Nanoscale zero-valent iron application for the treatment of soil, wastewater and groundwater contaminated with heavy metals: a review

Motasem Y.D. Alazaiza[a,*], Ahmed Albahnasawi[b], Nadim K. Copty[c], Mohammed J.K. Bashir[d], Dia Eddin Nassani[e], Tahra Al Maskari[a], Salem S. Abu Amr[f], Mohammed Shadi S. Abujazar[f,g]

[a]*Department of Civil and Environmental Engineering, College of Engineering, A'Sharqiyah University, 400 Ibra, Oman, emails: my.azaiza@gmail.com (M.Y.D. Alazaiza), tahra.almaskari@asu.edu.om (T. Al Maskari)*
[b]*Department of Environmental Engineering-Water Center (SUMER), Gebze Technical University, 41400 Kocaeli, Turkey, email: ahmedalbahnasawi@gmail.com*
[c]*Institute of Environmental Sciences, Bogazici University, Bebek, Istanbul, Turkey, email: ncopty@boun.edu.tr*
[d]*Department of Environmental Engineering, Faculty of Engineering and Green Technology (FEGT), Universiti Tunku Abdul Rahman, 31900 Kampar, Perak, Malaysia, email: jkbashir@utar.edu.my*
[e]*Department of Civil Engineering, Hasan Kalyoncu University, 27500 Gaziantep, Turkey, email: diaeddin.nassani@hku.edu.tr*
[f]*Faculty of Engineering, Karabuk University, Demir Campus, 78050 Karabuk, Turkey, email: sabuamr@hotmail.com*
[g]*Al-aqsa Community Intermediate college, Al-aqsa University, Gaza P.B.4051 – Palestinian Authority, email: mohammedshadi@hotmail.com*

ABSTRACT

Nanoscale zero-valent iron (nZVI) has been extensively investigated for the remediation of soil, wastewater, and groundwater contaminated with heavy metals. This paper presents a collective review of nZVI synthesis, nZVI interaction mechanisms with heavy metals, factors affecting nZVI reactivity, recent applications of nZVI for heavy metals removal, and the environmental concerns of nZVI application for soil microorganisms and plants. Modified nZVI, spatially biochar supported nZVI (BC@nZVI) and sulfidation nanoscale zero-valent iron (S-nZVI) showed high heavy metals removal efficiency and more stable performance compared to nZVI alone. The removal of heavy metals by nZVI is as a synergistic process where adsorption, oxidation/reduction and precipitation occur simultaneously or in series. pH and organic matter are the main factors that significantly affect nZVI reactivity. Toxic effects of nZVI are observed for the soil microorganisms as the direct contact may cause a decrease in cell viability and membrane damage. A low concentration of nZVI promotes the growth of plant whereas high concentration decreases root length. It is observed that, further research is needed to enhance nZVI recovery techniques, evaluate the effectiveness of novel modified nZVI and their effects on the environment, and the full-scale application of nZVI.

Keywords: Nanoscale zero-valent iron; Heavy metals; Groundwater; Wastewater

1. Introduction

Heavy metals are used in numerous industries such as dyeing, metallurgy, tanning, mining, pesticide synthesis, batteries, ceramics, and electroplating, leading to their discharge into environment [1,2]. These heavy metals are non-biodegradable, persistent and toxic. Thus, the application of chemical and biological degradation has had limited success [3]. The U.S. Environmental Protection Agency ranks toxic heavy metals (e.g., chromium (Cr), zinc (Zn), mercury (Hg), copper (Cu), cadmium (Cd), nickel (Ni) and lead (Pb) as top priority pollutants. Pollution by heavy metals presents a long-term health risk for both human health and environment such as electroplating, mining, pesticide synthesis, batteries, ceramics and paint result in the discharge of huge quantities of heavy metals into environment [4]. Heavy metals contamination is a great of concern as they are non-biodegradable, persistent and toxic as well. They tend to accumulate in the food chain which affects human health as well as ecosystems. Therefore, there is an urgent need to develop effective heavy metals immobilization/removal technologies to limit their harmful effect [5,6]

Conventional biological and chemical treatment methods cannot remove heavy metals as it is non-biodegradable [3]. Therefore, heavy metal remediation methods mainly focus on transforming them into less toxic species and/or less soluble/insoluble substances. Remediation could be implemented in situ or ex-situ. In situ heavy metals remediation usually aims at changing the stability state of those heavy metals to be stable. For heavily polluted soil, conventional remediation methods such as electrochemical separation, sediment washing, flotation, immobilization, ultrasonic-assisted extraction are costly and not effective [7,8] On the other hand, adsorption technologies have gained more attention as they are highly effective and cost-saving as well as no by-product formation (eco-friendly) [9,10].

Recently, the use of Fe-based nanomaterials for environmental remediation has gained significant attention due to these materials' high sorption sites, high specific area, and several surface interactions. Among the various Fe-based nanoparticles, nanoscale zero-valent iron (nZVI) is the most used one due to its high performance in degrading a wide range of pollutants [11–14]. nZVI has been demonstrated to be a good alternative for the remediation of a wide variety of organic and inorganic pollutants in soil and groundwater, showing a high efficiency and low economic and environmental costs [15,16]. For example, nitrate removal, organic dyes degradation, antibiotic remediation, and heavy metals removal. Including (Cd, Cr, As, Se and Pb) form the aqueous solutions [17–22].

Heavy metal that have been considered for remediation with nZVI include cadmium (Cd) [23], arsenic (As) [24], selenium (Se) [25], lead (Pb) [26], mercury (Hg) [27], corium (Cr) [28], zinc (Zn) [20], uranium (U) [29], nickel (Ni) [30] and copper (Cu) [31]. Despite the effectiveness of nZVI, problems such as agglomeration, limited mobility, and small size have limited the wide application of nZVI. To overcome these problems, surface modification, coating and supported nZVI have been considered to remove contaminants from soil and groundwater. The key mechanisms for heavy metals removal from soil and groundwater are adsorption, reduction and precipitation/co-precipitation [11]. nZVI is the most used one due to its high performance in degrading a wide range of pollutants. [11–14] For example, nitrate removal, organic dyes degradation, antibiotic remediation, and heavy metals removal. Including (Cd, Cr, As, Se and Pb) form the aqueous solutions. [17–22].

Because of the large volume of literature investigating the application of nZVI for heavy metals remediation from soil, wastewater and groundwater, there is a need for a collective synthesis of these studies to identify conditions under which nZVI are most effective and to identify lines of future review. Therefore, this review discusses and summarizes the recent application of nZVI for soil, wastewater, and groundwater remediation. The paper is organized as follows: Section 2 summarizes different nZVI synthesis methods. Section 3 describes the main interaction mechanisms between heavy metals and the nZVI. Section 4 reviews the environmental factors affecting the reactivity of nZVI. Section 5 discuss the application of nZVI for heavy metals removal from wastewater. Section 6 describes recent studies that applied nZVI for heavy metals remediation. Section 7 focuses on the environmental concerns associated with the use of nZVI. Finally, Section 8 outlines future research needs.

2. nZVI synthesis methods

Several methods have been developed for the synthesis of nZVI. Initially, physical methods such as abrasion, lithography as well as grinding were used [32,33]. Recently, more advanced methods have been used for nZVI synthesis such as nucleation from homogenous solution or gas, annealing at elevated temperature and separation of phases [11,34,35].

Synthesis methods of nZVI particles can be broadly classified as: bottom-up and top-down. Bottom-up methods utilize a growth-based approach molecule-by-molecule or atom-by-atom using chemical synthesis, positional assembling, self -assembling In top-down methods, large size materials are converted to nano-size particles by mechanical or/and chemical processes [36–38]. By physical methods, the formation of nZVI synthesis is done by the breakdown of iron materials using high energy and mechanical force. The previous physical method was severe plastic deformation (SPD). Nanostructure by SPD is formed under quasistatic pressure which resulted in significant refinement. One of the main drawbacks of this method is that the control of pressure is difficult [39]. latterly, evaporation condensation was invented in which raw material is gasified by utilizing vacuum evaporation, electron beam irrigation, laser heating evaporation, and sputtering, and rapidly condense to form nanostructure. The energy demand hindered the application of this method for full-scall [40]. Precision milling is a wildly used physical method for nZVI production. This method uses solid-state reaction or diffusion method to form superfine nanoscale particles. The produced nZVI by precision milling showed high reactivity towards organic pollutants. However, the irregular shape of formed nZVI limits their application [41]. Compared to physical methods, chemical methods are widely used due to their controllability and simplicity. The simple aqueous-phase reduction using Fe^{2+} and sodium borohydride as substrates was the commonly applied method. The high cost of this method

limited its application [42]. Compared to aqueous-phase reduction, carbothermal reduction is cost-effective as less expensive carbon materials are used. However, the electrolysis-based method is simpler and less expensive compared to carbothermal and aqueous-phase reduction. In the electrolysis method, electrodes (anode and cathode), electric current, and Fe^{2+}/Fe^{3+} salts are used to produce/aggregate nZVI at the cathode [25].

Reducing Fe^{2+}/Fe^{3+} using microorganisms and plant extracts have gained more attention in recent years. Such green synthesis methods overcome the limitation of the above methods (physical and chemical). The plant extracts have higher water solubility, less toxicity, and high yield. In addition, the synthesized nZVI using plant extracts have longer longevity and varied structure (irregular, square, and round), and varied morphology [43,44]. Two microbial approaches are used to form nZVI, the first one is biomineralization-inspired which use biochemical process in vivo. The second approach is biomineralization-induced which use the condition change (chemical and physical) of the surrounding microenvironment for coagulation, nucleation and precipitation of nZVI [45,46]. Table 1 summarizes the reported methods in literature.

3. Interaction mechanisms between nZVI and heavy metals

Although nZVI has been widely investigated for heavy metals contaminated soil and groundwater remediation and showed high prosperous application and tremendous protentional for in situ remediation, there is no consensus on the major mechanisms governing heavy metal remediation [56,57]. The main interaction mechanisms between nZVI and heavy metals assisted in the literature are adsorption (Ni, Cd, Pb), reduction (Ni, Cu, Pb) oxidation/reduction (U, As, Pb, Se) and precipitation (Cd, Pb, Cu). Each of these mechanisms is reviewed below.

3.1. Adsorption

Since nZVI possess large active sites and functional groups, nZVI is considering a feasible adsorbent for heavy metals removal [56,58]. Furthermore, iron oxides or hydroxides could be produced on the surface of nZVI, which could further enhance the adsorption process in a Fe^0-H_2O system [59]. Moreover, adsorption using iron-based materials is considered cost-effective and non-toxic. Thus, its environmental remediation application of nZVI contains to expand [9].

The adsorption mechanism is considered the dominant removal mechanism for a wide range of heavy metals. The main factor that affects the adsorption reaction mechanism between nZVI and heavy metals is the stander redox potential (E^0) of heavy metals. Heavy metals such as Cd and Zn which have similar or more negative E^0 than nZVI are being adsorbed. On the other hand, heavy metals such as Pb and Ni which have a more positive E^0 are reduced and precipitated in soil. Heavy metals such as Cr, Cu and As are adsorbed and also reduced [58,60,61].

Gue et al. [62] reported that nZVI based nanoparticles have high and selective adsorption for Cd^{2+}. The result showed that the maximum adsorption capacity of Cd^{2+} reached 290 mg/g after 5 h reaction time at 25°C. In another study, Abukhadra et al. [63] studied the adsorption of Zn^{2+}, Co^{2+}, and Cu^{2+} from an aqueous solution using nZVI based materials. The results showed that the adsorption isotherm fitted with the Langmuir model, and the maximum adsorption capacity was 149.25, 106.4 and 147.5 mg/g for the Zn^{2+}, Co^{2+}, and Cu^{2+} where the aquarium was reached at 240 min for Zn^{2+}, Co^{2+} and 120 min for Cu^{2+}.

3.2. Reduction

Reduction reactions are considered an important interaction between nZVI and heavy metals as it influences the physiochemical properties and valence of heavy metals in solutions [5,64]. Many studies have highlighted the reduction capacity of nZVI to be a promising alternative for heavy metals removal from aqueous solutions [65,66] In general, for multivalent heavy metals, the reduction process by nZVI is the main mechanism for heavy metal removal, where Fe^0 acts as an electron donor for the multivalent heavy metals [8]. Two different mechanisms controlled the reduction reaction of nZVI with heavy metals: 1) direct reduction with Fe^0 as the electron donor [67]: 2) the gradual reduction of heavy metals by Fe^{2+} after the primary adsorption through electrostatic interaction and surface complexation to nZVI core-shell [56,68]. For Cr^{2+} and Cr^{6+}, the reduction is the main removal mechanism by nZVI [59,69].

Li et al. [70] investigated the reduction of Cu^{2+} in an aqueous environment by nZVI. They used a pilot scale with a capacity of 1,600 L, the flow rat and initial Cu^{2+} concentration were 1,000–2,500 L/h and 70 mg/L. The results showed tremendous potential to reduce Cu^{2+} as the removal efficiency reached 96%. In another study, Fajardo et al. [71] indicated that two mechanisms are controlled the removal of Pb^{2+}, Cd^{2+} and Zn^{2+}. Firstly, these metals adsorbed to the surface of nZVI and then chemical reduction occurred. Many environmental factors such as organic matter, pH and co-exciting ions may affect the reduction interaction between nZVI and heavy metals. There are discussed in detail in Section 4 of this review.

3.3. Oxidation/reoxidation

In contrast to the reduction interaction, oxidation of heavy metals could occur but only in some special environmental systems. In the presence of oxygen, Fe^0-H_2O controlled by the Fenton reaction could oxidize heavy metals and could be considered as a possible reaction mechanism. In addition, Fe^0 could form various derivatives which have a great oxidizing capacity, thus, leading to the separation of heavy metal ions [56]. In the Fe-H_2O system, the oxidation of Fe^0 to Fe(II) and Fe(III), and reduction of Cr(VI) to Cr(III) were reported [72]. In some cases, direct oxidation of As^{5+} to As^{3+} by nZVI may decrease the toxicity of As since As^{3+} is less toxic than As^{5+} [73].

Bhowmick et al. [74] investigated the removal of arsenic from aquatic medium using nZVI. They found that As(III) was oxidized to As(V) along with the production of various oxidizing intermediates. The study concludes that nZVI can be effectively applied to remove heavy metals form the environment.

Table 1
nZVI preparation methods

Method	Description	Advantages	Disadvantages	References
Top-Down				
Precision milling method	Precision milling method consists of applying mechanical force to crush micro iron with steel shot in a high-speed rotary chamber for about 8 h without any chemical to achieve highly reactive nanoparticles of diameter 10–50 nm and surface area 39 m^2/g	Elimination of toxic reagents, short processing time, low energy consumption	Particles are deformed and cracked producing nanoparticles with irregular shapes and with strong tendency to aggregate because of their high surface energy	[47]
Lithography grinding	Break down bulk iron materials	Inexpensive method	Limited control over particle size distribution and morphology	[48]
Bottom-up				
Chemical reduction	Reduction of the iron salts using reducing reduction agent	Simple and easy to use in any laboratory	Use of toxic reducing agent; Not mentioned	[49]
Carbothermal reduction	Fe^{2+} are reduced to nZVI at elevated temperatures with the use of thermal energy in the presence of gaseous reducing agent	Spherical iron particles, cheap reducing agent – H_2, CO_2, CO	Not mentioned	[50]
Ultrasound method	Application of ultrasound waves and reducing agent uses reducing agents like sodium borohydride and ammonium hydroxide to produce small, uniform and equal-axe grains of iron nanoparticle of average size of 10 nm	Creation of small nanoparticles	Use of toxic reducing agent	[26]
Electrochemical method	Reduction of the iron salt in the presence of the electrodes and electrical	Inexpensive method	Tendency to form nZVI clusters	[51]
Green synthesis	Biosynthesis of nanoparticles using plant extracts	Inexpensive and environmentally friendly procedure where highly water soluble, less toxic, and biodegradable plant extracts are used to reduce iron to nanoscale	nZVI clusters; Irregular shape	[45,52–55]

3.4. Precipitation

Generally, Precipitation of heavy metals by nZVI is a co-precipitation mechanism where heavy metals are adsorbed to the nZVI iron shell, reduced and co-precipitated with nZVI particles [67,75]. For example, Cr(VI) removal in nZVI system includes oxidation of Fe, reduction of Cr(VI) and co-precipitation. In this system, the reduction process may occur before, during or after the co-precipitation [76,77],

Similarly, some heavy metals precipitate as hydroxides in high pH systems [57]. Cu removal by nZVI from aqueous solutions includes two mechanisms: (1) Cu is adsorbed to nZVI at pH 4–6, (2) after pH increase due to the release of OH^- from the reactions between oxygen, hydrogen and Fe^0, Cu(II) can precipitate as $Cu(OH)_2$ [68]. Similarly, U(VI) remediation by nZVI comprises reduction, adsorption and/ or precipitation. The precipitation of uranium occurs under alkaline conditions [78]. Similarly, Pb^{2+} removal mechanism

by nZVI includes adsorption over the porous structure of nZVI followed by the reduction and precipitation on nZVI particles [79]. For Ni(II) and Zn(II), the primary removal mechanism by nZVI is chemical adsorption and electrostatic attraction, co-precipitation within iron products and precipitation with hydroxide ions [13,80]. Han et al. [81] reported that the addition of BC to nZVI removal systems increases the pH, thus Cd immobilization in such systems is attributed to adsorption and precipitation [81]. Zhu et al. [82] stated that Cu^{2+} could be effectively removed from the aquatic environment using nZVI by replacement-co-precipitation from EDTA chelated Cu^{2+}.

To sum up, the removal mechanism of heavy metals by nZVI is as a synergistic process where adsorption, oxidation/reduction and precipitation take place simultaneously or in series. Nevertheless, the main removal mechanism could be attributed to one or two interactions. Hence, to understand the interaction mechanisms between nZVI and heavy metals, real reaction conditions should be implemented.

4. Environmental factors affecting the reactivity of nZVI with heavy metals

Environmental factors significantly affect the removal of heavy metals by nZVI [69]. In this section, the influence of environmental and operation conditions such as pH, contact time, reaction temperature, organic matter content, oxidation–reduction potential and co-exciting ions on the heavy metals removal from soil and groundwater is discussed.

4.1. pH effect

The soil/groundwater pH could affect the removal mechanism (adsorption, reduction and precipitation), and interaction between heavy metals and nZVI via changing the Fe^0 particles surface charge and the speciation and ionization degree of heavy metals [57,68,75]. Different pH values may control the removal mechanism of heavy metals [83–85]. For example, at low pH, the positive charge surrounds the nZVI surface which leads to electrostatic repulsion and reduces the adsorption of positive cations of heavy metals such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+}. Increased adsorption of heavy metals in anion form such as Cr^{6+} which exist as $HCrO_4^-$ or CrO_4^- [68,86,87]. On the other hand, high pH leads to formation of metal hydroxide species [59,68,88–90]. Similarly, for As(V) existing in the form $H_2ASO_4^-$ and $H_3AsO_4^{2-}$, the electrostatic interaction between As species and nZVI at low pH is high as the protonation degree of the nZVI is higher at low pH. As the initial pH increases, the degree of protonation is continuously decreased leading to weakening electrostatic interaction between nZVI and $H_2ASO_4^-/H_3AsO_4^{2-}$. At pH above 7 the high concentration of OH^- compete with $HASO_4^{2-}$ or AsO_4^{3-} for active sites on the nZVI surface [72,91]. Kumari et al. [17] studied the relationship between Cr(VI) removal and pH. At an initial pH of 4, the adsorption of Cr(VI) is high due to electrostatic interaction between nZVI and Cr(VI) species. As pH increases, the electrostatic attraction gradually decreased. Yuan et al. [92] found that the initial pH dramatically affects the removal of tetrabromobisphenol A (TBBPA) from

contaminated soil using nZVI. The degradation efficiency of TBBPA decreased from 89.4% to 39.8% when the initial pH increased from 3.5 to 10.5. Qiu et al. [93] stated that the Cr(III) can be removed completely from aqueous solution using nZVI when the solution pH was lower than 7.

4.2. Contact time

Generally, the removal efficiency and adsorption capacity of heavy metals improve with an increase of the contact time with nZVI as the dominant mechanism is adsorption [68]. Liu et al. [91] reported that for times exceeding 24 h (adsorption equilibrium time), As(V) adsorption by nZVI is almost negligible. The As(V) remediation include two steps in terms of contact time: 1) in the first stage (0 to 6 h), the adsorption rate is high while in the second-stage (6 to 24 h), the rate is reduced to 22% of the rate pf the first stage. This is attributed to the decrease of active sites on the surface of nZVI. Similarly, the removal efficiency of U(VI) by nZVI was 50% for the first 10 min of contact with the reaction equilibrium of about 60 min [85]. In the same way, Mahmoud et al. [94] reported that the sorption process of Co(II), Zn(II), Hg(II), Pb(II), Cd(II) and Cu(II) gradually rises with the increase of contact time. After 60 min contact time, the adsorption efficiency increased from 1,800 µmol/g to around 2,700 µmol/g for Zn(II). The quick adsorption during the first stages could be attributed to the high concentration of both adsorbate and adsorbent as well as the high amount of empty places attainable during this period [95,96].

Similarly, U(VI) removal by nZVI was high in the first 10 min to reach 50% removal efficiency. The removal rate decreased gradually by filling the active sites, reaching the equilibrium at 60 min [85]. However, the release of adsorbed heavy metals may occur after reaching the equilibrium. In a study by Calderon and Fullan [97], although the removal capacity of nZVI for Zn, Cr, Cu, Cd and Ni remediation from groundwater was high, some adsorbed heavy metals were released again to water. This could be attributed to the oxidation of nZVI by aging, which leads to nZVI surface crystallization.

4.3. Organic matter

Organic matter is an inherent constituent of water and soil, affecting the application and reactivity of nZVI for heavy metals removal. Organic matter content may affect the heavy metals removal through charged species such as humic and fulvic acids which are readily adsorbed on the surface of nZVI rather than heavy metals. In addition, humic acids may form soluble complexes with heavy metals through their carboxylate and phenate groups which increases the humic affinity for divalent metal ions [98]. These complexes increase the reduction effectiveness preventing the precipitation of heavy metals as well as the passivation of nZVI [99]. Thus, heavy metals contaminated soil with high organic matter content is not suitable for nZVI application as an inhibitory effect of organic matter is mentioned in many studies [100,101]. Gueye et al. [99] reported that the removal efficiency of Cr(VI) decreased from 91% to 12% after 2 h of treatment of soil containing 35.71 g/kg of organic matter. Similarly, Han et al. [102]

found that the reactivity of S-nZVI was decreased by 60% when the organic matter increased by 200 mg/L.

5. Oxidation–reduction potential

Oxidation–reduction potential (ORP) has an essential role in the bioavailability, mobility, toxicity, and oxidation state of heavy metals. ORP also controls the performance of nZVI for heavy metals removal [103]. Due to the high reduction potential of nZVI, it may consume dissolved oxygen when the nZVI is added to the subsurface system (soil or water) containing organic matter; thus, ORP also decreases as DO decrease [104,105]. In addition, nZVI acts as a two-electron donor system, consisting of Fe^0 and Fe^{2+}, indicating that nZVI react with numerous redox-responsive contaminants and common environmentally relevant electron acceptors as well [106].

5.1. Co-existing cations and anions

Natural soil and groundwater contain a variety of cations and anions which can affect heavy metals remediation [65,75]. Many studies have reported that nZVI performance for heavy metals remediation is affected by the presence of cations (Zn, Fe, Mg, and Ca) and anions (NO_3, HCO_3, SO_4 and PO_4) [69,107–112] For instance, the presence of Cl^-, NO_3^{2-}, SO_4^{2-} and CO_3^{2-} decreases the removal of Cr(VI) as these anions could compete with Cr(VI) for the adsorption sites on nZVI surface. On the other hand, the presence of metal ions, such as Pb^{2+}, Cu^{2+} and Cd^{2+} may also interfere with the removal of Cr(VI) [68]. In a study, it was reported that the presence of HCO_3^- did influence the Cr(VI) removal by S-nZVI by 10 % (decreased from 99% to 88%). This was attributed to the competition between Cr(VI) and HCO_3^- for the active sites on the S-nZVI surface. In addition, the produced Fe^{2+} may react with HCO_3^- and from $FeCO_3$ which precipitates due to its low solubility [16].

Conversely, co-existing ions may enhance the removal of some heavy metals by nZVI [30,90]. For example, the presence of Cu^{2+} improved the removal of Se(VI) as Cu^{2+} may act as a catalyst during the reaction. However, in the same study, the presence of Ca^{2+} inhibited the removal of Se(VI) due to the formation of passivate precipitate like $CaCO_3$ on the surface of iron particles which block the electron transfer surface [113]. Jiao et al.. [114] examined the effect of co-existing ions on Pb removal by nZVI.

The selectivity of nZVI toward heavy metals may be influenced by reduction potential. While the uptake capacity of nZVI for Hg(II) was not affected by the presence of Cd(II), Pb(II), Ni(II) and Cu(II), the Hg(II) removal efficiency was significantly decreased (from 58% to 27%) in the presence of Cr(VI) as it has positive reduction potential higher than Hg(II) [22].

6. Application of nZVI for heavy metal removal from wastewater

Many studies have reported the protentional of nZVI for heavy metals removal from wastewater. In this section, recent studies are presented highlighting the progress of using nZVI for heavy metals removal from wastewater.

In a study, Gao et al. [115] investigated the removal of U(VI) from nuclear industry wastewater by nZVI. The results showed that nZVI can effectively remove U(VI) from strongly alkaline wastewater (pH 10). The removal mechanism of U(VI) was the reductive precipitation. Finally, this study provided new insight into the reaction between nZVI and U(VI) in strong alkaline wastewater and demonstrated that nZVI is a promising treatment technology for heavy metals removal from nuclear industry watermaster. In another study, Zhou et al. [116] investigated the performance of sulfide-modified nanoscale zero-valent iron (nZVI)-supported ZSM zeolite composite (S-nZVI@ZSM) for the As(V) removal from acidic wastewater. The results pointed that S-nZVI@ZSM effectively removed As(V) from acidic wastewater as the removal efficiency reached 95%. The results demonstrated that the introduction of sulfur positively increased the surface area from 35.3 to 45.7 m^2/g which increase the activity of nZVI. In a recent study, Li et al. [117] examined the removal of lead and cadmium from wastewater using a biofunctionalized magnetic mesoporous silica (nZVI-SH-HMS). The result pointed out that the main removal mechanism was adsorption/precipitation and surface complexation. In addition, nZVI-SH-HMS showed high adsorption performance and sorption recyclability. These results indicated that nZVI-SH-HMS is a promising solution for heavy metal removal from real wastewater. In a recent study, Xie et al. [66] studied Cr(VI) removal using nano zero-valent iron assisted by schwertmannite (nZVI/Sch). The results showed that Cr(VI) removal by nZVI/Sch-AP was high pH-dependent. At pH 6.3 the removal efficiency reached 99.99%. The results from this study demonstrated nZVI/Sch as an effective treatment method for heavy metals removal from wastewater. In another study, Hernández et al. [118] studied the performance of nZVI and nZVI-functionalized zeolite (Z-nZVI) for As(V) removal from single and multi-component Se(VI) wastewater. The results indicated that the performance of Z-nZVI was higher than nZVI both in multi-component and single systems. The superiority of Z-nZVI was attributed to their high specific areas' sites than nZVI, which make Z-nZVI more effective than nZVI for As(V) removal from wastewater.

Table 2 summarizes the application of different types of nZVI for the removal of different types of heavy metals from wastewater.

7. Applications of nZVI for heavy metal removal from contaminated soil

nZVI has been applied for the remediation of different heavy metals from soil and groundwater. In this section, recent studies in this domain are presented with a focus on the used nZVI type, targeted heavy metals, experiment conditions and the main findings.

Industrial activities, mostly leather production and electroplating may release Cr into the environment [119,120]. Two forms of Cr are stable: Cr(VI) and Cr(III), Cr(VII) is more toxic, mutagenic and terato-genic than Cr(III) [121,122] Many studies investigated the remediation of Cr(VI) from soil and groundwater by Fe based nanomaterials. Ye et al. [123] investigated the performance of green tea (GT) and vitamin C(VC) modified nZVI (GT-nZVI@VC) for

Table 2
Application of nZVI for the removal of different types of heavy metals from wastewater

nZVI	Heavy metals	Conditions	Main results	References
nZVI	U(VI)	- U(VI) initial concentration 8.4×10^{-4} mol/L - pH 10; - Contact time 1 h.	nZVI is a promising solution for U(VI) form nuclear industry wastewater, specially at strong alkaline.	[115]
S-nZVI@ZSM	As(V)	- As(V) initial concentration 5 mg/L; - S-nZVI@ZSM dosage 100 mg/L; - pH (3–9); - Contact time (10–300) min.	Sulfur introducing can increase the reactivity time of nZVI and enhance the adsorption performance of S-nZVI@ZSM.	[116]
nZVI-SH-HMS	Pb(II), Cd(II)	- Pb and Cd initial concentration (100–150) mg/L; - nZVI-SH-HMS dosage 1 g/L; - pH (2–8).	- Reusability and regeneration tests indicated nZVI-SH-HMS maintained excellent adsorption performance and had a great potential for removing heavy metals from the actual water environment; - nZVI-SH-HMS regeneration and reusability characteristics make it as competitive adsorbent for heavy metals removal from wastewater.	[117]
nZVI/Sch	Cr(VI)	- Cr(VI) initial concentration (10, 20, 30, 50) mg/L; - pH (4.7, 5.5, 6.3); - nZVI/Sch mass ratio (1:0.5, 1:1, 1:2); - nZVI dosage 300 mg/L; - Contact time (0–60) min.	Main removal mechanism was a combination between immobilization and surface absorption–reduction.	[66]
Z-nZVI	As(V)	- Z-nZVI dosage 200 mg/L; - As(II) initial concentration (0.5–200) mg/L; - Contact time (5–180) min; - pH (3–10).	Because of its simple preparation methods and high adsorption capacity, Z-nZVI is an excellent alternative for heave metals removal form wastewater.	[118]

Cr(VI) removal from water-saturated heterogeneous porous media. The results pointed to the high Cr(VI) removal by GT-nZVI@VC. The high removal efficiency is attributed to the synergistic effects of tea polyphenols and VC that can enhance the releases of free electrons into solution leading to a high reduction of Cr(VI) to Cr(III). Li et al. [124] examined the performance of sodium oleate (NaOA) and poly-vinylpyrrolidone (PVP) modified nZVI for Cr(VI) groundwater remediation. The study showed the occurrence of synergistic effects for Cr(VI) removal as PVP and NaOA were used for nZVI modification. The Cr(VI) was totally reduced to Cr(III). Thus, this process is suitable for in situ Cr(VI) remediation from groundwater. In a subsequent study, Qiu et al. [93] studied nZVI supported biochar system for Cr(VI) from an aqueous solution. The result showed that the removal efficiency was 64.13% for Cr(VI) and 28% for Cr(III). Remarkably, the result indicated that the direct complexation with Fe(II) and sufficient adsorption site was the main factors that affect Cr(III) removal [93].

Lead has several industrial applications such as pigments and paints preparation, electroplating and battery manufacturing [110,125] As a result, it may be present in soil and aquatic systems [12,20] Lead may cause anemia chronic headaches and diarrhea; thus, it is necessary to remove lead from environment. A study by Li et al. [126] examined the performance of hydrophilic biochar (HPB) immobilized nZVI (nZVI-HPB) for the removal of Pb(II) from aqueous solution. The results indicated that the removal mechanisms include reduction reaction, co-precipitation and reduction reactions leading to a high removal efficiency by the nZVI-HPB system, Mandal et al. [127] developed nZVI impregnated magnetic green tea biochar (nZVI@GTBC) for Pb(II) removal from contaminated soil. The results demonstrated that nZVI@GTBC enhanced the Pb(II) immobilization by 19% compared to nZVI alone and 57% in combustion with GTBC. Li et al. [128] examined the performance of biochar loaded with nano-zero-valent iron (BC-nZVI) for remediation of Pb-contaminated soil. The result indicated that 8 g/kg is the optimum dosage for remediation of Pb where the removal efficiency was 66%.

Table 3 summarizes the application of different types of nZVI for the removal of different types of heavy metals from soil and groundwater.

Remarkably, Pb and Zn removal was high over short term scales but dropped with increased time [20]. Roncevic et al. [129] studied the removal of Cd by 2,6-pyridinedicarboxylic acid (PDC) functionalized nZVI (PDC@nZVI). The result revealed that the removal efficiency was 100% when Cd initial concentration was 5 mg/L, which corresponded to a removal capacity of 110.2 mg/g. In a subsequent study, Linang et al. [23] investigated the mechanism of Cd(II) removal from aqueous solution by sulfidated nanoscale zero-valent iron (S-nZVI) (Fig. 1). the results indicated that the Cd removal capacity by S-nZVI was 495 mg/L which is dramatically higher than other nZVI adsorbents. The co-existence of Mg^{2+}, NO_3^{2-} and humic acid slightly reduced the removal of Cd due to competition for the adsorption sites on the S-nZVI surface shell. Yang et al. [130] examined the performance of biochar-supported nanoscale zero-valent iron (BC-nZVI) for Cd and As removal from aqueous systems. The results indicated that, in a single adsorption system, the maximum Cd removal capacity was 33.81 mg/g in 2 h reaction time with an As removal capacity of 148.5 mg/g for 1 h contact time. Remarkably, in mixed adsorption systems, the adsorption capacity for Cd and As was dramatically enhanced to reach 179.9 and 158.5 mg/g, respectively.

Singh et al. [131] investigated the performance of S-nZVI for As removal from aqueous environments. The results demonstrated that the adsorption capacity of As(III) by S-nZVI was 89.29 and 79.37 mg/g for As(V). In addition, the removal mechanism of As(III) and As(V) was adsorption as arsenate and arsente, respectively.

Removal efficiency of Pb and Ni from soil using nZVI synthetized from neem leaves and mint leaves. the results showed that the removal efficiency of Pb by nZVI synthesized from neem and mint was 26.9% and 62.3%, respectively. The corresponding removal efficiencies for Ni were 33.2% for neem and 50.6% for min, respectively [132].

In another study, Mandal et al. [133] investigated the performance of low-cost biochar-supported nZVI and polysulfide (PS-nZVI@BC) for Se(VI) removal from contaminated soil.The result indicated that many interaction mechanisms were responsible for Se removal such as; reduction, adsorption and precipitation (Fig. 2). In addition, Ther results demonstrated that PS-nZVI@BC is better than nZVI@BC for Se control in contaminated soil as the Se concentration decreased by 77% after 30 d of contact time with PS-nZVI. In a recent study, Chen et al. [134] examined the performance of nZVI@Mg(OH)$_2$ for U(VI) removal from an aqueous solution. The authors reported a high removal efficiency of 97.8% and a removal capacity of 122.3 mg/g at 0.4 g/L dosage. Moreover, the results revealed that the main interaction mechanism between U(VI) and nZVI@Mg(OH)$_2$ was adsorption and reduction.

Shao et al. [42] investigated the removal of chlortetracycline (CTC) and copper Cu(II) from aqueous solution by nZVI supported on wheat straw (WS-nZVI) composites. The results showed that, in a single removal system, the removal capacity of Cu(II) and CTC was 376.4 and 1,280.8 mg/g, respectively, whereas in binary removal system, the removal efficiency of Cu(II) was influenced by the presence of CTC.

8. Environmental considerations of nZVI

Numerous studies have demonstrated nZVI's high performance for soil and groundwater heavy metal remediation. There is a need to assess the potential effects of implementing nZVI in the field on the environment [135]. In this section, recent studies that discuss the potential impacts of nZVI on environmental microorganisms and plants are summarized.

Lv et al. [136] studied the bacterial toxicity of nZVI on soil bacteria. *Pseudomonas putida* was chosen as an indicator. The results indicated that nZVI was toxic to *Pseudomonas putida*. However, the toxicity effects of nZVI decreased with the increase in DO. Moreover, the result suggested that oxidative stress and membrane disruption by direct stress is the main mechanism of bactericidal under aerobic conditions while membrane disputing is the primary mechanism under anaerobic conditions. Ravikumar et al. [137] investigated the ecotoxicity of nZVI on five native

Table 3
Application of nZVI for the removal of different types of heavy metals from soil and groundwater

nZVI	Heavy metals	Conditions	Main results	References
GT-nZVI@VC	Cr(VI)	- Cr(VI) initial concentration 25–200 mg/L; - GT-nZVI@VC dosage 0.5 g/L; - pH 2.2; - Contact time 3 h.	Transportability of GT-nZVI@VC in soil/sand system was high compering to nZVI.	[123]
PVP and NaOA modified nZVI	Cr(VI)	- Cr(VI) initial concentration 80 mg/L; - nZVI dosage 20 g/L; - Contact time 3 h.	- Acidic conditions enhance the Cr(VI) removal. - Removal efficiency was 99% with removing capacity 231.45 mg/g.	[124]
Biochar supported nZVI	Cr(VI)	- Temperature 25°C; - Cr(VI) and Cr(III) initial concentration 1,000 mg/L; - nZVI dosage 1 g/L; - pH 4.	Presence of Cu(II) and humic acid adversely affected the removal of Cr(VI) and Cr(III), whereas Na and Ca(II) present did not affect the removal efficiency.	[93]
nZVI-HPB	Pb(II)	- Pb(II) initial concentration 200 mg/L; - pH 6; - Temperature 25°C; - Adsorbent dosage 0.25 g/L.	- Adsorption capacity of nZVI-HPB was 480.9 mg/g; - High removal efficiency was attributed to good dispersibility, and abundant functional groups form hydrophilic biochar carrier as well as the antioxidation of nZVI.	[126]
nZVI@GTBC	Pb(II)	- Contact time 1, 15, 30 d; - nZVI@GTBC dosage 10 g/kg; - Pb(II) initial concentration 386 mg/kg.	- Immobilization studies over 30 d suggested effective immobilization of lead in soil natural pH conditions; - Alkaline and acidic pH dramatically affect the immobilization of Pb(II) in soil whereas natural soil pH did not affect the Pb(II) immobilization.	[127]
BC-nZVI	Pb(II)	BC-nZVI dosage 0.0, 2.0, 4.0, 8.0, 16.0 g/kg;	BC-nZVI is a promising technology for Pb immobilization in contaminated soil.	[128]
nZVI	Pb, Zn, Cd	- pH 5.7; - initial concentration Pb 2,700 mg/kg; Zn 4,200 mg/kg; and Cd 310 mg/kg; - nZVI dosage 5% w/w.	- Nanoremediation strategy applied to multiple HM-contaminated soil decreased Zn and Pb mobility, particularly in the short-term. However, over longer time scales of treatment (120 d), the efficiency of this strategy was low; - nZVI was effective for Pb and Zn immobilization in short term while in long term the efficiency was low.	[20]

(Continued)

Table 3 Continued

nZVI	Heavy metals	Conditions	Main results	References
PDC@nZVI	Cd	- Cd initial concentration 0.1–50 mg/L. - PDC@nZVI dosage 4.74, 2.37 g/L.	Adsorption of Cd by PDC@nZVI depended on (1) composition of mixed magnetite, (2) feroxyhyte oxide layers on the core–shell structure.	[129]
S-nZVI	Cd	- Cd initial concentration 50–400 mg/L; - Mg^{2+}/NO_3 concentration 30–480 mg/L; - Humic acid concentration 10–50 mg/L.	Sulfur plays a significant role in Cd transformaton in the environment. S-nZVI is a promosing technology for Cd removal from environment.	[23]
BC-nZVI	Cd, As	- pH 2–8; - Adsorbent dosage 0.25 g/L; - Temperature 25°C.	Adding biochar to nZVI system could inhibit the oxidation and aggergate of nZVI, enhancing thus, the stability of nZVI.	[130]
S-nZVI	As	- S-nZVI dosage 0.5 g/L; - As(III) and As(V) initial concentration 10–50 mg/L; - pH 5–9.	Dominant uptake mechanism of As by nZVI involves adsorption and reduction of the adsorbed As(III) and As(V) to lower valence state including As(0).	[131]
nZVI	Pb, Ni	- Initial Ni and Pb concentration 250 mg/kg; - Contact time 30 d; - nZVI dosage 0.1 g/kg.	nZVI based green leave is a promosing green technology for heavy meatls removal from contaminated soil, espicially, Pb and Ni.	[132]
PS-nZVI@BC	Se	- Se initial concentration 125 mg/kg; - PS-nZVI@BC dosage 10 mg/L; - Moisture content 40%; - Temperature 25°C; - Contact time 1, 7, 15, 30 d.	PS-nZVI@BC is an effective technology for Se-contaminated soil.	[133]
nZVI@Mg(OH)₂	U(VI)	- U(VI) initial concentration 5–50 mg/L; - Temperature 25°C; - pH 3–8; - nZVI@Mg(OH)₂ dosage 0.1–2 g/L; - Contact time 10–60 min.	$Mg(OH)_2$ coating imporoved the mobility and stability of nZVI. nZVI@Mg(OH)₂ is a promosing technology for in-situ U(VI) remedation.	[134]
WS-nZVI	CTC, Cu(II)	- WS-nZVI dosage 0.1, 0.25, 0.5 g/L; - Temperature 25°C; - CTC/Cu(II) initial concentration 50–950 mg/L.	Removal mechansim of CTC and Cu(II) includes (1) adsorption of CTC and Cu(II) into WS-nZVI surface, (2) Fe^0 reduced Cu(II) to Cu^0 at the same time degraded CTC.	[42]

bacteria. The result indicated that a decrease in cell viability and membrane damage was observed after contact with nZVI. The nZVI action against microorganisms could be attributed to oxidative pressure caused by reactive oxidative species produced from the reduction of Fe and oxygen [138]. Gómez-Sagasti et al. [139] conducted a three-month experiment in two types of soil: sandy-loam and clay-loam soils, to see how nZVI concentration (ranging from 1 to 20 mg/gL) affected soil microbial properties. The findings showed that the type of soil can influence the degree of potential toxic effects of nZVI on soil microbial communities. The results revealed that nZVI has a stronger inhibitory effect on soil microorganisms in sandy-loam soil than in clay-loam soil. This may be due to the clay-loam soil's high organic content, which acts as a protective barrier when nZVI is added to the soil, rendering nZVI active and preventing interaction with soil microorganism cells. The use of nZVI to remediate sandy-loam soil had a negative impact on bacterial biomass, arylsulphatase activity, diversity, and richness. In terms of concentration, they discovered that nZVI application had no discernible concentration-response effect on soil. To gain a clear understanding of the effect of soil properties and type on the impact of nZVI on soil Bactria communities, the study suggests that numerous investigations using a wide range of soil types and soil proprieties are required.

Cheng et al. [140] investigated the toxicity of sulfide-modified nanoscale zero-valent iron (S-nZVI) in aqueous solution to *E. coli*. The results showed that sulfidation could reduce the toxicity of nZVI, as S-nZVI showed less toxicity at lower F/S molar ratios, owing to higher iron oxide and sulfate content and lower Fe^0 content. The findings suggest that common groundwater constituents (such as Ca^{2+}, HCO_3^-, SO_4^{2-}, and humic acid) may reduce nZVI toxicity. In addition, S-nZVI toxicity was low in the presence of groundwater mix components. The findings suggest that S-presence nZVI's could pose a low toxicity risk to the ecosystem.

A number of studies investigated the effect of nZVI on plants[141–146] Most of these studies revealed that adding limited amounts of nZVI to contaminated soil not only removed heavy metals but also enhance the growth of plants. However, high concentrations of nZVI pose a negative effect on plant growth [147]. Kashtiban et al. [148] found that the low dosage of nZVI enhanced the growth of plants by increasing the root length and leaf area. In contrast, the high dosage negatively affects seedling growth. Similarly, Tolaymat et al. [149] stated that the low concentration of nZVI may stimulate both the seeds and the growth of peanut plants. This was attributed to nZVI particles penetrating the peanut seed to increase water uptake and enhance germination activity of the seed by rise seedling development. Libralato et al. [119] found that the used concentration of 2.3–33 g/L did not have adverse toxic effects on plant growth as bio-stimulation phenomena generally happened at high concentrations of Fe [150]. Huang et al. [21] also investigated the effect of nZVI on plant growth. The results demonstrated that the root length decreased with the increase of nZVI dosage especially above 1,000 mg/kg. In a recent study, Zhang et al. [151] studied the effect of nZVI concentration on root length. It was reported that the root length increased by adding nZVI up to 250 mg/L whereas further increasing of nZVI concentration decreased the root length.

Wang et al. [152] investigated the effect of nZVI concentration (0, 100, 250, 500, 750 and 1,000 mg kg/L) on seedling growth, germination, toxicity mechanisms and physiology. The results demonstrated that at nZVI dosage less than 500 mg/L), no effect on germination, and seedling growth was observed, whereas at a concentration higher than 750 mg/L, the rice seedling was inhabited, and visible iron deficiency was observed.

9. Recommendations and future prospective

Although the application of nZVI for heavy metals has been successfully applied in the lab and in the field, the following connected issues should be addressed in future research; (1) synthesis of modified nZVI that improve the removal of heavy metals efficiencies; (2) evaluating the potentially hazardous effect of nZVI remediation on soil microorganisms and plants; (3) development of cost-effective nZVI preparation methods and in situ application including the delivery of nZVI to zones of high heavy
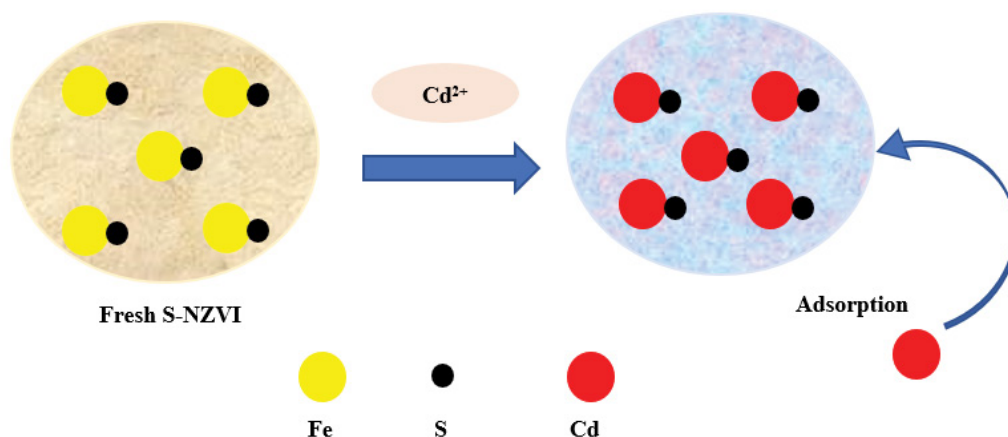

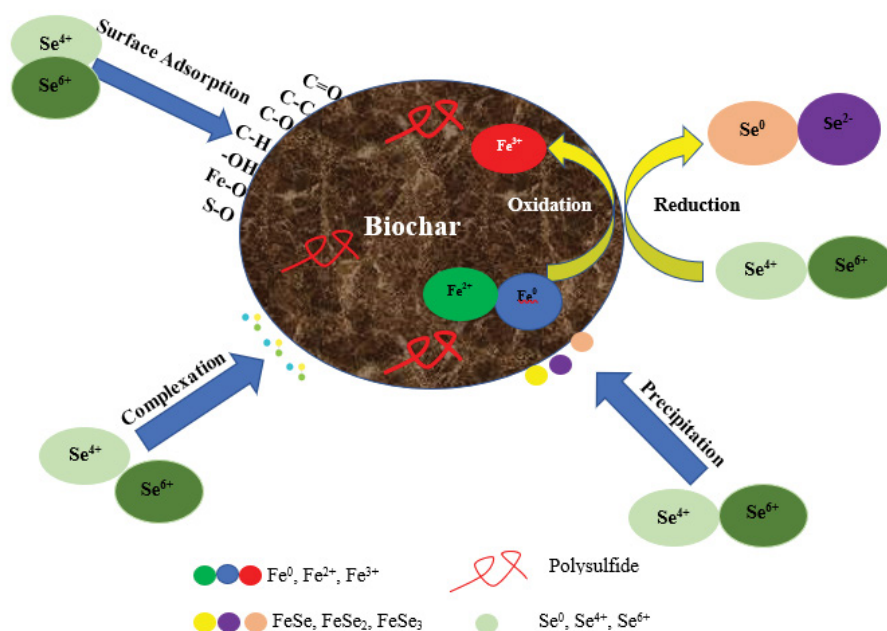Fig. 1. Cd removal mechansim by S-nZVI.

Fig. 2. PS-nZVI@BC interaction mechnsim with Se.

metal concentrations; (4) Specific attention should focus on green synthesis of nZVI as this is important towards sustainable remediation practices. In addition, future studies should focus on the nZVI fate and transport with more attention on toxicity behavior during those processes. Moreover, the long-term evolution of nZVI, especially under field conditions should be examined.

10. Conclusions

Because of their toxic effects on human health and the environment, heavy metals contaminated soil, wastewater, and groundwater have gotten a lot of attention. The development of effective heavy metals removal technologies from the subsurface environment is a pressing need, given the scope of the problem. nZVI has been extensively researched as a method of removing heavy metals from the environment. This review compiles information on the synthesis of nZVI, the mechanism of heavy metal interaction, the factors influencing nZVI's reactivity, its application for heavy metal removal, and the environmental concerns associated with nZVI's use in soil microorganisms and plants. Overall, the studies show that modified nZVI is more efficient at removing heavy metals and has a more stable performance than nZVI alone. nZVI's heavy metal removal mechanism is a complicated one in which adsorption, oxidation/ reduction, and precipitation all happen at the same time or in sequence. pH, organic matter, and co-existing ions are the most important environmental factors affecting nZVI reactivity. nZVI has a negative impact on soil microorganisms. Low concentrations of nZVI encourage plant growth, whereas high concentrations inhibit plant growth by shortening root length. Finally, more research is needed into the applicability of restoring nZVI, as well as the green development

of effective modified nZVI, their long-term environmental impact, and field scale application.

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