Review

Xilu Chen, Xiaomin Li, Dandan Xu, Weichun Yang, and Shaoyuan Bai*

Application of nanoscale zero-valent iron in hexavalent chromium-contaminated soil: A review

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Abstract: Chromium (Cr) is a common toxic heavy metal that is widely used in all kinds of industries, causing a series of environmental problems. Nanoscale zero-valent iron (nZVI) is considered to be an ideal remediation material for contaminated soil, especially for heavy metal pollutants. As a material of low toxicity and good activity, nZVI has been widely applied in the *in situ* remediation of soil hexavalent chromium (Cr(VI)) with mobility and toxicity in recent years. In this paper, some current technologies for the preparation of nZVI are summarized and the remediation mechanism of Cr(VI)-contaminated soil is proposed. Five classified modified nZVI materials are introduced and their remediation processes in Cr(VI)-contaminated soil are summarized. Key factors affecting the remediation of Cr(VI)-contaminated soil by nZVI are studied. Interaction mechanisms between nZVI-based materials and Cr(VI) are explored. This study provides a comprehensive review of the nZVI materials for the remediation of Cr(VI)-contaminated soil, which is conducive to reducing soil pollution.

Keywords: Cr(VI)-contaminated soil, nanoscale zero-valent iron (nZVI), soil remediation, modified nano-iron

1 Introduction

Chromium (Cr) is one of the most common heavy metals, which are widely utilized in wood preservatives, metallurgy, chromium plating, chromate manufacturing, alloys, textiles, printing, dyeing, and other industrial manufacturing sectors [1]. Nevertheless, during these industrial production processes, a large amount of Cr gets released into soils, which brings about a series of environmental problems and arouses widespread concern [2].

In soils, Cr may be soluble in the solution, exchangeable on the solid phase, bound to organic substance or oxides and clay-like mineral, and trapped in a crystal lattice core [3]. The species of Cr mentioned above is related to its chemical form and is attributed to its bioavailability and toxicity. Cr has several oxidation states in the natural environment, the most common and stable of which in the environment and biosystem are Cr(III) and Cr(VI) [3].

Cr(III) is an essential trace element for human nutrition and has low toxicity [4]. It is easy to be hydrolyzed in aqueous solution, usually in the form of precipitates (i.e., Cr(OH)₃ and Cr₂O₃) in an alkaline or even in a weakly acidic environment, as shown in the Eh–pH diagram of Cr in solution (Figure 1) [5]. In contrast, Cr(VI) is soluble in water over a wide pH range, mainly in the form of hydrogen–chromate ion (HCrO₄[−]) under acidic conditions or in the form of chromate ion (CrO₄^{2−}) under neutral and alkaline conditions [6]. Therefore, the bioavailability of Cr(VI) is higher than that of Cr(III) since it is hard to be precipitated or adsorbed on soil colloids. Besides, Cr(VI) is also known as a strong oxidant and has a 400-fold higher toxicity than Cr(III) [7]. It is one of the 17 most dangerous toxic substances and a Class A carcinogen [8]. In addition, according to a document released by the United States Environmental Protection Agency [9], Cr(VI) is identified as the most important hazardous pollutant [10].

The Cr(VI) pollution in the soil is mainly caused by an unlawful leakage and illegal dumping of the chromium residue of industries. Once Cr(VI) enters the food chain

* **Corresponding author: Shaoyuan Bai**, Department of Environmental Engineering, College of Environmental Science and Engineering, Guilin University of Technology, Guilin, 541006, China, e-mail: baishaoyuan@163.com

Xilu Chen, Dandan Xu: Department of Environmental Engineering, College of Environmental Science and Engineering, Guilin University of Technology, Guilin, 541006, China

Xiaomin Li: Department of Environmental Engineering, School of Metallurgy and Environment, Central South University, Lushan South Road 932, Changsha 410083, China

Weichun Yang: Department of Environmental Engineering, School of Metallurgy and Environment, Central South University, Lushan South Road 932, Changsha Hunan 410083, China; Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Lushan South Road 932, Changsha Hunan 410083, China

Figure 1: Eh-pH diagram of Cr in the solution [3].

through plants [11], it will be detrimental to the ecological environment, and eventually, pose a potential threat to the health of human and other living organisms, due to its mutagenicity, teratogenicity [6], and carcinogenicity [12]. Therefore, how to eliminate the Cr(vi) pollution in the soil has become a high-profile issue [13].

Several approaches have been exploited to remediate Cr(vi) contamination and they can be divided into *in situ* remediation and *ex situ* remediation. *Ex situ* remediation refers to the excavation and treatment of the polluted soil at the contaminated site [14]. *Ex situ* remediation, however, will significantly increase the transportation cost, and there is also a risk of pollutant diffusion during transportation and transfer. Technologies for *in situ* remediation [15], such as phytoremediation, bacterial remediation, chemical flushing, and chemical reduction [16], are more promising because of the lower cost and higher efficiency [17]. Moreover, soil disturbance can be minimized, which is better for the subsequent application of soil. Nevertheless, these *in situ* technologies [18] inevitably have shortcomings, such as long remediation period, difficult operation, unstable effects, and secondary pollution [19], which will limit their practical applications. Because the bioavailability and toxicity of Cr depend on its chemical form, the reduction of Cr(vi) to Cr(III) is an important process for Cr(vi)-contaminated soil remediation, as shown in the following reaction [5].

Experiments have proved that Cr(vi) can be reduced to Cr(III) by the common wood preservative solution of chromate copper arsenate and three soil types (sandy soil, organic soil, and clayey soil) [20]. In addition, adding calcium polysulfide [21] or acidified hydrazine hydrate [13]

can also reduce the content of hexavalent chromium in soil. Nevertheless, these materials are still not the most ideal due to various defects.

Nowadays, nanotechnology and nanomaterials have showed great potential to solve the water, air, and soil pollution problems [22,23]. In recent years, the application of nanoscale zero-valent iron (nZVI) in the *in situ* remediation of Cr(vi)-contaminated soil has attracted extensive attention [24]. nZVI is a kind of material, which is generally in powder form, and its particle size generally lies within the range of 10–100 nm [25]. The original nZVI was prepared by reducing iron [26] with NaBH_4 , and in the laboratory [27], the original nZVI was synthesized by reducing FeCl_3 with NaBH_4 . Furthermore, the production of nanocomposites with controllable shapes, sizes, and surface properties is important for different practical applications [28]. nZVI is a promising *in situ* remediation material [29] with a flexible particle size, a large specific surface area [30], fast reaction speed, a strong reduction ability, and an ideal cost-effectiveness [31]. Moreover, nZVI can effectively overcome the shortcomings of *in situ* remediation, such as long repair cycle and unstable effect. Therefore, it is an ideal repair material and has been widely applied to the *in situ* remediation of heavy metal pollutants as a reaction medium [32]. Nevertheless, the current research works on the treatment of Cr(vi) by nZVI are mainly concentrated in the water field, and there has been little progress in research works in the soil field in recent years.

In this paper, applications of nZVI in Cr(vi)-contaminated soil remediation are comprehensively introduced. First, the synthesis and properties of nZVI are briefly introduced. Moreover, some typical methods for nZVI application in Cr(vi)-polluted soil remediation and their influencing factors are summarized and evaluated. Furthermore, the basic remediation mechanisms of nZVI application in Cr(vi)-contaminated soil are explored. Finally, some suggestions for potential remediation technologies are proposed.

2 nZVI for the remediation of Cr(vi)-contaminated soil

2.1 Preparation and properties of nZVI

Nowadays, nanomaterials are widely applied in pollution control. Extensive studies have been carried out on nanomaterials, especially the correlation between the

properties of nanomaterials and their chemical or physical properties [33]. In the past decade, nZVI has been used for the treatment of various common environmental pollutants existing in contaminated soil [34], groundwater and wastewater [35], such as chlorinated organic solvents, polychlorinated biphenyls, organochlorine pesticides [36], and heavy metal inorganic anions [37]. Due to its large surface area [38], fast reaction speed, and a strong reduction ability, nZVI can be used as the reaction medium of Cr(vi), with prospects of wide application [39].

There are many methods for preparing nZVI. Physical methods, such as grinding, abrasion, and lithography, were initially used. Currently, homogeneous solution or gas nucleation, and phase separation or high-temperature annealing are also widely used [40].

In addition to the physical methods described above, the most commonly used method to obtain nZVI is chemical reduction for its simplicity. The product obtained by this method is characterized by the uniform structure and high reaction activity. For example, sodium borohydride (NaBH_4) is used as the reducing agent [41], and nZVI is obtained by the following reaction [42]:

Besides, there are still some less commonly used methods, such as precision grinding, carbothermal reduction, ultrasonic-assisted production, electrochemical generation, and green synthesis, whereas due to their advantages, they may become popular in the future [42].

2.2 Classification and features of different modified nZVIs

In the application of nZVI, the surface quality and structure of nZVI undoubtedly play a key role in its function [43]. However, pristine nZVI is thermodynamically unstable due to its small size, large surface energy, and surface curvature [44]. nZVI particles tend to aggregate and react quickly with non-target compounds in the surrounding media, which may reduce the activity and stability of nZVI. Each particle has a magnetic field. So, it produces a magnetic field and the particles get stuck in an agglomerated form. Therefore, some nZVI-based materials have been fabricated to remove the pollutants from the environment [25]. The common modified nZVI morphologies are shown in Figure 2(a). nZVI can be

divided into organic modified nZVI, bimetallic modified nZVI, and materials loaded on modified nZVI.

2.2.1 Organic modified nZVI

The interaction of organic matter with nano-iron can reduce the gravity of nano-iron particles, prevent the agglomeration of nano-iron particles, and improve the dispersion performance [45].

2.2.1.1 Carboxymethyl cellulose (CMC)-supported nZVI

Figure 2(b) shows the TEM image of CMC-nZVI. Among the modified materials of nZVI, CMC is inexpensive and environment-friendly. The use of CMC-stabilized nZVI can improve the fluidity and diffusion of nanoscale zero-valent iron particles; thus, CMC-stabilized nZVI is especially suitable for *in situ* remediation of chromium-contaminated soil [46,47].

The CMC-stabilized nZVI is prepared by the sodium borohydride reduction method from steel pickling wastewater. The specific synthesis steps are as follows: first, CMC is dissolved in deionized water, the diluted waste liquid is sucked out by purging with purified nitrogen, and then the environment is kept as anaerobic. Finally, the sodium borohydride solution is added dropwise during violent mixing of the mixture to obtain the stable CMC-stabilized nZVI [48].

Some studies have observed the TEM images of CMC-nZVI [49]. It is found that the size of CMC-nZVI is large, and the particle size is generally distributed between 80 and 120 nm. The particles are not in chain structure, but are more evenly distributed. This shows that the CMC can effectively prevent the aggregation of nZVI nanoparticles [46].

2.2.1.2 Vinegar residue (VR) supported nZVI

Vinegar residue is composed of by-products and additives (rice bran, bran, and sorghum husk) produced by vinegar fermentation. According to the study of Pei *et al.* [32], VR is rich in such organic acids as acetic acid, malic acid, lactic acid, and tartaric acid. Figure 2(c) shows the SEM image of VR-nZVI.

The nZVI supported on a VR (nZVI@VR) is prepared in the following steps. First, ferrous sulfate and VR are stirred in rotating magnetic field at room temperature, and then the potassium borohydride (KBH_4) solution is added slowly

Figure 2: TEM image of nZVI. (a) [46]; TEM image of CMC-nZVI (b) [46]; SEM image of VR-nZVI (c) [32]; TEM images of Fe⁰-Cu (d) [56].

while stirring. Subsequently, nZVI@VR samples are separated from the mixture by vacuum filtration and finally dried in vacuum. It should be noted that in order to ensure that the nZVI@VR sample is not oxidized, nitrogen should be injected continuously during the process [32].

The feasibility of loading nZVI on VR composite to eliminate Cr(VI) in soil is tested by the settlement experiment. The results show that loading nZVI on VR could avoid aggregation and maintain the reactivity of particles. Furthermore, VR has a positive impact on soil properties and thus can be employed to improve soil pollution properties [32].

2.2.1.3 Rice husk-derived biochar-supported nZVI

It is a simple and economical one-step reduction method to directly use waste rice husk as the carrier of iron salt and the

source of reducing agent. Using the polarity and hydrophilicity of carbon materials can reduce the energy consumption and reduce the adverse effects of biochar recarbonization [50], so that the waste rice husk can be fully reused.

The production process can be summarized as follows. First, nitrogen is introduced as the protective gas in the production process, then the rice husk is mixed with Fe₂(SO₄)₃ solution under specific pressure. The excess iron salt is filtered and washed out under vacuum after vibration, and finally the target sample is obtained [39].

2.2.1.4 Other organics-supported nZVI

In addition, chitosan [51] can form nanocomposites with other materials through electrostatic interaction [52], covalent crosslinking, macromolecular compounding, adsorption,

and hydrogen bonding. Sucrose, vegetable oil, green tea, biochar [53], MCM-41 [54], and other extracts [55] can also be used as nZVI composite materials [21]. However, these materials were rare and less successful in treating $\text{Cr}(\text{VI})$, so they are not described in detail here.

2.2.2 Bimetallic modified nZVI

It has been proved that an additional metal material on the surface of nZVI can accelerate its reduction rate and effectively improve its performance [57]. The reaction activity of bimetallic particles is higher than that of nZVI [58]. Bimetallic modified nano-iron can delay the oxidation rate of nZVI and accelerate the reduction rate. There are many kinds of bimetallic modified materials [59], such as nano Ni/Fe bimetallic [60], nano Cu/Fe bimetallic [56], nano Pd/Fe bimetallic [61], nano Fe/Au bimetallic [62], and so on [63]. In this paper, the nano Cu/Fe bimetallic material nZVI/Cu is introduced. The TEM image of $\text{Fe}^0\text{-Cu}$ is shown in Figure 2(d).

nZVI/Cu is synthesized by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. At room temperature and under nitrogen gas condition, CuSO_4 is put into alcohol and stirred continuously. NaBH_4 is dissolved in deionized water. The mixture is added and stirred vigorously. After stirring, the black solid particles are obtained. Subsequently, they are pumped and filtered, then washed with deionized water and ethanol, and finally sent to the vacuum dryer for drying [64].

2.2.3 Materials loaded on modified nZVI

Bentonite is a nZVI-loading material. It is a kind of silicate with a sheet structure, is non-toxic, offers

environmental protection, and holds abundant reserves. When the bentonite is used as the support material of nZVI, a large amount of nZVI can be adsorbed on the surface of nZVI itself, which can promote the dispersion of nZVI particles and reduce their agglomeration. Thus, the final composite nZVI has a very good adsorption performance and improves the decontamination ability of nZVI [65]. Figure 3 shows the structure and morphology of nZVI@Bent's.

The study of Leupin *et al.* [65] introduces the preparation method. The specific steps are as follows. Under the protection of nitrogen, the solid with the mass ratio of Fe^{2+} to bentonite of 1:1 is weighed and added with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to the mixture of quantitative absolute ethanol and ultrapure water, and stirred. During continuous stirring, 2 mol/L of NaBH_4 solution is added into the mixture. Finally, the target sample is prepared by vacuum filtration, fast rinsing with absolute ethanol, and drying in vacuum drying oven (Table 1).

3 Remediation of $\text{Cr}(\text{VI})$ -contaminated soil by nZVI

In the process of remediation of $\text{Cr}(\text{VI})$ -contaminated soil by nZVI, in order to prevent iron agglomeration as well as to improve the remediation efficiency of nZVI, modified materials are generally used to stabilize nZVI, including CMC-stabilized nZVI, nZVI@VR, and nZVI-RBC. Various tests were performed to evaluate the remediation effect of $\text{Cr}(\text{VI})$ -contaminated soil from different aspects. The $\text{Cr}(\text{VI})$ will adsorb on nZVI, through the surface pores and oxygen-containing functional

Figure 3: nZVI@Bent before reaction (a); nZVI@Bent after reaction (b) [66].

Table 1: Summary of modified nZVI

Modified nZVI	Short description	Synthesis methods	Advantages	Side effects	size
CMC-stabilized nZVI [46]	Sodium carboxymethyl cellulose (CMC)	Sodium borohydride reduction from steel pickling wastewater	Improve the fluidity and diffusion of nZVI particles	CMC-stabilized nZVI achieved a target remediation effect on Cr	80–120 nm
Vinegar residue supported nZVI [32]	By-products and additives produced by vinegar fermentation	Stirring mixture of ferrous sulfate, VR, and KBH_4 solution	Avoid agglomeration and keep the activity of particles	It takes a long time to be effective	400 nm
Rice husk-derived biochar-supported nZVI [39]	Waste rice husk	Mixed solution of rice husk and $\text{Fe}_2(\text{SO}_4)_3$	Reduce energy consumption and biochar recarbonization	The processes proceed slowly	100 nm
Bimetallic modified nZVI (nZVI/Cu) [56]	Nano Cu/Fe bimetal material	Mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, CuSO_4 , and NaBH_4	Speed up the reduction of nZVI	It is easy to form new heavy metal pollution	20–50 nm
Materials loaded on modified nZVI (Bentonite) [66]	Silicate with a lamellar structure	Mixture of bentonite and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Promoting the dispersion of nZVI particles	The effect of reaction temperature is great	100 nm

groups, and then react directly with the surface to reduce to Cr(III) , whereas nZVI is oxidized to Fe^{2+} and indirectly reduced with Cr(VI) [66]. For example, toxicity characteristic leaching procedure is used to examine the leaching ability of Cr, and the immobilization and bioaccumulation of Cr in the improved soil are discussed through *in vitro* and plant experiments [67].

3.1 Remediation of Cr(VI) -contaminated soil by CMC-stabilized nZVI

In vitro and plant experiments show that the application of CMC–nZVI to remove Cr(VI) from contaminated soil can significantly enhance the immobilization of Cr by converting Cr(VI) to Cr(III) [15], thereby reducing its bioavailability, leaching ability, and plant bioaccumulation, and finally realize the remediation of Cr(VI) -contaminated soil [46].

As suggested by Zhang et al. [46], the speciation of Cr in soil changes from relatively high availability (exchangeable) to relatively lower availability (carbonate binding and iron manganese oxide binding). The results show that Cr(OH)_3 or Cr(III)/Fe(III) hydroxides are the main forms of Cr(OH)_3 or Cr(III)/Fe(III) hydroxides [68]. After the application of modified nZVI, Cr(VI) are adsorbed and fixed by soil particles, so that the remediation of Cr(VI) -contaminated soil is achieved.

The effects of biochar addition on CMC–nZVI and CMC–nZVI alone are compared. The results show that the conversion efficiency of Cr(VI) declines slightly, whereas the immobilization efficiency of total chromium increases. This is because biochar can adsorb a small amount of CMC–nZVI, which leads to a decrease in the effective contact area between nZVI and Cr, thereby further reducing the conversion efficiency of Cr(VI) . However, the reduction reaction after adding biochar [69] prolongs the total remediation time and increases the immobilization efficiency of total chromium [70].

CMC–nZVI has a significant effect on the remediation of Cr(VI) -contaminated soil. nZVI modified by CMC and addition of biochar into CMC–nZVI can realize the remediation of Cr(VI) -contaminated soil, and also greatly reduce the leaching of Cr in a contaminated soil by more than 95%. Finally, the experimental results of Zhang et al. [46] show that when the content of Cr(VI) in soil is 800 mg/kg (w/W), the optimal dosage of CMC–nZVI/BC for remediation of Cr(VI) -contaminated soil is 11 g/kg.

3.2 Remediation of Cr(vi)-contaminated soil by vinegar residue supported nZVI

The specific process of Cr(vi) immobilization by nZVI with VR (nZVI@VR) as support material is as follows. First, highly toxic Cr(vi) is adsorbed on the surface of nZVI@VR through the surface pores and oxygen-containing functional groups, such as C–O, COO[–], or –OH. Then the content of Cr(vi) is reduced by the zero-valent iron. Finally, (Cr_xFe_{1–x})(OH)₃ and Cr_xFe_{1–x}OOH are precipitated [71].

In the practical application of nZVI@VR, if the nZVI@VR powder is used as an improver, it is not easy to pack and will be blown away by the wind, which will negatively impact the health of people without a cover. Therefore, nZVI@VR powder needs to be transformed into a nZVI@VR particle.

The specific transformation process can be summarized as follows. nZVI@VR and attapulgite are mixed and water is added in proportion. The mixture is stirred until it is completely homogeneous. nZVI@VR particles are produced by a granulator at room temperature and air-dried at 50°C.

After granulation, the granular nZVI@VR is used for remediation, and it is found that the conversion rate of the available Cr to low-availability components is accelerated, significantly reducing the bioavailability of Cr.

The results of Pei *et al.* [27] show that the fixation efficiency of nZVI@VR without granulation is 98.68%. When the content of Cr(vi) in soil is 198.20 mg/kg, the best dosage of nZVI@VR is 50 g/kg, i.e., 5%.

3.3 Remediation of Cr(vi)-contaminated soil by rice husk-derived biochar-supported nZVI

In recent years, biochar has also been used as the carrier of nZVI for the reuse of waste biomass.

In order to remediate Cr(vi)-contaminated soil, waste rice husk is used as an iron carrier and reductant [39]. When the main form of Cr in contaminated soil is acid soluble, it is found that during the reduction of Cr(vi) by nZVI–RBC, the redox products of Fe and Cr form, and the residual Cr in soil accounts for 47.5%, 24.6%, and 27.9%, respectively. Cr in soil is transformed into a low-bioavailability form, and the leaching of Cr is greatly inhibited. nZVI–RBC has long-term remediation ability to Cr(vi)-contaminated soil.

The final experimental results show that when the concentration of Cr(vi) in the leachate is 62.4 mg/L and the dosages of modified nZVI are 8% and 12%,

respectively, in which case, the best remediation effect of Cr(vi)-contaminated soil can be achieved. Under these two dosages, nZVI–RBC could completely remove Cr(vi) in 120 and 30 min, respectively, and no Cr(vi) can be detected in the soil leachate for 6 consecutive days.

3.4 Remediation of Cr(vi)-contaminated soil by bimetallic-modified nZVI

Copper–iron bimetallic particles can be formed by coating copper on the surface of nZVI. The study showed that compared with other oxidation pollutants, nZVI needs a higher copper content to remove Cr(vi). Under acidic conditions, Cr(vi) is further reduced by Fe²⁺ and Cu⁰ formed in the reaction of nZVI/Cu and Cr(vi). The deposition of iron oxide on the surface of the material can be effectively inhibited, and the active sites on the surface of nZVI/Cu can be exposed, and finally the reduction reaction of Cr(vi) is promoted.

The results show that when the contaminated soil contains 120 mg/kg Cr(vi), the Cr(vi) reduction exceeded 99% at a pH of 5, temperature of 303 K, and nZVI/Cu dose of 0.06 g [64].

3.5 Remediation of Cr(vi)-contaminated soil by bentonite-supported nZVI

In the process of remediation of Cr(vi)-contaminated soil by nZVI@Bent [32], Cr(vi) will adsorb on nZVI and react directly with the surface containing nZVI to be reduced to Cr(III), while nZVI is oxidized to Fe²⁺ and indirectly reduced with Cr(vi) [72].

The experimental results of Leupin *et al.* [65] show that when the ratio of iron to bentonite is 1:0.5 and the dosage is 5 g/L, the removal rate of Cr(vi) in the soil suspension is the highest, which is the best reaction condition for removing Cr(vi) (Table 2).

4 Factors affecting the remediation of Cr(vi)-contaminated soil by nZVI

In the application of nZVI, there are many factors which will affect the removal effect, including the initial pH

Table 2: Remediation of Cr(vi)-contaminated soil by nZVI

nZVI	Remediation process	Content of Cr(vi) in soil	Optimum dosage of modified nZVI	Advantages
CMC-stabilized nZVI [46]	Carbonate binding and iron manganese oxide binding	800 mg/kg (w/w)	11 g/kg	Enhancing the immobilization of Cr by converting Cr(vi) to Cr(III), reducing plant bioaccumulation
Vinegar residue supported nZVI [32]	nZVI@VR reduces the content of Cr(vi) through surface pores and oxygen-containing functional groups	198.20 mg/kg	50 g/kg	Reducing the bioavailability of Cr
Rice husk-derived biochar-supported nZVI [39]	Formation of redox products of Fe and Cr	62.4 mg/L	8–12%	Long-term remediation ability to Cr(vi)-contaminated soil
Bimetallic modified nZVI (nZVI/Cu) [64]	Cr (vi) is reduced by Fe ²⁺ and Cu ⁰	120 mg/kg	0.06 g	Inhibiting the deposition of iron oxide on the surface of the material.
Bentonite-supported nZVI [66]	nZVI is oxidized to Fe ²⁺ and indirectly reduced with Cr(vi)	The ratio of iron to bentonite is 1:0.5	5 g/L	Avoiding secondary iron pollution, acidification of paddy fields, and high removal cost

value, temperature, nZVI dosage, the chemical composition of surrounding organic matter, etc. [73].

4.1 Effect of the initial pH value

It is found that the initial pH value has a significant impact on the removal rate of Cr(vi) in soil, no matter what kind of nZVI is wrapped by modified materials [74]. More specifically, the pH value and the Cr(vi) removal rate show a negative correlation [75], that is, with the rising pH value, the Cr(vi) removal rate declines [76].

In the experiment of remediating Cr(vi)-contaminated soil with nZVI and copper bimetallic particles, it is found that the Cr(vi) removal rate is much higher at pH 5 than at pH 7 or 9, and the reduction rate could reach 99.9% within 5 min. Due to the release of Fe²⁺ under acidic conditions, the deposition of iron oxide on the material's surface is well inhibited, the active sites on the surface of nZVI/Cu are exposed, and the reduction rate of Cr(vi) is accelerated [77]. In an alkaline condition, however, owing to the precipitation of nZVI/Cu, a passivation layer is easily formed on the surface of nZVI/Cu, which hinders the contact between nZVI/Cu and Cr(vi), and meanwhile affects the formation of the codeposition of ferrochromium, thereby lowering the reduction rate [64].

The reason is due to the fact that the acidic environment will corrode the oxide layer of Fe₂O₃ and FeOOH attached to the surface of nZVI@Bent, thereby exposing more reaction sites. A large amount of free H⁺ in the soil suspension promotes the reaction direction of nZVI removal, and the removal efficiency of Cr(vi) in soil is improved. Nevertheless, the contact between nZVI@Bent and Cr(vi) in an alkaline environment is reversed [65].

To sum up, the conclusion can be drawn that the soil is acidic, which is conducive to remediating Cr(vi)-contaminated soil [78].

4.2 Effect of the reaction temperature

As a key factor, temperature has a profound influence on the Cr(vi) removal rate and chemical reaction rate [20]. It is found that the temperature and Cr(vi) removal rate are in a positive correlation, that is, the Cr(vi) removal rate increases with the rising temperature.

After describing the reaction by the Langmuir–Hinshelwood first-order kinetic model or half-life, it can be concluded that the activation of reactant molecules increases as the temperature rises. That is, the reaction rate constant increases with the rising temperature. Some studies have confirmed that the concentration of Cr(VI) in soil should be reduced to the same concentration (2 mg/L), and it should be used for 30 min at 298 K and 10 min at 303 K. When the temperature is above 303 K, the Cr(VI) removal rate continues to increase slowly [64].

In the experiment of nZVI@Bent materials mentioned above, it is found that with the increasing reaction temperature, the removal rate of Cr(VI) in soil solution by nZVI@Bent presents an ascending trend. The specific reason is that after the temperature rises, the energy in the reaction system increases correspondingly; thus, the number of reaction molecules increases and the reaction rate accelerates [66].

To sum up, with the increase of reaction temperature, the reaction will advance backward, which is conducive to accelerating the remediation of Cr(VI)-contaminated soil [64,79].

4.3 Effect of other factors

In addition to pH and temperature, there are many other factors that affect the Cr(VI) removal rate [80]. For example, the dosage of nZVI [81], the contact time between nZVI and soil environment, the concentration of nZVI, the initial concentration of Cr(VI), and the chemical composition of surrounding organic matter, heavy metal, ion species, and other media will impact the reaction rate [82].

The results show that when the amount of nZVI increases, the active molecules will increase as well [26], and a large amount of Cr(VI) will adhere to the nZVI particles, resulting in a higher reaction rate [83].

In addition, the concentration of Cr(VI) is inversely proportional to the removal rate of Cr(VI). Under high Cr(VI) concentration, the immobilization efficiency of Cr(III) in the reduced soil liquid phase is low, and the surface area of nZVI is limited. In this case, there isn't enough position for excess Cr(III), which leads to the slow removal rate of Cr(VI) [66].

It should be pointed out that there are many factors affecting the Cr(VI) removal rate, and the combination of each factor is more complex than that of the current one, which needs to be analyzed in detail [65].

5 Interaction mechanism between nZVI-based materials and Cr(VI)

In the treatment of Cr(VI)-contaminated soil, nZVI-based materials have been widely studied and show great potential and broad application, as mentioned above.

The methods and applications of various modified nZVIs for the remediation of Cr(VI)-contaminated soil have been introduced. According to these introductions, many researchers have speculated and verified the mechanism, but the systematic summaries are few. The mechanisms of these methods can be divided into adsorption mechanism and reduction mechanism.

5.1 Reduction mechanism

In fact, the major removal mechanism of nZVI on Cr(VI) in soil is reduction [84]. It is found that the removal of heavy metal ions is generally attributed to the reduction process when nZVI is used as the repair material [85]. The reduction of Cr(VI) by zero-valent iron is a multistep process, in which the zero-valent iron acts as an electron donor of heavy metal ions [86].

According to the theme of this paper, the process of Cr(VI) reduction in soil can be classified into direct reduction and indirect reduction. The final products from reduction are Cr(OH)₃ and Fe(III)–Cr(III) complexes [66].

First, in the process of direct reduction, Cr(VI) in soil adsorbs on the curved surface of nZVI and reacts directly with the surface containing nZVI to form Cr(III) [87]; second, in the indirect reduction process, nZVI will be oxidized to Fe²⁺ first [88], and to Fe³⁺ subsequently [89], both with the reduction from Cr(VI) to Cr(III). Cr(III) will combine with OH[−] and Fe³⁺, to form Cr(OH)₃ and Fe(III)–Cr(III) complexes [66].

In addition, when Cr(VI) is present in the curved particle system and soil suspension, the reduction process is stronger than the adsorption process. In the process of Cr(VI) reduction, most of the Cr(VI) will be removed, accordingly, the residual Cr(VI) in soil will be reduced [90].

The specific reaction is as follows [91]. (1) Cr(VI) was adsorbed on the surface of nZVI through surface pores and oxygen-containing functional groups. (2) Cr(VI) in soil was reduced by FeO (equations (3)–(5)). (3) Precipitation of (Cr_xFe_{1-x})(OH)₃ and Cr_xFe_{1-x}OOH (equations (6) and (7)):

On the other hand, zero-valent iron and Cr(vi) can also carry out charge transfer through biochar to maintain the redox reaction, but the difference is that in this process, the removal rate of hexavalent chromium in soil is relatively low [39].

5.2 Adsorption mechanism

Compared with other methods, adsorption method is simple and efficient, thus it is the most commonly used technology for organic pollutants' removal [92]. Due to the rich oxygen-containing functional groups on the surface of various adsorbents [93], adsorption technology is considered to be a typical reaction process for removing Cr(vi) and other heavy metal ions [94]. The adsorption performance of adsorbents depends on the morphology and structure of porous materials, such as specific surface area, pore volume, pore distribution, and special pore surface chemistry [92]. The main principle of adsorption is related to the large specific surface area of nZVI and adsorption sites on its surface [95]. It has been proved that nZVI-based materials physically [96] contain a large number of active sites or functional groups [97].

Based on the analysis of the results and material characterization of the removal of Cr(vi) by nZVI (nZVI-RBC) supported by biochar, the reaction mechanism can be inferred as follows: on the surface of biochar, when CrO_4^{2-} diffuses to the surface of nZVI-RBC in the reaction system, some ions unite with the function and react with nZVI [98], CrO_4^{2-} . On the one hand, the electrons provided by the zero-valent iron can be directly obtained and will be oxidized into ferrous iron and trivalent iron. At this time, CrO_4^{2-} combined with

functional groups will be gradually reduced to trivalent chromium, so the concentration of Cr(vi) in soil will be rapidly reduced [39].

In addition, part of biochar as modified material will be dissolved to form dissolved organic carbon, and part of Cr(vi) will be reduced to Cr(III). The dissolution of biochar also results in the lack of coating materials for nZVI; thus, nZVI is gradually exposed to the reaction system and could directly participate in the reduction of Cr(vi). Despite the fact that these processes are much slower than other processes, they are still a continuous and effective way to remediate Cr(vi)-contaminated soil [30].

In fact, the position of nZVI reaction surface may be the corrosion products of stable or metastable iron (II), mixed iron (II)/(III), or iron (III) oxide, hydroxide, or hydroxide. These iron hydroxide and oxide could enhance their adsorption capacity under natural environment [39].

During adsorption, the Cr(vi) in the soil can be directly adsorbed by nZVI, and the $\text{Cr}(\text{OH})_3$ and Fe (III)–Cr(III) complexes produced in the reduction process described later will also be adsorbed by nZVI. Through the above process, Cr(vi) pollution in the soil will be further reduced [66].

After the synthesis of microcrystalline cellulose (MCC) immobilized nZVI (c-nZVI), the reductive adsorption of Cr(vi) on MCC is studied. nZVI adsorbs Cr(vi) to Fe (III) by zero-valent iron redox. Fe(III) is reduced and regenerated to zero-valent iron by the *in situ* oxidation of cellulose to cellulose dialdehyde [99].

5.3 Other interaction mechanism

More occasionally, van der Waals force, magnetic force, specific surface bonding, and electrostatic interaction control the main mechanism in some natural environmental reaction systems [100].

In addition, the coprecipitation theory can also support the remediation mechanism of Cr(vi)-contaminated soil by nZVI or nZVI-modified materials. When Fe^{2+} reduces Cr(vi) in the soil suspension to Cr(III), Cr(III) can combine with OH^- in the soil suspension to form $\text{Cr}(\text{OH})_3$, while Fe^{2+} is oxidized to Fe^{3+} , and Fe^{3+} combines with free OH^- to form $\text{Fe}(\text{OH})_3$. Finally, both of them combine with Cr(III) in the soil suspension to form a Fe(III)–Cr(III) complex to remediate Cr(vi)-contaminated soil [101].

6 Future prospective and conclusions

In the practical application of nZVI to repair Cr(VI), in addition to its advantages, there are some disadvantages as well. Pure nZVI is easy to agglomerate and passivate. Besides, it has poor transport capacity and can reduce electron transfer, which will weaken its remediation effect [46]. Although the modified nZVI can avoid some of the above problems, it also gives rise to some other new problems. For example, it may inhibit the reaction between nZVI and target pollutants or cause other new environmental pollution problems. Many modified materials can be prepared only under extremely strict conditions. Some of them are easy to oxidize and difficult to preserve, and the reduction selectivity of the nanoscale zero-valent iron is poor. For example, the use of sulfidation [88]-modified materials may induce corrosion of the nZVI core and increase the particle size. The application of bimetallic particles [64] as modified materials is also likely to increase corrosion, reduce the service life of nZVI, and even introduce other heavy metals, resulting in a serious environmental pollution. If borohydride is used as a common reducing agent, the cost of wet synthesis method is too high to be used on a large scale and may cause secondary pollution [32]. These are the problems that need to be addressed at present or they will hinder the further development of nZVI to a certain extent [102].

In order to make the nZVI system fully competitive, major improvements and upgrades should be carried out. First of all, the reaction between nZVI and soil pollutants is very complex [103], and its remediation efficiency needs improvement [104]. Therefore, the research work on its reaction mechanism, such as the possible properties of soil itself [105], the potential impact of nZVI on soil pollutants [106], and the influence of combined application of nZVI and biotechnology on soil remediation, should be further studied.

Second, although nZVI has been widely used, its preparation method is too complex and time-consuming, so the cost is high. Thus, in order to prepare nZVI on a large scale, it is necessary to explore new preparation methods to obtain nZVI with higher quality and performance at the lowest cost [107]. Future research works must seek to establish a sound evidence system, on which one can accurately predict the liquidity, responsiveness, fate, and ecological impact of nZVI [35].

In addition, due to the complexity and variability of the natural environment [108], most application sites of

nZVI are carried out only on the laboratory scale, and field applications are lacking. Furthermore, other models are needed to detect the potential risks of nZVI to plants and microorganisms [29] in the soil during pollutant remediation [109–112].

However, in general, nZVI is a very promising and widely used reductant, which can also be used in any other heavy metal remediation. The mechanism of nZVI repair is not only limited to reduction mechanism and adsorption mechanism, but also to oxidation mechanism. The oxidation mechanism is realized by the Fenton reaction, forming various derivatives of iron, oxidizing various target pollutants, and finally realizing the separation of heavy metal ions.

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