as the studies are still in their initial stages, and this will pave the way for better understanding of the synergistic potential of plants and NPs in the remediation of contaminants [14].

2.4. Rhizodegradation of Heavy Metals

The bioavailability of metals in the rhizosphere is governed by several factors such as the pH of the native soil, the ionic state and concentration of metal ions, the nature of the microbial population, the plant species and their root secretions, etc. The rhizosphere facilitates the degradation of contaminants through symbiotic relationships between plants and soil microbes [42,43]. The process of rhizodegradation involves pollutants being accumulated in the rhizosphere of soil by the action of microbes and their breakdown for getting energy and nutrition. Through this mechanism, microbes can decompose hazardous pollutants into harmless and nontoxic substances [44]. The root systems of plants release natural carbon compounds such as alcohols, sugars, and acids, thus providing microorganisms with additional nutrients and stimulating the process of rhizodegradation [45]. The secretions of root exudates may result in a decreased pH of the rhizosphere, which further facilitates the absorption of HMs [46]. It has been found that *Zea mays* is more capable of bioaccumulating mercury than other plants [47]. There are some plants that provide the most favorable conditions for mycorrhizae and bacteria to associate and degrade toxins effectively. This degradation results in the volatilization or incorporation of components into the soil matrix [48]. Sugars and organic acids released by plants promote the growth of bacteria and fungi [49]. It is possible to enhance rhizodegradation by improving soil characteristics such as moisture content and soil aeration [49]. It was recently found that rhizomes of *Typha latifolia* are capable of phytodegrading terbuthylazine (TER) in a wetland contaminated with terbuthylazine (TER) [50]. A study by Sampaio et al. found that a *Rhizophora mangle* mangrove under the influence of plant-growth-promoting rhizobacteria (*Bacillus* sp. and *Pseudomonas aeruginosa*) was capable of degrading polycyclic aromatic hydrocarbons (PAHs) in contaminated sediment [51]. As a result of rhizodegradation, contaminants are dissolved in their natural environment, which is its most significant benefit. Further, plant species related to the oil family have been found to have a positive effect on the removal of heavy metals from contaminated soils. In one such study, the application of nZVI particles in a rhizospheric region of sunflowers resulted in a positive impact on the arsenic mobility in the plant, which was due to a decreased percentage of accumulation into the roots and shoots of the test plants as compared to the control plants [52]. The rhizospheric regions of plants grown in heavy-metal-contaminated soils are inhabited by heavy-metal-tolerant microflora such as arbuscular mycorrhizal fungi (AMF), mycorrhizal-helping bacteria (MHB), and plant-growth-promoting rhizobial microbes (PGPR), which have been reported to be beneficial for the process of nano-phytoremediation [53]. Hence, the fundamental mechanism of rhizodegradation-assisted heavy metal removal from contaminated water and soil relies on the synthesis and secretion of HM-affinity transporter nanomaterials by inhabitant microflora, which can further bind and mobilize the available HMs into root cells [54].

3. Types of Nanomaterials Used in the Removal of Heavy Metals

NMs are categorized into inorganic and carbon-based NMs [55]. There has been a great deal of success with their application in the field of environmental remediation (Table 1). The most commonly used and studied NMs are TiO_2, nZVI, and carbon nanotubes (CNTs) [56,57].

Table 1. List of nano-adsorbents used for the removal of heavy metals/pollutants from contaminated sites.

Sr. No.	Adsorbent	Target Heavy Metals/Pollutants	Percentage Removal	Source	pH	References
1	nZVI	Cr (VI)	98	Soil	5	[27]
2	nZVI + Carboxymethyl cellulose	DDT	25	Soil		[34]
3	Technosol	Cu, Cd, Zn, Pb, As	75	Soil		[58]
4	nZVI + Carboxymethyl cellulose	TCE	44	Soil		[34]
5	nZVI + Cellulose	Cr(VI)	30	Soil	5	[59]
6	TiO_2	Fe(III)	91.99	Mining waste water	-	[60]
		Mn(II)	89.37	Mining waste water	-	[60]
		Pb(II)	32.39	Mining waste water	-	
		Cu(II)	81.95	Mining waste water	-	[45]
		Cd(II)	96	Wastewater	7	[46]
		Pb(II)	99.1	Wastewater	7	[46]
		Cr(II)	94	Wastewater	7	[46]
		Th(IV)	94	Soil	4	[21]
7	Biochar + nZVI	Cr (VI)	66	Soil		[21]
8	Biochar	Phenol		Mining waste water	5.8	[47]
		Cd		Mining waste water	7	[47]
9	Graphite oxide	Cd	88.33	Soil	3	[48]
		Pb	85	Soil	3	[48]
		Cr	63	Soil	3	[48]
		Ni	89.9	Soil	3	[48]
		Zn	85.6	Soil	3	[48]
10	Silver-iron oxide NPs	Cr (VI)	97	Soil	4	[49]
11	Magnetite	Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}	$\approx$90	Soil	6	[50]
12	Carbon nanotubes	Cu	79	Acid Mine drainage	5.5	[51]
		Mn	78	Acid Mine drainage	5.5	[51]
		Zn	48	Acid Mine drainage		[51]
		Mn	100	-	3	[52]
		Cr(VI)	-	Soil	5	[53]
		DDT	59	Soil	-	[54]
		HCH	75	Soil	-	[54]

3.1. Nano Zero-Valent-Iron-Based Nanomaterials

nZVI is the most widely studied and applied NM for environmental remediation. There is a wide range of contaminants that can be adsorbed, reduced, and catalyzed with nZVI, including pharmaceuticals, HM ions, organic dyes, and halogenated organic compounds [61–63]. Nano zero-valent iron consists of a core–shell structure that consists of Fe(II), Fe(III), and zero-valent iron [64]. The various mechanisms involved in the removal of heavy contaminants include precipitation, reduction, etc. [65–67]. These NMs have been found to be effective in the removal of HM ions from contaminated soils and have proven to be effective in the remediation of soil contaminated with chromium. Nano zero-valent iron NMs have also been reported to stabilize the levels of arsenic and zinc in soils rich in these microcontaminants [52]. NMs can also facilitate the remediation of acid mine water by reducing the concentrations of microcontaminants [68]. The mine drainage sites treated using technosols showed promising results and offered an alternative to conventional removal processes. Technosols consisting of a mixture of iron-rich soils and plant-based green-synthesized multicomponent NMs showed a 75% removal of HMs via adsorption, which followed a pseudo-second-order model in a 4.24 min contact time [58].

Nanoremediation with zero-valent iron has proven successful in treating acidic water polluted with several HMs [69]. nZVI immobilizes HMs dissolved in mine water by quickly and effectively neutralizing them. It has been found that the adsorption of HMs onto the surface of iron-based NMs is the main mechanism for removing HMs. The corrosion products of iron also serve as adsorption sites on unreacted metal surfaces. The metal uptake process slows down with time, but bacteria that reduce sulfate can accelerate it even further [70]. However, the traditional methods for preparing these iron NPs have the drawback of agglomerating and reacting quickly with the substrate, reducing their mobility and reactivity. Due to their micron-scale size, agglomerated iron NPs cannot be transported or delivered in soils, so in situ treatment is not possible [71]. Another problem that is limiting the engineering applications of iron-based materials is the cost factor due to the large amount of chemical reagents such as ferrous sulfate and ferrous chloride that are consumed during the material's conventional preparation technologies [72].

3.2. Magnetic Nanomaterials

Magnetic NMs based on iron oxide may be more effective at removing HMs depending on their size, surface area, and magnetic properties [73,74]. Adsorbents can be easily separated from the system due to their magnetic character. Iron oxide NPs (Fe_2O_3 and Fe_3O_4) have been found to remove a wide variety of HMs, such as arsenic and Cu(II) [75,76]. Coprecipitation-produced maghemite (γ Fe_2O_3) NPs have been proven to be suitable for selectively removing toxic metals from wastewater [77], whereas hydrothermal preparations of Fe_3O_4 NPs functionalized with amino groups have been found to be useful for adsorbing HMs such as cadmium, lead, and copper [78]. Polymer-fused Fe_2O_3 NPs have been proven to be effective in the expulsion of divalent metal microparticles of Co, Ni, and Cu at pH levels ranging from 3 to 7. HMs such as arsenic have also been demonstrated to be decontaminated by iron oxide NPs. Fan et al. [79] examined novel MNPs (core–shell $Fe_3O_4@SiO_2$ NPs coated with iminodiacetic acid chelators) as potential remediators of contaminated soil.

3.3. Carbon Nanotubes (CNTs)

CNTs are made up of a graphitic sheet that is rolled and shaped into a cylindrical shape [80,81]. CNTs are extremely durable substances that are six times lighter and over 100 times more resistant in comparison to steel [82]. A significant advantage of CNTs is their ability to bind strongly to the functional groups of pollutants, making them highly effective adsorbents [83]. CNTs can be classified into two categories based on how many cylindrical shells they contain, namely single-wall CNTs (SWCNTs) and multi-wall CNTs (MWCNTs). CNTs are considered to be excellent NMs for the removal of various organic and inorganic pollutants due to their extraordinary characteristics such as their unique morphology, high reactivity, and a large specific surface area [84,85]. A variety of methods can be used to manufacture CNTs, including arc discharge, chemical vapor deposition, and laser ablation. Different methods of synthesizing CNTs with different reactants and catalysts have a large impact on their adsorption capacities [86]. Rodríguez and Leiva [87] studied the application of oxidized and double-oxidized MWCNTs for the removal of Zn^{2+}, Cu^{2+}, and Mn^{2+} from acid waters, where the latter showed a higher adsorption rate close to neutral pH as compared to the former and hence can be utilized as an alternative with a high performance rate.

The successful usage of TFN membranes for the removal of HM ions from acid mine drainage holds promising results for the future. In a recent study, the use of multi-walled carbon nanotubes (MWCNTs) in the manufacture of TFN membranes further enhanced their capacity owing to an increase in the diffusion of target monomers to the interface, restricting the change in pH and increasing the rejection affinity for HM ions [88,89].

3.4. Metal Oxide Nanomaterials

Metal oxide NMs are considered as the primary choice for the removal of HMs via surface complexation from varied targets on account of their promising physicochemical properties. The surface complexation process increases with the decrease in the pH of the soil, thus promoting the removal of contaminants at a higher pace. For the production of NMs, raw materials are a major challenge, which is gradually being replaced by alternatives such as biopolymers produced from plants, microorganisms, or microbial sources. Ease of synthesis, chemical stability, reactivity, and photocatalysis make TiO_2 NMs the most widely studied candidate for removal of HMs from a variety of sources [90,91].

Soil-augmented TiO_2 NMs resulted in a 2.6 times increase in the removal of cadmium and its accumulation in aerial parts of *Glycine max* via phytoremediation [92]. In an another study, a 94 percent removal rate for Th(IV) was reported by the application of TiO_2 at 4.0 pH [93]. A similar impact of acidic pH on cadmium removal was observed for iron(III) oxide NMs at a pH of 6.0 [25]. A variety of iron oxide NMs have been designed and successfully applied for the remediation of soil and water systems owing to their ease of synthesis and negligible environmental impact. Some of the members of the iron oxide family that have been successfully employed for the removal of HMs such as As^{5+}, As^{3+}, Cr^{6+}, Cr^{3+}, and Pb^{2+} include magnetite, geothite, and maghemite [94]. A widely accepted mechanism behind the removal of HMs from aqueous environments is the ability of NMs to confiscate HM ions via adsorption, thus restricting their availability for further reaction. The low toxicity of iron oxides to living organisms is another factor contributing to their increased application in soil and water treatment schemes.

Studies on the impact of size of iron oxide NMs on a human cell line A549 involving various parameters such as DNA lesions and damage and mitochondrial damage documented a low toxicity with a negligible impact of size on the cell line [95]. The low toxicity of maghemite was attributed to its organic coating, which prevented the direct exposure of the NMs to the cells [96]. The oxidizable fraction of HMs present in acid mine drainage was successfully removed by employing Fe and Mn oxides, which were further recovered by a series of chemical reactions [58]. The availability of wide structures and a uniform size distribution resulting in an increased adsorption capacity make CuO-based NMs demanding candidates for the successful removal of some prominent HMs ions such as As^{5+}, As^{3+}, and Cr^{6+} from various matrices [97]. The advancement in technology leads to the production of organic surfactant-bearer SiO_2 NMs. An organic carrier with cyano as the prominent functional group acting as the adsorption site resulted in an enhanced Cr^{3+} ion removal from a polluted site [98]. Metal-oxide-based NMs showed varying behaviors under different environments and may be prone to losing their activity. For example, Fe and Mn showed a reduction in their valent states in wetland environments. Similarly, acidic environments resulted in a decreased activity in Al and Zn oxides [99].

4. Impact of Environmental Factors

Environmental factors play a prominent role in governing the impact of the activity of NMs. The contaminant's persistence and removal tendency are impacted by its surroundings and the composition of the matrix. Some of the vital governing physicochemical factors are temperature, pH, and contact time.

4.1. Temperature

The removal of HMs by NMs is aided by the adsorption process, which is impacted by a change in temperature. A temperature rise beyond a threshold limit resulted in reduced activity due to a rise in the rate of redox reactions. A temperature increase to 40 °C reduced the removal rate of Hg(II) from chitosan–alginate NMs [100]. In some cases, a reverse trend was observed, where the efficiency increased with the increase in temperature. The dimensions, optical activity, and photocatalytic activity of titanium oxide NMs vary with an increase in temperature. NM powder treated at 800 °C exhibited decreased photocatalytic activity as compared to those treated with a 100 and 450 °C exposure due to the higher recombination of photo-generated electrons and holes [101]. The effect of heat treatment on the confiscation of metal ions from mine drainage using cobalt and ferrite NMs revealed that heating facilitates the formation of magnetic NMs, thereby removing a significant proportion of the contaminant metal ions such as Mg, Mn, and Al [102].

4.2. pH

pH is another crucial aspect in determining the activity and efficiency of NMs. The adsorption capacity of NPs, their ionic state, and the availability of HM is primarily governed by the environmental pH [103]. The rate at which HMs are removed is highly influenced by pH changes, and it was observed that phenomena such as precipitation and electrostatic sorption become more prominent at neutral pH conditions [104]. Different NMs showed varied trends at a similar pH. Su et al. [105] reported a positive effect of S-nZVI on the removal of cadmium at a pH of 5. However, a reverse increasing trend was observed for Cr(VI) involving similar NPs [106]. Similar observations were reported in NZVI-treated samples containing Cr(VI) and Hg(II), in which the former led to a reduction in the removal rate while the latter showed an increasing trend on raising the pH from 3.1–8.1 [107]. In another study carried by Xu and Zhao [59], a pH change from 9.0 to 5.0 had an alarming impact on the cellulose-stabilized NZVI-aided immobilization of Cr(VI), thus reducing its leaching rate from initially 30% to 20%. The acidic pH of acid mine drainage is the biggest challenge for its treatment. Graphene oxide (GO) has been successfully employed for the treatment of such waters and shows a high removal capacity at a lower pH. Furthermore, the complexation of GO with zinc nanocomposites under different pH ranges was studied [108]. In similar studies, divalent metals' adsorption using GO was studied from a pH range of 2 to 8, and a 90% removal rate was achieved with the maximum activity being at an acidic pH followed by a constant trend and a steady decline at pH 8 [109].

4.3. Contact Time

The contact time is an important aspect in determining the efficiency of NM-mediated HMs removal from the target sites. An increased contact time is generally accompanied by an increased removal rate, as is evident from the increased adsorption rate. The impact of contact time was studied using different models such as the Zeldowitsch model and pseudo-first- and second-order models [110]. The trend of the adsorption of HMs ions on the surface of NMs reported a rise during the initial stages followed by a snag until the sorption equilibrium was reached. Similar findings were reported by Khoso et al. [111], where nickel ferrite NMs were employed for the removal of Cd(II), Cr(VI), and Pb(II). Their studies reported that the removal of metal ions increased with a rise in contact time, but after 90 min, a reverse phenomenon of the desorption of metal ions began and adsorption forces started to diminish as soon as the maximum equilibrium was attained. At a constant adsorbent dosage of 10 mg and a 90 min contact time of nickel ferrite, a maximum removal efficiency up to 85.21% and 84.45% was achieved for Cr(VI) and Cd(II) ions, respectively whereas for Pb(II) ions, this rate was 77.41% in 120 min. In another study, nZVI–Fe_3O_4 NMs eliminated Cr(VI) within 2 h followed by a declining trend after attaining equilibrium [112]. Mine and farmland soils contaminated with Pb(II), Cd(II), and Zn(II) treated with organic acids combined NZVI reported an increased removal efficiency in 120 min followed by a steady decrease until the point of equilibrium was attained [61].

5. Conclusions

The increasing accumulation of contaminants at all levels of the environment has increased demands for sustainable technology. NMs hold a promising future in this direction owing to their inertness, eco-friendly nature, high efficiency, and size flexibility, which gives them an edge over conventional techniques. They can be easily applied across different matrices, i.e., soil, surface, or ground water as remediation tools. Other characteristics which make NMs a preferred means of decontamination are their high adsorption abilities and reusability, which remain unaffected by rapid changes in pH and temperature, thus making them suitable for highly acidic acid mine treatment. As the research on NMs is still in its infancy, there are certain disadvantages and possible risks linked with their use. The major limitations associated with use of NMs include accumulation and toxicity, owing to their possible interaction with the environmental components and thus posing another challenge for researchers in terms of their potential role as decontaminants. NMs get easily mobilized and hence can be dispersed across long distances, because of which they may be difficult to track and might pose a risk of bioaccumulation in non-target species resulting in ecotoxicity. NMs may further get oxidized on encountering microbial entities and varying environmental factors resulting in the production of reactive oxygen species, which may have a detrimental effect on plants and other living organisms. Hence, detailed studies are needed to determine the precise fate of NPs in the environment in order to establish their utility in harmony with nature and in order to obtain sustainable solutions for environmental remediation.

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References

1. Vilardi, G.; Ochando-Pulido, J.M.; Verdone, N.; Stoller, M.; Di Palma, L. On the removal of hexavalent chromium by olive stones coated by iron-based nanoparticles: Equilibrium study and chromium recovery. *J. Clean. Prod.* **2018**, *190*, 200–210. [CrossRef]
2. Yu, G.; Liu, J.; Long, Y.; Chen, Z.; Sunahara, G.I.; Jiang, P.; You, S.; Lin, H.; Xiao, H. Phytoextraction of cadmium-contaminated soils: Comparison of plant species and low molecular weight organic acids. *Int. J. Phytoremediation* **2019**, *22*, 383–391. [CrossRef] [PubMed]
3. Zhu, S.; Khan, M.A.; Kameda, T.; Xu, H.; Wang, F.; Xia, M.; Yoshioka, T. New insights into the capture performance and mechanism of hazardous metals Cr3+ and Cd2+ onto an effective layered double hydroxide based material. *J. Hazard. Mater.* **2022**, *426*, 128062. [CrossRef] [PubMed]
4. Zhu, S.; Xia, M.; Chu, Y.; Khan, M.A.; Lei, W.; Wang, F.; Muhmood, T.; Wang, A. Adsorption and Desorption of Pb(II) on l-Lysine Modified Montmorillonite and the simulation of Interlayer Structure. *Appl. Clay Sci.* **2018**, *169*, 40–47. [CrossRef]
5. Volesky, B.; Holan, Z.R. Biosorption of Heavy Metals. *Biotechnol. Prog.* **1995**, *11*, 235–250. [CrossRef]
6. Selvi, A.; Rajasekar, A.; Theerthagiri, J.; Ananthaselvam, A.; Sathishkumar, K.; Madhavan, J.; Rahman, P. Integrated Remediation Processes Toward Heavy Metal Removal/Recovery From Various Environments-A Review. *Front. Environ. Sci.* **2019**, *7*, 66. [CrossRef]
7. Johnson, D.B.; Hallberg, K.B. Acid mine drainage remediation options: A review. *Sci. Total Environ.* **2005**, *338*, 3–14. [CrossRef]
8. Gaikwad, R. REVIEW ON REMOVAL OF HEAVY METALS FROM ACID MINE DRAINAGE. *Appl. Ecol. Environ. Res.* **2008**, *6*, 81–98. [CrossRef]
9. Nordstrom, D.K.; Southam, G. Geomicrobiology of sulfide mineral oxidation. *Rev. Mineral. Geochem.* **1997**, *35*, 361–390.
10. Das, P.K. Phytoremediation and Nanoremediation: Emerging Techniques for Treatment of Acid Mine Drainage Water. *Def. Life Sci. J.* **2018**, *3*, 190–196. [CrossRef]
11. Singh, G. Mine water quality deterioration due to acid mine drainage. *Mine Water Environ.* **1987**, *6*, 49–61. [CrossRef]
12. Valdés, J.; Pedroso, I.; Quatrini, R.; Dodson, R.J.; Tettelin, H.; BlakeII, R.; Eisen, J.A.; Holmes, D.S. Acidithiobacillus ferrooxidans metabolism: From genome sequence to industrial applications. *BMC Genom.* **2008**, *9*, 597. [CrossRef]
13. Chauhan, G.; González-González, R.B.; Iqbal, H.M. Bioremediation and decontamination potentials of metallic nanoparticles loaded nanohybrid matrices—A review. *Environ. Res.* **2021**, *204*, 112407. [CrossRef]
14. Sharma, T.; Sharma, N. *Nanoparticles: Uptake, Translocation, Physiological, Biochemical Effects in Plants and their Molecular Aspects*; Springer: Cham, Switzerland, 2022; pp. 103–116. [CrossRef]
15. Khan, I.; Saeed, K.; Khan, I. Nanoparticles: Properties, applications and toxicities. *Arab. J. Chem.* **2019**, *12*, 908–931. [CrossRef]
16. Nogueira, S.S.; de Araujo-Nobre, A.R.; Mafud, A.C.; Guimarães, M.A.; Alves, M.M.M.; Plácido, A.; Carvalho, F.A.A.; Arcanjo, D.D.R.; Mascarenhas, Y.; Costa, F.G.; et al. Silver nanoparticle stabilized by hydrolyzed collagen and natural polymers: Synthesis, characterization and antibacterial-antifungal evaluation. *Int. J. Biol. Macromol.* **2019**, *135*, 808–814. [CrossRef]

17. Cecchin, I.; Reddy, K.R.; Thomé, A.; Tessaro, E.F.; Schnaid, F. Nanobioremediation: Integration of nanoparticles and bioremediation for sustainable remediation of chlorinated organic contaminants in soils. *Int. Biodeterior. Biodegrad.* **2017**, *119*, 419–428. [CrossRef]
18. Raffa, C.; Chiampo, F.; Shanthakumar, S. Remediation of Metal/Metalloid-Polluted Soils: A Short Review. *Appl. Sci.* **2021**, *11*, 4134. [CrossRef]
19. Gong, Z.; Chan, H.; Chen, Q.; Chen, H. Application of Nanotechnology in Analysis and Removal of Heavy Metals in Food and Water Resources. *Nanomaterials* **2021**, *11*, 1792. [CrossRef]
20. Abebe, B.; Murthy, H.C.A.; Amare, E. Summary on Adsorption and Photocatalysis for Pollutant Remediation: Mini Review. *J. Encapsul. Adsorpt. Sci.* **2018**, *08*, 225–255. [CrossRef]
21. Desiante, W.L.; Minas, N.S.; Fenner, K. Micropollutant biotransformation and bioaccumulation in natural stream biofilms. *Water Res.* **2021**, *193*, 116846. [CrossRef]
22. Filote, C.; Roșca, M.; Hlihor, R.M.; Cozma, P.; Simion, I.M.; Apostol, M.; Gavrilescu, M. Sustainable Application of Biosorption and Bioaccumulation of Persistent Pollutants in Wastewater Treatment: Current Practice. *Processes* **2021**, *9*, 1696. [CrossRef]
23. RoyChowdhury, A.; Sarkar, D.; Datta, R. Remediation of Acid Mine Drainage-Impacted Water. *Curr. Pollut. Rep.* **2015**, *1*, 131–141. [CrossRef]
24. Yan, A.; Wang, Y.; Tan, S.N.; Yusof, M.L.M.; Ghosh, S.; Chen, Z. Phytoremediation: A Promising Approach for Revegetation of Heavy Metal-Polluted Land. *Front. Plant Sci.* **2020**, *11*, 359. [CrossRef]
25. Qian, Y.; Qin, C.; Chen, M.; Lin, S. Nanotechnology in soil remediation—Applications vs. implications. *Ecotoxicol. Environ. Saf.* **2020**, *201*, 110815. [CrossRef] [PubMed]
26. Rabbani, M.M.; Ahmed, I.; Park, S.-J. Application of Nanotechnology to Remediate Contaminated Soils. In *Environmental Remediation Technologies for Metal-Contaminated Soils*; Springer: Tokyo, Japan, 2016; pp. 219–229. [CrossRef]
27. Chrysochoou, M.; Johnston, C.P.; Dahal, G. A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron. *J. Hazard. Mater.* **2012**, *201–202*, 33–42. [CrossRef] [PubMed]
28. Rajput, V.D.; Kumari, A.; Minkina, T.; Barakhov, A.; Singh, S.; Mandzhieva, S.S.; Sushkova, S.; Ranjan, A.; Rajput, P.; Garg, M.C. A practical evaluation on integrated role of biochar and nanomaterials in soil remediation processes. *Environ. Geochem. Health* **2022**, 1–15. [CrossRef]
29. Lobzenko, I.; Burachevskaya, M.; Zamulina, I.; Barakhov, A.; Bauer, T.; Mandzhieva, S.; Sushkova, S.; Minkina, T.; Tereschenko, A.; Kalinichenko, V.; et al. Development of a Unique Technology for the Pyrolysis of Rice Husk Biochar for Promising Heavy Metal Remediation. *Agriculture* **2022**, *12*, 1689. [CrossRef]
30. Elbehiry, F.; Darweesh, M.; Al-Anany, F.S.; Khalifa, A.M.; Almashad, A.A.; El-Ramady, H.; El-Banna, A.; Rajput, V.D.; Jatav, H.S.; Elbasiouny, H. Using Biochar and Nanobiochar of Water Hyacinth and Black Tea Waste in Metals Removal from Aqueous Solutions. *Sustainability* **2022**, *14*, 10118. [CrossRef]
31. Awasthi, G.; Nagar, V.; Mandzhieva, S.; Minkina, T.; Sankhla, M.S.; Pandit, P.P.; Aseri, V.; Awasthi, K.K.; Rajput, V.D.; Bauer, T.; et al. Sustainable Amelioration of Heavy Metals in Soil Ecosystem: Existing Developments to Emerging Trends. *Minerals* **2022**, *12*, 85. [CrossRef]
32. Burachevskaya, M.; Mandzhieva, S.; Bauer, T.; Minkina, T.; Rajput, V.; Chaplygin, V.; Fedorenko, A.; Chernikova, N.; Zamulina, I.; Kolesnikov, S.; et al. The Effect of Granular Activated Carbon and Biochar on the Availability of Cu and Zn to *Hordeum sativum* Distichum in Contaminated Soil. *Plants* **2021**, *10*, 841. [CrossRef]
33. Zhang, R.; Zhang, N.; Fang, Z. In situ remediation of hexavalent chromium contaminated soil by CMC-stabilized nanoscale zero-valent iron composited with biochar. *Water Sci. Technol.* **2018**, *77*, 1622–1631. [CrossRef] [PubMed]
34. El-Temsah, Y.S.; Sevcu, A.; Bobcikova, K.; Cernik, M.; Joner, E.J. DDT degradation efficiency and ecotoxicological effects of two types of nano-sized zero-valent iron (nZVI) in water and soil. *Chemosphere* **2016**, *144*, 2221–2228. [CrossRef] [PubMed]
35. Rizwan, M.; Ali, S.; Zia ur Rehman, M.; Adrees, M.; Arshad, M.; Qayyum, M.F.; Ali, L.; Hussain, A.; Chatha, S.A.S.; Imran, M. Alleviation of cadmium accumulation in maize (*Zea mays* L.) by foliar spray of zinc oxide nanoparticles and biochar to contaminated soil. *Environ. Pollut.* **2019**, *248*, 358–367. [CrossRef] [PubMed]
36. Sun, T.Y.; Bornhöft, N.A.; Hungerbühler, K.; Nowack, B. Dynamic Probabilistic Modeling of Environmental Emissions of Engineered Nanomaterials. *Environ. Sci. Technol.* **2016**, *50*, 4701–4711. [CrossRef] [PubMed]
37. Jabeen, R.; Ahmad, A.; Iqbal, M.F. Phytoremediation of Heavy Metals: Physiological and Molecular Mechanisms. *Bot. Rev.* **2009**, *75*, 339–364. [CrossRef]
38. Rascio, N.; Navari-Izzo, F. Heavy metal hyperaccumulating plants: How and why do they do it? And what makes them so interesting? *Plant Sci.* **2011**, *180*, 169–181. [CrossRef]
39. Upadhyay, S.K.; Ahmad, M.; Srivastava, A.K.; Abhilash, P.C.; Sharma, B. Optimization of eco-friendly novel amendments for sustainable utilization of Fly ash based on growth performance, hormones, antioxidant, and heavy metal translocation in chickpea (*Cicer arietinum* L.) plant. *Chemosphere* **2021**, *267*, 129216. [CrossRef]
40. Usman, K.; Al-Ghouti, M.A.; Abu-Dieyeh, M.H. The assessment of cadmium, chromium, copper, and nickel tolerance and bioaccumulation by shrub plant Tetraena qataranse. *Sci. Rep.* **2019**, *9*, 5658. [CrossRef]
41. Kisku, G.C.; Kumar, V.; Sahu, P.; Kumar, P.; Kumar, N. Characterization of coal fly ash and use of plants growing in ash pond for phytoremediation of metals from contaminated agricultural land. *Int. J. Phytoremediation* **2018**, *20*, 330–337. [CrossRef]
42. Das, S.; Chou, M.-L.; Jean, J.-S.; Yang, H.-J.; Kim, P.J. Arsenic-enrichment enhanced root exudates and altered rhizosphere microbial communities and activities in hyperaccumulator Pteris vittata. *J. Hazard. Mater.* **2017**, *325*, 279–287. [CrossRef]

43. Caracciolo, A.B.; Grenni, P.; Garbini, G.L.; Rolando, L.; Campanale, C.; Aimola, G.; Fernandez-Lopez, M.; Fernandez-Gonzalez, A.J.; Villadas, P.J.; Ancona, V. Characterization of the Belowground Microbial Community in a Poplar-Phytoremediation Strategy of a Multi-Contaminated Soil. *Front. Microbiol.* **2020**, *11*, 2073. [CrossRef]
44. Ojuederie, O.B.; Babalola, O.O. Microbial and Plant-Assisted Bioremediation of Heavy Metal Polluted Environments: A Review. *Int. J. Environ. Res. Public Health* **2017**, *14*, 1504. [CrossRef] [PubMed]
45. Rai, G.K.; Bhat, B.A.; Mushtaq, M.; Tariq, L.; Rai, P.K.; Basu, U.; Dar, A.A.; Islam, S.T.; Dar, T.U.H.; Bhat, J.A. Insights into decontamination of soils by phytoremediation: A detailed account on heavy metal toxicity and mitigation strategies. *Physiol. Plant.* **2021**, *137*, 287–304. [CrossRef] [PubMed]
46. Upadhyay, S.K.; Rajput, V.D.; Kumari, A.; Espinosa-Saiz, D.; Menendez, E.; Minkina, T.; Dwivedi, P.; Mandzhieva, S. Plant growth-promoting rhizobacteria: A potential bio-asset for restoration of degraded soil and crop productivity with sustainable emerging techniques. *Environ. Geochem. Health* **2022**, 1–24. [CrossRef] [PubMed]
47. Benavides, L.C.L.; Pinilla, L.A.C.; Serrezuela, R.R.; Serrezuela, W.F.R. Extraction in laboratory of heavy metals through rhizofiltration using the plant Zea mays (maize). *Int. J. Appl. Environ. Sci.* **2018**, *13*, 9–26.
48. De Farias, V.; Maranho, L.T.; De Vasconcelos, E.C.; Filho, M.A.D.S.C.; Lacerda, L.G.; Azevedo, J.A.M.; Pandey, A.; Soccol, C.R. Phytodegradation Potential of Erythrina crista-galli L., Fabaceae, in Petroleum-Contaminated Soil. *Appl. Biochem. Biotechnol.* **2009**, *157*, 10–22. [CrossRef] [PubMed]
49. Kirk, J.L.; Klironomos, J.N.; Lee, H.; Trevors, J.T. The effects of perennial ryegrass and alfalfa on microbial abundance and diversity in petroleum contaminated soil. *Environ. Pollut.* **2005**, *133*, 455–465. [CrossRef]
50. Papadopoulos, N.; Zalidis, G. The Use of Typha Latifolia L. in Constructed Wetland Microcosms for the Remediation of Herbicide Terbuthylazine. *Environ. Process.* **2019**, *6*, 985–1003. [CrossRef]
51. Sampaio, C.J.S.; de Souza, J.R.B.; Damião, A.O.; Bahiense, T.C.; Roque, M.R.A. Biodegradation of polycyclic aromatic hydrocarbons (PAHs) in a diesel oil-contaminated mangrove by plant growth-promoting rhizobacteria. *3 Biotech* **2019**, *9*, 155. [CrossRef]
52. Vítková, M.; Puschenreiter, M.; Komárek, M. Effect of nano zero-valent iron application on As, Cd, Pb, and Zn availability in the rhizosphere of metal(loid) contaminated soils. *Chemosphere* **2018**, *200*, 217–226. [CrossRef]
53. Khan, A.; Kuek, C.; Chaudhry, T.; Khoo, C.; Hayes, W. Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. *Chemosphere* **2000**, *41*, 197–207. [CrossRef]
54. Khan, A.G. In Situ Phytoremediation of Uranium Contaminated Soils. In *Phytoremediation*; Springer: Berlin/Heidelberg, Germany, 2020; pp. 123–151. [CrossRef]
55. Stone, V.; Nowack, B.; Baun, A.; Brink, N.V.D.; von der Kammer, F.; Dusinska, M.; Handy, R.; Hankin, S.; Hassellöv, M.; Joner, E.; et al. Nanomaterials for environmental studies: Classification, reference material issues, and strategies for physico-chemical characterisation. *Sci. Total Environ.* **2010**, *408*, 1745–1754. [CrossRef]
56. Ren, X.; Chen, C.; Nagatsu, M.; Wang, X. Carbon nanotubes as adsorbents in environmental pollution management: A review. *Chem. Eng. J.* **2011**, *170*, 395–410. [CrossRef]
57. Fu, F.; Dionysiou, D.D.; Liu, H. The use of zero-valent iron for groundwater remediation and wastewater treatment: A review. *J. Hazard. Mater.* **2014**, *267*, 194–205. [CrossRef]
58. Guerrón, D.B.; Capa, J.; Flores, L.C. Retention of heavy metals from mine tailings using Technosols prepared with native soils and nanoparticles. *Heliyon* **2021**, *7*, e07631. [CrossRef]
59. Xu, Y.; Zhao, D. Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water Res.* **2007**, *41*, 2101–2108. [CrossRef]
60. Ajala, M.A.; Abdulkareem, A.S.; Tijani, J.O.; Kovo, A.S. Adsorptive behaviour of rutile phased titania nanoparticles supported on acid-modified kaolinite clay for the removal of selected heavy metal ions from mining wastewater. *Appl. Water Sci.* **2022**, *12*, 19. [CrossRef]
61. Cao, Y.; Zhang, S.; Zhong, Q.; Wang, G.; Xu, X.; Li, T.; Wang, L.; Jia, Y.; Li, Y. Feasibility of nanoscale zero-valent iron to enhance the removal efficiencies of heavy metals from polluted soils by organic acids. *Ecotoxicol. Environ. Saf.* **2018**, *162*, 464–473. [CrossRef]
62. Moosa, A.; Ridha, A.; Moosa, A.A.; Ridha, A.M.; Hussien, N.A. Removal of Zinc Ions from Aqueous Solution by Bioadsorbents and CNTs Removal of Zinc Ions from Aqueous Solution by Bioadsorbents and CNTs. *Am. J. Mater. Sci.* **2016**, *6*, 105–114. [CrossRef]
63. Alimohammady, M.; Jahangiri, M.; Kiani, F.; Tahermansouri, H. Design and evaluation of functionalized multi-walled carbon nanotubes by 3-aminopyrazole for the removal of Hg(II) and As(III) ions from aqueous solution. *Res. Chem. Intermed.* **2017**, *44*, 69–92. [CrossRef]
64. Crane, R.A.; Scott, T.B. Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *J. Hazard. Mater.* **2012**, *211–212*, 112–125. [CrossRef] [PubMed]
65. Elsner, M.; Chartrand, M.; VanStone, N.; Couloume, G.L.; Lollar, B.S. Identifying Abiotic Chlorinated Ethene Degradation: Characteristic Isotope Patterns in Reaction Products with Nanoscale Zero-Valent Iron. *Environ. Sci. Technol.* **2008**, *42*, 5963–5970. [CrossRef] [PubMed]
66. Luo, S.; Lu, T.; Peng, L.; Shao, J.; Zeng, Q.; Gu, J.-D. Synthesis of nanoscale zero-valent iron immobilized in alginate microcapsules for removal of Pb(ii) from aqueous solution. *J. Mater. Chem. A* **2014**, *2*, 15463–15472. [CrossRef]
67. Mueller, N.C.; Braun, J.; Bruns, J.; Černík, M.; Rissing, P.; Rickerby, D.; Nowack, B. Application of nanoscale zero valent iron (NZVI) for groundwater remediation in Europe. *Environ. Sci. Pollut. Res.* **2011**, *19*, 550–558. [CrossRef] [PubMed]

68. Klimkova, S.; Cernik, M.; Lacinova, L.; Filip, J.; Jancik, D.; Zboril, R. Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching. *Chemosphere* **2011**, *82*, 1178–1184. [CrossRef] [PubMed]
69. Morrison, S.J.; Metzler, D.R.; Dwyer, B.P. Removal of As, Mn, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: Reaction progress modeling. *J. Contam. Hydrol.* **2001**, *56*, 99–116. [CrossRef]
70. Wilkin, R.T.; McNeil, M.S. Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. *Chemosphere* **2003**, *53*, 715–725. [CrossRef]
71. Reyhanitabar, A.; Alidokht, L.; Khataee, A.R.; Oustan, S. Application of stabilized Fe^0nanoparticles for remediation of Cr(VI)-spiked soil. *Eur. J. Soil Sci.* **2012**, *63*, 724–732. [CrossRef]
72. Fang, Z.; Qiu, X.; Chen, J.; Qiu, X. Degradation of the polybrominated diphenyl ethers by nanoscale zero-valent metallic particles prepared from steel pickling waste liquor. *Desalination* **2011**, *267*, 34–41. [CrossRef]
73. Xu, P.; Zeng, G.M.; Huang, D.L.; Feng, C.L.; Hu, S.; Zhao, M.H.; Lai, C.; Wei, Z.; Huang, C.; Xie, G.X.; et al. Use of iron oxide nanomaterials in wastewater treatment: A review. *Sci. Total Environ.* **2012**, *424*, 1–10. [CrossRef]
74. Warner, C.L.; Chouyyok, W.; Mackie, K.E.; Neiner, D.; Saraf, L.V.; Droubay, T.; Warner, M.G.; Addleman, R.S. Manganese Doping of Magnetic Iron Oxide Nanoparticles: Tailoring Surface Reactivity for a Regenerable Heavy Metal Sorbent. *Langmuir* **2012**, *28*, 3931–3937. [CrossRef] [PubMed]
75. Hao, Y.-M.; Man, C.; Hu, Z.-B. Effective removal of Cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles. *J. Hazard. Mater.* **2010**, *184*, 392–399. [CrossRef] [PubMed]
76. An, B.; Liang, Q.; Zhao, D. Removal of arsenic(V) from spent ion exchange brine using a new class of starch-bridged magnetite nanoparticles. *Water Res.* **2011**, *45*, 1961–1972. [CrossRef]
77. Dave, P.N.; Chopda, L.V. Application of Iron Oxide Nanomaterials for the Removal of Heavy Metals. *J. Nanotechnol.* **2014**, *2014*, 398569. [CrossRef]
78. Xin, X.; Wei, Q.; Yang, J.; Yan, L.; Feng, R.; Chen, G.; Du, B.; Li, H. Highly efficient removal of heavy metal ions by amine-functionalized mesoporous Fe3O4 nanoparticles. *Chem. Eng. J.* **2012**, *184*, 132–140. [CrossRef]
79. Fan, L.; Song, J.; Bai, W.; Wang, S.; Zeng, M.; Li, X.; Zhou, Y.; Li, H.; Lu, H. Chelating capture and magnetic removal of non-magnetic heavy metal substances from soil. *Sci. Rep.* **2016**, *6*, 21027. [CrossRef]
80. Kang, S.; Pinault, M.; Pfefferle, L.D.; Elimelech, M. Single-Walled Carbon Nanotubes Exhibit Strong Antimicrobial Activity. *Langmuir* **2007**, *23*, 8670–8673. [CrossRef]
81. Li, J.; Chen, C.; Zhang, S.; Wang, X. Surface functional groups and defects on carbon nanotubes affect adsorption–desorption hysteresis of metal cations and oxoanions in water. *Environ. Sci. Nano* **2014**, *1*, 488–495. [CrossRef]
82. Trojanowicz, M. Analytical applications of carbon nanotubes: A review. *TrAC Trends Anal. Chem.* **2006**, *25*, 480–489. [CrossRef]
83. Savage, N.; Diallo, M.S. Nanomaterials and Water Purification: Opportunities and Challenges. *J. Nanoparticle Res.* **2005**, *7*, 331–342. [CrossRef]
84. Lv, X.; Xu, J.; Jiang, G.; Xu, X. Removal of chromium(VI) from wastewater by nanoscale zero-valent iron particles supported on multiwalled carbon nanotubes. *Chemosphere* **2011**, *85*, 1204–1209. [CrossRef] [PubMed]
85. Helland, A.; Wick, P.; Koehler, A.; Schmid, K.; Som, C. Reviewing the Environmental and Human Health Knowledge Base of Carbon Nanotubes. *Environ. Health Perspect.* **2007**, *115*, 1125–1131. [CrossRef]
86. Sheng, G.; Alsaedi, A.; Shammakh, W.; Monaquel, S.; Sheng, J.; Wang, X.; Li, H.; Huang, Y. Enhanced sequestration of selenite in water by nanoscale zero valent iron immobilization on carbon nanotubes by a combined batch, XPS and XAFS investigation. *Carbon* **2015**, *99*, 123–130. [CrossRef]
87. Rodríguez, C.; Leiva, E. Enhanced Heavy Metal Removal from Acid Mine Drainage Wastewater Using Double-Oxidized Multiwalled Carbon Nanotubes. *Molecules* **2019**, *25*, 111. [CrossRef] [PubMed]
88. Oakes, K.; Shan, Z.; Kaliaperumal, R.; Zhang, S.X.; Mkandawire, M. *Nanotechnology in Contemporary Mine Water Issues*; Springer: Cham, Switzerland, 2014; pp. 307–361. [CrossRef]
89. Al-Hobaib, A.S.; Al-Sheetan, K.M.; Shaik, M.R.; Al-Suhybani, M.S. Modification of thin-film polyamide membrane with multi-walled carbon nanotubes by interfacial polymerization. *Appl. Water Sci.* **2017**, *7*, 4341–4350. [CrossRef]
90. Dong, H.; Zeng, G.; Tang, L.; Fan, C.; Zhang, C.; He, X.; He, Y. An overview on limitations of TiO_2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. *Water Res.* **2015**, *79*, 128–146. [CrossRef]
91. Nguyen, V.N.H.; Amal, R.; Beydoun, D. Effect of formate and methanol on photoreduction/removal of toxic cadmium ions using TiO2 semiconductor as photocatalyst. *Chem. Eng. Sci.* **2003**, *58*, 4429–4439. [CrossRef]
92. Singh, J.; Lee, B.-K. Influence of nano-TiO2 particles on the bioaccumulation of Cd in soybean plants (Glycine max): A possible mechanism for the removal of Cd from the contaminated soil. *J. Environ. Manag.* **2016**, *170*, 88–96. [CrossRef]
93. Tan, X.; Wang, X.; Chen, C.; Sun, A. Effect of soil humic and fulvic acids, pH and ionic strength on Th(IV) sorption to TiO2 nanoparticles. *Appl. Radiat. Isot.* **2007**, *65*, 375–381. [CrossRef] [PubMed]
94. Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *J. Hazard. Mater.* **2012**, *211–212*, 317–331. [CrossRef]
95. Karlsson, H.L.; Gustafsson, J.; Cronholm, P.; Möller, L. Size-dependent toxicity of metal oxide particles—A comparison between nano- and micrometer size. *Toxicol. Lett.* **2009**, *188*, 112–118. [CrossRef] [PubMed]

96. Auffan, M.; Decome, L.; Rose, J.; Orsiere, T.; De Meo, M.; Briois, V.; Chaneac, C.; Olivi, L.; Berge-Lefranc, J.-L.; Botta, A.; et al. In Vitro Interactions between DMSA-Coated Maghemite Nanoparticles and Human Fibroblasts: A Physicochemical and Cyto-Genotoxical Study. *Environ. Sci. Technol.* **2006**, *40*, 4367–4373. [CrossRef] [PubMed]
97. Gupta, V.K.; Chandra, R.; Tyagi, I.; Verma, M. Removal of hexavalent chromium ions using CuO nanoparticles for water purification applications. *J. Colloid Interface Sci.* **2016**, *478*, 54–62. [CrossRef] [PubMed]
98. Gervas, C.; Mubofu, E.B.; Mdoe, J.E.G.; Revaprasadu, N. Functionalized mesoporous organo-silica nanosorbents for removal of chromium (III) ions from tanneries wastewater. *J. Porous Mater.* **2015**, *23*, 83–93. [CrossRef]
99. Liu, R.; Lal, R. Nanoenhanced Materials for Reclamation of Mine Lands and Other Degraded Soils: A Review. *J. Nanotechnol.* **2012**, *2012*, 461468. [CrossRef]
100. Dubey, R.; Bajpai, J.; Bajpai, A. Chitosan-alginate nanoparticles (CANPs) as potential nanosorbent for removal of Hg (II) ions. *Environ. Nanotechnology, Monit. Manag.* **2016**, *6*, 32–44. [CrossRef]
101. Velardi, L.; Scrimieri, L.; Serra, A.; Manno, D.; Calcagnile, L. Effect of temperature on the physical, optical and photocatalytic properties of TiO2 nanoparticles. *SN Appl. Sci.* **2020**, *2*, 707. [CrossRef]
102. Kefeni, K.K.; Kefeni, K.K.; Mamba, B.; Mamba, B.; Msagati, T.A.; Msagati, T.A. Magnetite and cobalt ferrite nanoparticles used as seeds for acid mine drainage treatment. *J. Hazard. Mater.* **2017**, *333*, 308–318. [CrossRef]
103. Feng, Y.; Gong, J.-L.; Zeng, G.-M.; Niu, Q.-Y.; Zhang, H.-Y.; Niu, C.-G.; Deng, J.-H.; Yan, M. Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. *Chem. Eng. J.* **2010**, *162*, 487–494. [CrossRef]
104. Chen, J.; Qiu, X.; Fang, Z.; Yang, M.; Pokeung, T.; Gu, F.; Cheng, W.; Lan, B. Removal mechanism of antibiotic metronidazole from aquatic solutions by using nanoscale zero-valent iron particles. *Chem. Eng. J.* **2011**, *181–182*, 113–119. [CrossRef]
105. Su, Y.; Adeleye, A.S.; Keller, A.A.; Huang, Y.; Dai, C.; Zhou, X.; Zhang, Y. Magnetic sulfide-modified nanoscale zerovalent iron (S-nZVI) for dissolved metal ion removal. *Water Res.* **2015**, *74*, 47–57. [CrossRef] [PubMed]
106. Lv, D.; Zhou, J.; Cao, Z.; Xu, J.; Liu, Y.; Li, Y.; Yang, K.; Lou, Z.; Lou, L.; Xu, X. Mechanism and influence factors of chromium(VI) removal by sulfide-modified nanoscale zerovalent iron. *Chemosphere* **2019**, *224*, 306–315. [CrossRef] [PubMed]
107. Liu, T.; Wang, Z.-L.; Yan, X.; Zhang, B. Removal of mercury (II) and chromium (VI) from wastewater using a new and effective composite: Pumice-supported nanoscale zero-valent iron. *Chem. Eng. J.* **2014**, *245*, 34–40. [CrossRef]
108. Rodríguez, C.; Tapia, C.; Leiva-Aravena, E.; Leiva, E. Graphene Oxide–ZnO Nanocomposites for Removal of Aluminum and Copper Ions from Acid Mine Drainage Wastewater. *Int. J. Environ. Res. Public Health* **2020**, *17*, 6911. [CrossRef] [PubMed]
109. Sitko, R.; Turek, E.; Zawisza, B.; Malicka, E.; Talik, E.; Heimann, J.; Gagor, A.; Feist, B.; Wrzalik, R. Adsorption of divalent metal ions from aqueous solutions using graphene oxide. *Dalton Trans.* **2013**, *42*, 5682–5689. [CrossRef]
110. Sivaranjanee, R.; Saravanan, A. Carbon sphere: Synthesis, characterization and elimination of toxic Cr(VI) ions from aquatic system. *J. Ind. Eng. Chem.* **2018**, *60*, 307–320. [CrossRef]
111. Khoso, W.A.; Haleem, N.; Baig, M.A.; Jamal, Y. Synthesis, characterization and heavy metal removal efficiency of nickel ferrite nanoparticles (NFN's). *Sci. Rep.* **2021**, *11*, 3790. [CrossRef] [PubMed]
112. Lv, X.; Xu, J.; Jiang, G.; Tang, J.; Xu, X. Highly active nanoscale zero-valent iron (nZVI)–Fe3O4 nanocomposites for the removal of chromium(VI) from aqueous solutions. *J. Colloid Interface Sci.* **2012**, *369*, 460–469. [CrossRef]