

Reductive Remediation of Cr(VI)-Contaminated Soils in the Presence of Zero-Valent Metals and Bimetals

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ABSTRACT: *The time-dependent efficiency of Zero-Valent Metals (ZVMs) including Al^0 and Zn^0 and their bimetals (Fe/Al and Fe/Zn, 0.1 g shell metal/g core metal) to reduce Cr(VI) in three contaminated soils (calcareous, non-calcareous near neutral and slightly acidic) was studied. The Cr(VI)-contaminated soils (100 and 500 mg/kg) were amended with the reductants (0, 5, and 10 g/kg) and the concentration of exchangeable Cr(VI) was determined after 0.5, 4, 24, 48 and 168 hours. It was found that the average reducing capacity of the bimetallic particles (11.4 mg Cr/g) was much higher than the ZVMs (3.3 mg Cr/g). The ZVMs showed rapid passivation within only a few minutes, while the bimetallic particles preserved their reactivity even up to one hour. In addition, the efficiency of ZVMs in the slightly acid soil was much higher than in two other soils. There was a good performance of Fe/Al in the calcareous soil with a higher hazard potential than the two other soils. The Cr(VI) reduction capacity of the bimetallic particles in non-calcareous near-neutral soil was two times more than in calcareous soil. The pseudo-first-order Cr(VI) reduction rate constant for the bimetals (0.248 h^{-1}) was on average higher than those of the ZVMs (0.074 h^{-1}).*

KEYWORDS: *Bimetallic particles; Cr(VI) reduction; Cr(VI)-contaminated soil; Zero-valent metal.*

INTRODUCTION

A combination of surface adsorption and reduction may be currently the best strategy to clean up Cr(VI)-contaminated environments [1]. Some Zero-Valent Metals (ZVMs) have a high electron-donating tendency to various contaminants, including Cr(VI). Most of the Cr(VI) reduction studies have focused on zero-valent iron (ZVI), because it is expected to be more cost-effective [2] and less environmentally disruptive [3]. However, ZVI has some disadvantages such as a relatively high dose of application

and long reaction time [4]. Likewise, the Cr(VI) reduction by ZVI is a self-inhibiting reaction due to the formation of Fe(III)-Cr(III) oxy/hydroxide thin layer on ZVI surface. The insulating nature of the layers hinders electron transfer from the ZVI to the surface, thereby stopping the redox reaction [5]. Furthermore, the efficiency of Cr(VI) reduction is low under alkaline conditions. This is because of proton consuming nature of the reaction [6] and the fact that the pH may be high enough to maintain durable

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passive film [7], but simultaneously alkaline pH enhances the Cr(III) co-precipitation in the form of insoluble oxy/hydroxides [8]. Apart from the deteriorated nature, ZVIs provided from different sources may have different reactivities [9]. For example, the Cr(VI)-removal efficiency of laboratory reagent grade microscale ZVI in our results was only 6.9% [10]. Utilization of other ZVMs with lower standard reduction potential (E^0) than ZVI ($E^0 = -0.44$ V) exhibits good prospects to be an alternative way for Cr(VI) decontamination. ZVMs like Al ($E^0 = -1.66$ V), Zn ($E^0 = -0.76$ V) and Mg ($E^0 = -2.37$ V) appear strong reductants to be easily oxidized by some environmental contaminants including chlorinated organic compounds [11], perchlorate [12], chromate [13] and nitrate [4].

When Cr(VI) comes in contact with ZVMs under favorable conditions, Cr(VI) reduces to Cr(III). This reaction is linked to the reaction of ZVMs oxidation. Eventually, Cr(III) is released into the solution and precipitated as hydroxides covering the surface of the soil at $\text{pH} > 5.5$ [14]. With respect to this, the ZVMs like Al^0 and Zn^0 can be easily oxidized by oxygen in the air to create an oxide layer (passivation layer) on the surface which inhibits their reactivity [15]. Acid-washing of ZVMs and deposition of secondary metals on ZVM surfaces are the methods commonly used to overcome this problem [16]. Coating of the primary metal surface with a second catalytic metal such as Pd, Cu, and Ni which are nobler than the primary metal has been reported in some studies [17]. However, because of the toxic behavior of noble metals, some investigators have preferred to use another type of bimetallic particle in which a metal with a high thermodynamic driving force (e.g. Al or Zn) is coated with iron. In these bimetallic systems, electron transfer from core to shell facilitates the removal performance [18].

Most research on Cr(VI) decontamination has been focused on aqueous solutions and there are few attempts to deal with the Cr(VI) contaminated soils [19, 20]. ZVMs and bimetals are much less toxic than mobile chromate and may be potential amendment candidates to alleviate the migration of Cr(VI) in these soils. However, failure of low ZVI dosages for efficient Cr(VI) removal has recently been demonstrated [21]. For this, it is required to test some other metals as well as bimetals with lower E^0 values that may guarantee an efficient Cr(VI) removal from contaminated soils. In this research, first, two ZVMs (Al^0 and Zn^0) and two bimetals from both groups (Fe/Al and

Fe/Zn) were used for reducing Cr(VI) in an aqueous solution. Then, a time-dependent experiment was conducted to investigate the efficiency of these reductants to reduce Cr(VI) in three Cr(VI)-contaminated soils.

EXPERIMENTAL SECTION

Materials and chemicals

Zero-valent aluminum (Al^0) with particle size less than $70 \mu\text{m}$ (Art. no. 1056, $\geq 99\%$ purity) and zero-valent zinc (Zn^0) with particle size less than $45 \mu\text{m}$ (Art. no. 108789, $\geq 95\%$ purity) were obtained from Merck company. Other reagents with analytical grade or better were purchased from Merck Company.

Acid pretreatment of zero-valent metals (ZVMs)

Acid-washed Al^0 and Zn^0 were used in all the experiments. For the preparation of activated Al^0 , 13 mL of concentrated HCl was added to 5.0 g Al^0 powder soaked in about 10 mL of deionized water. The suspension was mixed thoroughly by a stirrer until the fume evolution was detected. Thereafter, a small amount of deionized water was added and the acid-washed Al^0 was filtered and then rinsed successively with 500 mL of deionized water. Finally, the pretreated Al^0 was dried under a stream of N_2 for 2 hours and immediately used [12]. To prepare acid-washed Zn^0 , 2.0 g of Zn^0 was stirred in 5 mL 2% HCl for 1 min and then filtered. After that, the activated Zn^0 was washed with 5 mL of 2% HCl, 3 times with 5 mL of deionized water, twice with 5 mL of 95% ethanol, and once with 5 mL of absolute ether. Finally, it was dried under N_2 stream for 2 hours and immediately used [22].

Preparation and characterization of bimetallic particles (Fe/Al and Fe/Zn)

The bimetallic Fe/Al particles (0.1 g Fe/g Al) were prepared as follows [23]: 1- A 30 mL aqueous solution containing 1.30 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was immediately added to 2.70 g of the acid-washed Al^0 , 2- The suspension was mixed on a stirrer for 20 minutes, 3- The bimetallic Fe/Al particles were then consecutively rinsed with 1000 mL deionized water and 30 mL acetone and allowed to dry in a stream of N_2 for 2 hours. For the preparation of bimetallic Fe/Zn particles (0.1 g Fe/g Zn) the following procedure was used [24]: 1-A respective amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.70 g) was dissolved in 25 mL of absolute ethanol containing 2% HCl and then 5 g of the acid-washed zinc were added to it,

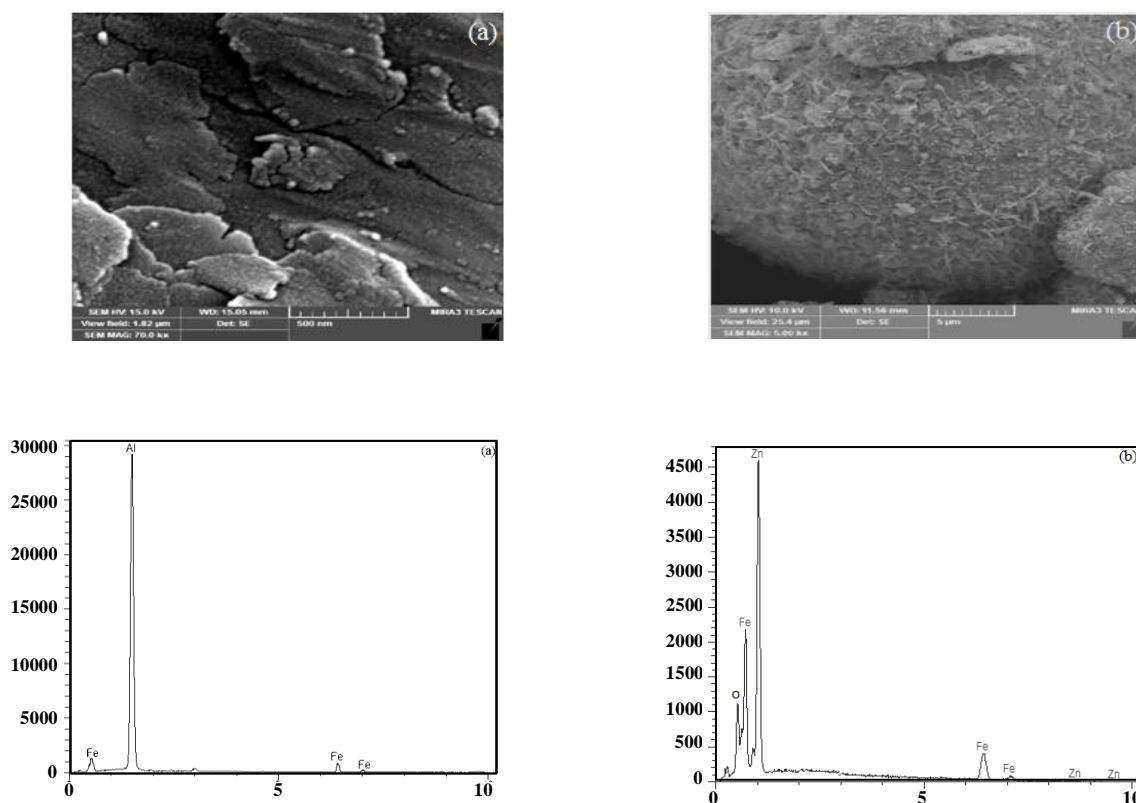


Fig. 1: SEM images and EDX spectra of bimetallic particles (0.1 g shell metal/g core metal) (a) Fe/Al, (b) Fe/Zn

2- The suspensions were shaken at 180 rpm for 20 min before being rinsed with deionized water and acetone,
 3- Finally, the prepared bimetals were dried by purging with N_2 gas for 2 hours.

The residual concentration of covering metals in each precursor solution was much less than the concentration of the stock solutions and could be considered negligible. Hence, assuming that all the covering metals were deposited onto the surface of the core metals, the content of the covering metals in the core metals will be 10% by weight [25]. Elemental and morphological analyses of two bimetallic particles were conducted using a Scanning Electron Microscope (SEM) (MIRA3 FEG-SEM, Tescan, Czech) with Energy-Dispersive X-ray (EDX) at 10 kV (for Fe/Zn) or 15 kV (for Fe/Al).

Characterization of the bimetallic particles

The Scanning Electron Microscopic (SEM) images of the bimetallic particles (Fe/Al and Fe/Zn) are present in Fig. 1. The micrograph of Fe/Al bimetallic particles

in Fig. 1 (a) shows particles with relatively smooth surfaces, but meanwhile, some bright knobs can be clearly seen on the surface of the aluminum core, which may be considered the deposition of an iron shell. By contrast, the Fe/Zn particles exhibited a dispersed spherical morphology with deposition of Fe onto the zinc surface which increases their total surface area (Fig. 1(b)). The content of metallic elements in the synthesized bimetallic particles was estimated by Energy Dispersion X-ray (EDX) procedure. The Energy Dispersion Spectrum (EDS) of the Fe/Al specimen is presented in Fig. 1(a). The EDS exhibits distinct peaks for Al and Fe indicating the presence of both elements. Additionally, in contrast to some reports in the literature [23] no oxygen peak was detected in the spectrum. The spectrum of Fe/Zn sample shows expected distinct peaks of the corresponding metals, but meanwhile, oxygen peaks (about 0.52 keV) were detected, which may be originated from the partial oxidation of the surface due to its exposure to the ambient atmosphere and diffusion of the molecular oxygen [26].

Table 1: Some properties of the studied soils.

Soil	pH _{1:1}	Easily reducible Mn (mg/kg)	Texture	CEC ¹ (cmol _c /kg)	OC ² (g/kg)	CCE ³ (g/kg)
1	8.15	207	Sandy clay loam	14.4	9.0	68
2	7.05	323	Loam	20.7	19.5	nil*
3	6.10	196	Silty loam	42.3	35.0	nil*

1: Cation exchange capacity, 2: Organic carbon, 3: Calcium carbonate equivalent

*The soils did not produce vigorous effervescence of CO₂ when treated with 0.1 N HCl.

Cr(VI) reduction in aqueous solutions by ZVMs and bimetallic particles

0.05 g of activated ZVMs or bimetallic particles (with a compositional ratio of 10%) were added to 50 ml of aqueous solutions containing 20.0 mg Cr(VI)/L and mixed at 120 rpm in a shaker incubator (25±0.5 °C) for 24 hours. After that, supernatants were harvested by centrifugation and filtration to analyze the final Cr(VI) concentration as described below. The Cr(VI) reduction efficiency, which is the percent ratio of (*initial [Cr(VI)] - final [Cr(VI)]*)×100/*initial [Cr(VI)]*, was calculated. No attempt was made to adjust pH.

The soils under investigation

Three different soils regarding pH values and organic carbon contents were taken from 0-20 cm depth of agricultural lands in the provinces of East Azerbaijan (soil 1, calcareous soil, Calcaric Cambisols) and Gilan (soils 2 and 3, non-calcareous near neutral and slightly acid soils, respectively, Haplic Luvisols) in northwest and north of Iran, respectively. The sampled soils were air-dried, ground, and homogenized to pass a 2-mm sieve. Particle size distribution [27], Field Capacity (FC) moisture content [28], electrical conductivity (EC) (1:1, w/v) [29], pH (1:1, w/v) [30], Organic Carbon (OC) content [31], Cation Exchange Capacity (CEC) [32], Calcium Carbonate Equivalent (CCE) [33] and easily reducible manganese [34] were determined in the soils. Exchangeable Cr(VI) in the soils was extracted using the method described by James and Bartlett [35], and then the Cr(VI) concentration was measured by the diphenyl carbazide method [36]. The absorbance was read at 540 nm on a spectrophotometer (HACH, DR 2000). None of the three soil samples had detectable exchangeable Cr(VI).

Some physical and chemical characteristics of the investigated soils are shown in Table 1. The soils differed in pH, CCE, and organic carbon. Soil 1 with less than 10 g/kg

organic carbon was alkaline (pH = 8.15) and calcareous (CCE = 68 g/kg), whereas soils 2 and 3 (both free of calcium carbonate) were near neutral (pH = 7.05) and slightly acidic (pH=6.1) and contained 19.5 and 35 g/kg organic carbon, respectively.

Spiking the soils with Cr(VI)

One kg of each of the three soils was contaminated with desired amounts of K₂CrO₄ to establish the levels of 100 and 500 mg Cr(VI)/kg (abbreviated as Cr₀). The volume of Cr(VI)-containing solutions added was adjusted to make FC condition. The soils were incubated and exposed to several cycles of wetting and drying at room temperature for one month. This was done to minimize self-attenuation of Cr(VI)-contaminated soils during the batch experiment. Complete reduction of Cr(VI) at the above levels occurred within the incubation period in soil 3 and hence, an excessive level of Cr(VI) (1000 mg Cr(VI)/kg) was added in order to maintain a residual amount of Cr(VI). Following that, the soils were mixed thoroughly to pass a 2 mm sieve and kept in plastic bags in the refrigerator at 4°C until use. Before batch experiments, the concentration of exchangeable Cr(VI) in the soils (*Cr_{exch.}*) was determined. Moreover, in order to find the maximum concentration of Cr(VI) in which complete reduction occurs, different initial concentrations of Cr(VI) were added to the soils.

Batch experiments

These experiments were performed in 250 mL Erlenmeyer flasks containing 45 mL of 0.03 M KCl (as background solution) and 5.0 g of the contaminated soils that were left to stand for 24 hours for equilibration [37]. This prevents the participation of different initial changes following wetting in the chemical reaction involved. Following this pre-equilibration, 0 (control), 5 and 10 g/kg of different reductants including Al⁰, Zn⁰, Fe/Al

(0.1 g Fe g⁻¹ Al) and Fe/Zn (0.1 g Fe g⁻¹ Zn) were added to the suspensions. All reductants were passed through a 325 mesh sieve before the experiment. The soil suspensions were agitated at 120 rpm for 0.5, 4, 24, 48, and 168 hours at 25±0.5°C. The flasks were opened once a day and the suspensions were thoroughly stirred to keep away from anaerobic conditions. After that, 5 mL of 1.6 M (0.8 M KH₂PO₄/0.8 M K₂HPO₄) buffer solution (pH=7.2) was added to the suspensions [35]. In a preliminary experiment, the desired concentration and volume of extraction phosphate buffer solution were achieved. The soil suspensions were agitated at 120 rpm for 2 hours. Finally, the supernatants were passed through a 0.45 µm filter paper (Whatman UK). Aliquots of the soil extracts were taken to measure Cr(VI) concentration as described above.

Calculations

The efficiency of Cr(VI) self-attenuation (R_s) that indicates the reducing ability of the soil itself was calculated as follows [38]:

$$R_s = \frac{C_{r_0} - C_{r_{exch.}}}{C_{r_0}} \times 100 \quad (1)$$

Where C_{r_0} is the concentration of added Cr(VI) to the soils (mg/kg) and $C_{r_{exch.}}$ is the concentration of exchangeable Cr(VI) (mg/kg) after incubation for one month.

The amendment-induced Cr(VI) reduction efficiency (R_a) that indicates the performance of reducing agents was computed with the following formula:

$$R_a = \frac{C_{r_{exch.}}^{control} - C_{r_{exch.}}^{amended}}{C_{r_{exch.}}^{control}} \times 100 \quad (2)$$

where, $C_{r_{exch.}}^{control}$ and $C_{r_{exch.}}^{amended}$ are the concentration of exchangeable Cr(VI) at zero and any specified level of the amendment at given times of batch experiment, respectively. Because of self-attenuation, the values of this efficiency were not calculated based on the initial concentration of Cr(VI).

The Cr(VI) reducing capacity (R_c) of metals or bimetal (mg/g) was calculated as follows [39]:

$$R_c = \frac{C_{r_{exch.}}^{control} - C_{r_{exch.}}^{amended}}{A} \quad (3)$$

Where A is the rate of added reducing agent (g/kg).

Finally, the pseudo-first-order equation was fitted to the data (R_a vs. time) by a nonlinear procedure using SPSS software, and values of the rate constants were obtained [40]:

$$R_a = R_{ae} (1 - e^{-kt}) \quad (4)$$

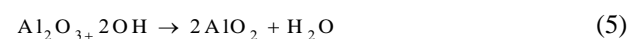
Where R_a and R_{ae} are the Cr(VI) reduction efficiency at a given time (t) and at the equilibrium, respectively and k is the rate constant (h⁻¹).

All experiments were conducted in duplicate and mean values with standard deviation error bars were reported.

RESULTS AND DISCUSSION

Cr(VI) reduction efficiency of ZVMs and bimetal in aqueous solutions

The Cr(VI) reduction efficiency of ZVMs and bimetallic particles in solutions containing Cr(VI) is presented in Fig. 2. Results showed the following order of Cr(VI) reduction efficiency: Fe/Al(80.5%) > Fe/Zn(49.0%) ≈ Al⁰(42.3%) > Zn⁰(13.5%). Bimetallic particles were significantly more efficient than ZVMs in reduction of Cr(VI), which is previously reported for the treatment of chlorinated organic compounds [41]. The combination of two metals allows the primary metal to act as an electron donor and the secondary metal serves as a catalyst or assistant to enhance the efficiency of Cr(VI) reduction [42]. This is not true for ZVMs in which the metal itself is consumed to form a passive layer slowing down or ceasing the remediation process. The Fe/Al bimetallic particles showed the highest Cr(VI) reduction efficiencies. *Fu et al.* [18] reported a fast and highly efficient removal of Cr(VI) by Fe/Al in aqueous solutions. The reactivity of Fe/Al microparticles toward Cr(VI) was expected to be low, as it is deduced from its smooth morphology. Nevertheless, no build-up of iron corrosion products on the Fe/Al surface greatly increased its reactivity. This may be because of the low standard reduction potential (E^0) of Al⁰ leading to the protection of iron from corrosion. The Fe/Zn bimetal and Al⁰ exhibited statistically the same reduction efficiencies that were much higher than that of Zn⁰. The better performance of Al⁰ compared with Zn⁰ under high pH conditions may also be due to the role of OH⁻ ions to remove aluminum oxide from the surface of Al⁰ [43]:



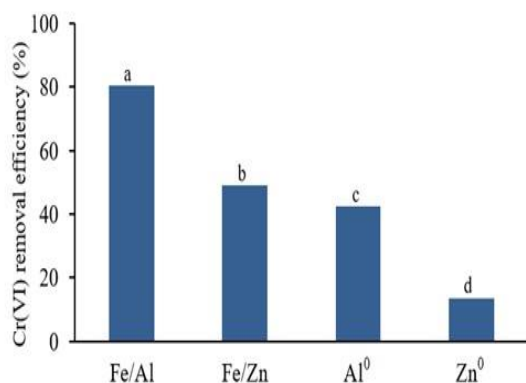


Fig. 2: The Cr(VI) reduction efficiency of metals and bimetals in aqueous solutions (20 mg Cr(VI)/L with a reductant dosage of 1 g/L). Bimetallic particles were synthesized as 0.1 g shell metal/g core metal.

As a whole result, bimetallic particles had much more reactivity compared with their core metals. The iron coating on Al⁰ increased its reduction efficiency nearly two-fold. Also, Zn⁰ coating with iron enhanced Cr(VI) reduction efficiency 3.6 fold, respectively.

Reduction of Cr(VI) in the contaminated soils

The self-attenuation efficiencies of the Cr(VI)-contaminated soils (R_s values) after one-month incubation ranged from 13 to 100% and decreased significantly ($p < 0.01$) with increasing the level of added Cr(VI). The average value of R_s at 50 and 500 mg Cr(VI)/kg for the three soils showed the order of soil 3(100%) > soil 2(78.3) > soil 1(27%). The figure was 96.2% at 1000 mg Cr(VI) kg⁻¹ for soil 3. Soil 3 with a lower pH and higher organic carbon content had higher self-attenuation efficiency than soils 1 and 2. In the presence of soil organic matter, Cr(VI) reduces to Cr(III), especially under acidic and neutral conditions [14]. This is the reason for the extra application of Cr(VI) (1000 mg/kg) in this soil. Complete Cr(VI) reduction for soils 1, 2, and 3 was observed at maximum Cr(VI) concentrations of 1, 50 and 500 mg Cr(VI)/kg, respectively. This finding indicates that to ensure no emission of Cr(VI) into the aquatic environments, the exchangeable Cr(VI) concentration in the soils under study should not exceed the limits specified above.

Reduction of Cr(VI) by ZVMs and bimetallic particles

Figs. 3 and 4 present the amendment-induced Cr(VI) reduction efficiencies of ZVMs and their bimetallic

particles (R_a values) as a function of time. Treatments without the addition of reductants (controls) showed no detectable change in the concentration of exchangeable Cr(VI) over the experiment time. The reduction process in treatments containing reductants began with a fast initial reaction followed by a subsequent slow reaction. At short times, when active sites on the surface of the particles were free to contact with Cr(VI), the reaction was fast. At longer times, a passivating film of oxy/hydroxides may be deposited on the surface of metals and bimetals which impedes the electron transfer, and eventually, the Cr(VI) reduction is hindered [18]. The ZVMs showed rapid passivation within only a few minutes, while the bimetallic particles preserved their reactivity even up to one hour. An exception was observed in the case of soil 3 (a slightly acid soil with a higher amount of organic matter), where ZVMs provided much better efficiency than that in two other soils. Furthermore, little difference in the time-trend of Cr(VI) reduction between ZVMs and bimetals was observed in this soil. More availability of protons in this soil not only facilitates the reduction of Cr(VI) [1] but disfavors the formation of the passivating film [44]. Also, more complexation of Cr(III) with humic substances [45] that forces the forward reduction reaction could be responsible. Application of Fe/Al bimetallic particles caused a significant increase ($p < 0.01$) in mean values of maximum Cr(VI) reduction efficiency after 168 hours when compared with application of Al⁰ (16.8%, 48.8%, and 37.4% in soils 1, 2 and 3, respectively). Also, supplementation of Fe/Zn particles in soils 1, 2 and 3 provided respectively 22%, 60.7% and 22.3% higher Cr(VI) reduction efficiency ($p < 0.01$) than Zn⁰. The highest difference was observed in soil 2 (a non-calcareous near-neutral soil that contains a medium amount of organic matter). However, increasing the initial concentration of Cr(VI) from 100 to 500 mg Cr(VI)/kg in this soil was concomitant with a great decrease in Cr(VI) reduction efficiency (72.6% and 48.5% for Fe/Al and Fe/Zn, respectively). However, in the case of soil 1 (a calcareous soil with low organic matter content), a little decrease was observed. As illustrated by the drawing in Fig. 5, the Al metal particles could capture Cr(VI) from suspension and convert it to less soluble precipitates. Meanwhile, bimetallic particles have limited active sites which become saturated only at high Cr(VI) concentrations [6]. However, because of high pH and resulting low anion adsorption

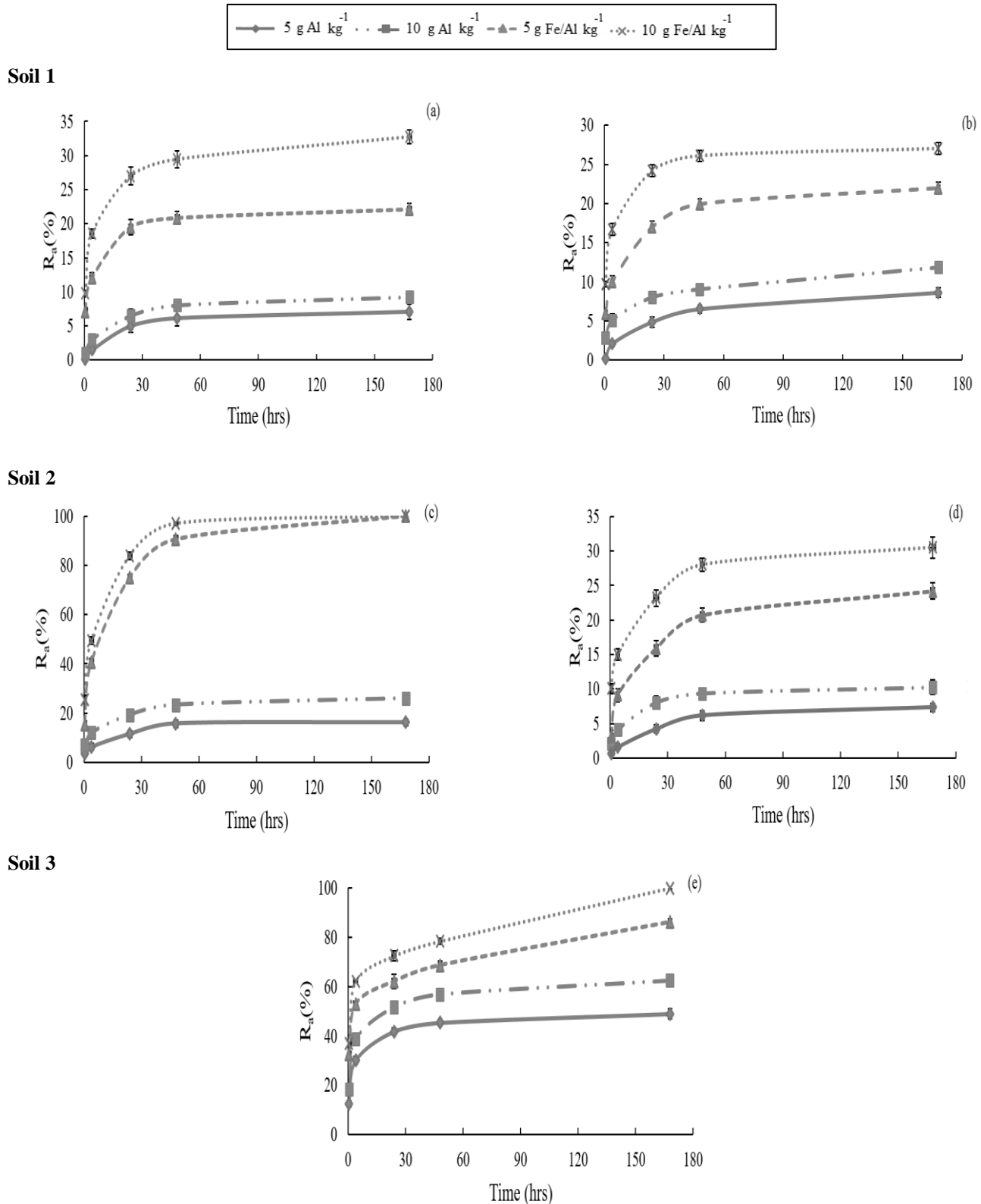


Fig. 3: The Cr(VI) reduction efficiency (R_a values) of Al^0 and Fe/Al with different dosages (5 and 10 g/kg soil) versus time: (a) and (b) 100 and 500 mg Cr(VI)/kg soil 1, respectively, (c) and (d) 100 and 500 mg Cr(VI)/kg soil 2, respectively. Fe/Al bimetallic particles were synthesized as 0.1 g shell metal/g core metal.

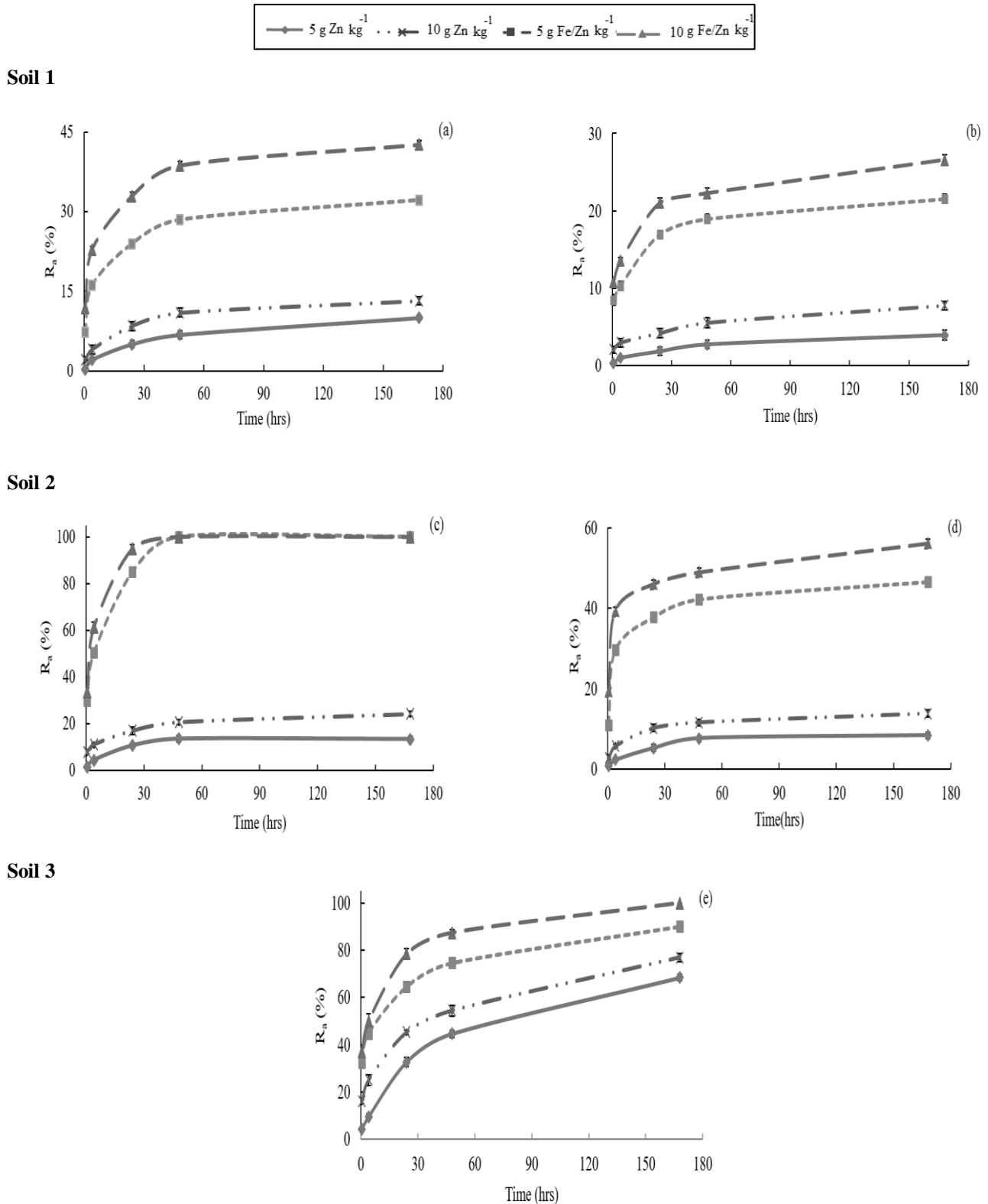


Fig. 4: The Cr(VI) reduction efficiency (R_a values) of Zn^0 and Fe/Zn with different dosages (5 and 10 g/kg soil) versus time: (a) and (b) 100 and 500 mg Cr(VI)/kg soil 1, respectively, (c) and (d) 100 and 500 mg Cr(VI)/kg soil 2, respectively. Bimetallic particles were synthesized as 0.1 g shell metal/g core metal.

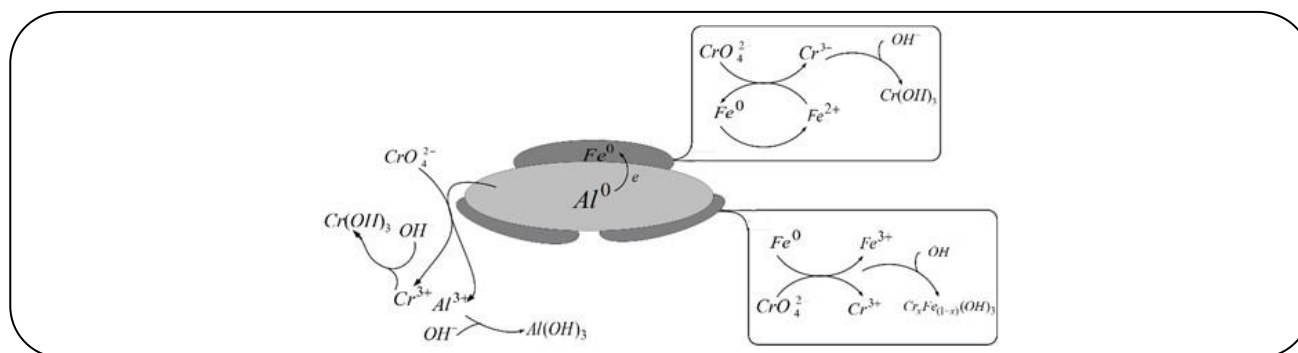


Fig. 5: The mechanism of iron catalysis to improve the Cr(VI) reduction by aluminum.

the capacity of soil 1, it is expected that a large portion of added Cr(VI) should be present in the soil solution. The higher presence of Cr(VI) in soil solution at its higher concentrations tends towards higher access of reducing particles to Cr(VI) which could lead to an easy reduction process. Bimetallic particles reduced Cr(VI) two times, on average, higher in soil 2 than in soil 1. This may be due to the rapid passivation of bimetals in soil 1. The effectiveness of bimetallic particles is deeply affected by the formation of precipitates, especially Cr(OH)_3 , on their surfaces [46]. The calcareous nature of soil 1 may be the reason for the very low efficiency of bimetallic particles in this soil. Higher concentrations of bicarbonate and calcium in soil 1 compared with two other soils likely played a major role in surface passivation. The impact of bicarbonate ions on bimetallic particles for Cr(VI) reduction may be attributed to the passivation from carbonate precipitates on the bimetallic particles. Another explanation is the competition between bicarbonate and chromate ions for the reactive sites on the bimetallic particles [16]. Moreover, the oxidizing ability of bicarbonate adsorbed on the Fe^0 has been well known [47]. In addition, the coexistence of bicarbonate and calcium and thereby calcium carbonate (CaCO_3) precipitation further enhances the passivation, leading to deterioration in Cr(VI) reduction by bimetallic particles [16]. Soil 3 exhibited a quite different situation of Cr(VI) reduction. The efficiency of bimetals in this soil was, on average, lower than soil 2. This might be attributed to the application of a higher level of Cr(VI) in soil 3 compared to soil 2. Although, this was not the case for ZVMs. Soil 3 with slightly acidic conditions allows to more easily remove of the passivating film, but in the meanwhile, complexation of organic compounds with active surface sites of bimetallic particles can decrease Cr(VI) reduction [48].

However, indirect favorable effects of organic matter on Cr(VI) reduction can be found in the literature. In fact, the varied nature of soil organic matter greatly influences the reaction mechanisms involved in the Cr(VI) reduction. Humic substances enriched with acidic functional groups, generally favored the Cr(VI) reduction effectiveness, by forming complexes with Fe(III) and Cr(III) and preventing their precipitation on the bimetallic particles. Conversely, in the presence of non-humic substances, the reduction inhibition may be due to the adsorption of dissolved organic compounds on to the surface of bimetallic particles, thus reducing the availability of free active reaction sites [49]. The addition of Fe/Al and Fe/Zn bimetallic particles into the contaminated soil 2 (100 mg Cr(VI)/kg) at a dosage of 5 g/kg, led to the complete removal of Cr(VI). Also, the addition of Fe/Al and Fe/Zn at the dosage of 10 g/kg in soil 3 led to complete Cr(VI) reduction. The differences between the Cr(VI) reduction efficiency of ZVMs and their bimetallic particles augmented with increasing the reductant dosage and the initial Cr(VI) concentration in soil 1 and especially in soil 2. Conversely, these differences diminished with increasing the reductant dosage in soil 3 as discussed above. Table 2 presents the Cr(VI) reducing capacity (R_c values) of metals and bimetals. In order to compare the values of Cr(VI) removal capacity (g/kg), the reductant dosage of 5 g/kg was considered for the contaminated soils 1 and 2 (500 mg Cr(VI)/kg) and for the contaminated soil 3 (1000 mg Cr(VI)/kg) after 48-hour contact time. Among the five reductants, the reducing capacity of Zn^0 in soil 1 and that of Al^0 in soils 2 and 3 were the lowest. The highest capacity was observed for either Fe/Al or Fe/Zn or both in all three soils. The order of R_c values observed was as follows: $\text{Fe/Al} \approx \text{Fe/Zn} > \text{Al}^0 > \text{Zn}^0$ in soil 1, $\text{Fe/Zn} > \text{Fe/Al} > \text{Zn}^0 \approx \text{Al}^0$ in soil 2 and $\text{Fe/Al} \approx \text{Fe/Zn} > \text{Al}^0 \approx \text{Zn}^0$ in soil 3.

Table 2: The Cr(VI) reducing capacity (mg/g) of the reductants.

Soil		Al ⁰	Zn ⁰	Fe/Al	Fe/Zn
	1	5.66±0.53	2.40±0.56	17.32±0.65	16.49±0.83
	2	2.31±0.20	2.59±0.28	7.05±0.41	14.37±0.66
	3	3.19±0.15	3.75±0.112	6.40±0.07	6.91±0.16

Initial concentration of Cr(VI): 500 mg Cr(VI)/kg in soils 1 and 2, 1000 mg Cr(VI)/kg in soil 3. Reductant dosage: 5 g/kg. Bimetallic particles were synthesized as 0.1 g shell metal/g core metal.

Table 3: Rate constants of pseudo-first order reaction of Cr(VI) reduction by ZVMs and bimetallic particles.

Soil	Initial concentration of Cr(VI) (mg/kg)	1				2				3	
		100		500		100		500		1000	
		5	10	5	10	5	10	5	10	5	10
Al ⁰	k	0.049±0.004	0.056±0.006	0.034±0.002	0.052±0.004	0.074±0.005	0.125±0.003	0.038±0.004	0.094±0.006	0.225±0.001	0.263±0.010
	r ²	0.998	0.973	0.988	0.825	0.923	0.874	0.993	0.942	0.942	0.914
Zn ⁰	k	0.027±0.002	0.045±0.004	0.028±0.004	0.035±0.001	0.080±0.003	0.083±0.001	0.047±0.005	0.072±0.006	0.025±0.001	0.035±0.001
	r ²	0.980	0.952	0.967	0.782	0.991	0.785	0.984	0.904	0.990	0.873
Fe/Al	k	0.217±0.006	0.235±0.004	0.137±0.023	0.295±0.009	0.803±0.006	0.177±0.005	0.054±0.002	0.177±0.005	0.286±0.011	0.303±0.007
	r ²	0.948	0.901	0.887	0.925	0.945	0.939	0.931	0.845	0.716	0.716
Fe/Zn	k	0.162±0.012	0.21±0.009	0.184±0.007	0.212±0.008	0.192±0.011	0.285±0.009	0.274±0.010	0.380±0.034	0.185±0.005	0.198±0.012
	r ²	0.884	0.883	0.795	0.768	0.926	0.944	0.937	0.886	0.736	0.801

k: Rate constant (h⁻¹), *: Reduction of Cr(VI) was completed in less than 0.5 h.

These results indicate that ironed aluminum (Fe/Al) can be an attractive candidate for the reduction of Cr(VI) in contaminated soils. In the present research, the complete Cr(VI) removal was attained at the (Fe/Al)/Cr(VI) ratio of 5000/100 (mg/mg) in soil 2. In a recent investigation, the same result appeared at the nZVI/Cr(VI) ratio of 1000/11 (mg/mg) [21] in an acid soil that was approximately twice that of Fe/Al in a near-neutral soil. The corresponding ratio (nZVI/Cr(VI)) in another acid soil was reported to be about 50000/200 (mg/mg) which was much greater than that observed for Fe/Al in our study [50]. Nevertheless, ratios as low as 60/120 (mg/mg) can be found when using bimetallic modified nZVI (Fe/Cu) [51]. The pseudo-first-order kinetic model was considered

to be the best fit for the reaction, and the values of rate constants are presented in Table 3. The average value of rate constants in soil 1 was in the order of Fe/Al > Fe/Zn >> Al⁰ > Zn⁰. The figure in soil 2 was in the order of Fe/Zn > Fe/Al > Al⁰ ≈ Zn⁰. The average value of rate constants in soil 3 was in the order of Fe/Al > Al⁰ > Fe/Zn >> Zn⁰. The Fe/Al application instead of using Al⁰ increased the rate constant by a factor of 4.6, 1.5, and 1.2 in soils 1, 2, and 3, respectively. Similarly, with the use of Fe/Zn rather than Zn⁰, the rate constant increased by a factor of 5.8, 4.2, and 6.5 in soils 1, 2, and 3, respectively. The results indicate that the Fe/Al showed its rapid performance in soil 1, whereas the speed of Cr(VI) reduction by Fe/Zn bimetal was almost the same for all three soils.

CONCLUSIONS

A number of previous reports showed that the removal of Cr(VI) by metals (e.g. ZVI) is inefficient because of the low rate of Cr(VI) reduction. The incorporation of a second metal with a high thermodynamic driving force can improve the performance of such amendments. In this research, two ZVMs (Al^0 and Zn^0) and their bimetallics (Fe/Al and Fe/Zn) were evaluated to reduce the soil Cr(VI) to Cr(III) in a batch experiment. The ZVMs showed relatively low Cr(VI) reduction efficiency in two non-acid soils, except in slightly acid soil. This is consistent with the fact that acid conditions favor Cr(VI) reduction. The efficiency of bimetallic particles to reduce Cr(VI) was higher in non-calcareous near-neutral soil than in calcareous soil. The findings of our research revealed difficulties in dealing with the remediation of calcareous Cr(VI)-contaminated soils. Reasonable reduction of Cr(VI) contamination was achieved by Fe/Al and Fe/Zn in both aqueous and soil environments. But, the Fe/Zn bimetallic particles are not environmentally friendly as compared to Fe/Al. In addition to superior reduction capacity, Fe/Al provided a high speed of Cr(VI) reduction, particularly in calcareous soil. According to the results of this study, it is expected that bimetallic particles would be promising candidates for the remediation of Cr(VI)-contaminated soils. Further research is, however, required to find safe alternatives that are not only highly efficient and stable but rapid in action to reduce Cr(VI) over a wide range of pH in soil and sediment environments.

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