



Efficient reduction of hexavalent chromium with microscale Fe/Cu bimetals: Efficiency and the role of Cu

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ABSTRACT

Microscale zero valent iron (mFe⁰) is one of the most potential water pollution remediation materials, but the effective utilization ability of electrons released by mFe⁰ in the reduction of hexavalent chromium (Cr(VI)) is not satisfactory. Here, we find the microscale iron-copper (mFe/Cu) bimetals coated with copper on the surface of mFe⁰ can significantly improve the effective utilization of electrons released by mFe⁰. Electrochemical analysis displays that copper plating on the surface of mFe/Cu can promote the release of the electrons from mFe⁰ and reduce the impedance of mFe⁰. Spin-polarized density functional theory (DFT) calculation reveals that Cu on the surface of mFe/Cu bimetals promotes the release of electrons from mFe⁰ and reduces the adsorption energy of Fe to Cr. As the electron transporter, moreover, Cu can always attract Cr to the hollow position near itself of the Fe surface, which could promote the effective utilization of electrons released by Fe. Effective utilization ability of electrons in mFe/Cu system is 12.5 times higher than that in mFe⁰ system. Our findings provide another basis for the efficient reduction of Cr(VI) by mFe/Cu bimetals, which could promote the application and popularization of mFe/Cu bimetals.

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Due to the low standard reduction potential of -0.441 V for $\text{Fe}^{2+}/\text{Fe}^0$, zero valent iron (Fe^0) releases electrons quickly and is often used as a reducing agent in chemical reactions [1]. With characteristics of eco-friendly, inexpensive, and easy operation, Fe^0 is widely used to remove a great deal of pollutants from water, such as heavy metals [2,3], nitrate [4], nitrobenzene [5,6]. The removal of contaminations mainly depends on the corrosion of Fe^0 , and during this corrosion, Fe^0 releases electrons and converts to $\text{Fe}^{2+}/\text{Fe}^{3+}$. In practical application, however, the activity of Fe^0 is low due to the formation of iron oxides and hydroxides on the surface of Fe^0 , which leads to the formation of a passivation layer on the surface [7,8]. This passivation layer makes Fe^0 hide in the core, reducing the ability of Fe^0 to release electrons and efficiency of electron transfer. Many methods have been developed to improve the electron releasing properties and activity of Fe^0 , such

as combining Fe^0 with strong oxidizer (e.g., H_2O_2 , persulfate, O_3) [6,9], apposition magnetic field or electric field [10,11], and assembling other elements on the surface of Fe^0 (i.e., Cu, Pd, S) [12–14]. Among all these strategies to improve the properties of Fe^0 , Fe/Cu bimetals (assembled Cu on the surface of Fe^0) have attracted extensive attention because of the simple preparation, low cost and high electron selectivity [15]. For example, Fe/Cu bimetals are superior to Fe^0 in the removal of nitrophenols in wastewater or reductive dechlorination of haloacetamides in drinking water [16,17]. In studies of Cu modified Fe^0 , the role of Cu is simplified to promote the corrosion of Fe^0 due to the potential between Fe^0 and Cu^0 (0.777 V), which is higher than that between Fe^0 and Fe^{2+} (0.441 V) [17,18]. However, the role of Cu on the interface between Fe/Cu bimetal and water, and the role of Cu on contaminants and electron transfer have been neglected.

Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) as the two main forms of chromium in aqueous solution, Cr(VI) has attracted more and more attention because of its high toxicity, generally soluble and easy to migration [19]. According to en-

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vironmental protection agency of the World Health Organization and Ministry of Health of China, concentration of Cr(VI) in drinking water is must less than 0.1 mg/L and 0.05 mg/L, respectively [20]. Hence, it is significant to develop efficient and economical methods for the removal of Cr(VI) from aqueous solution.

Generally, methods to reduce the concentration and toxicity of Cr(VI) in aqueous solution include adsorption, post-reduction flocculation and sedimentation, ion exchange and membrane separation [21–23]. Among these methods for removal Cr(VI), adsorption is the most widely used because of its economy, while it carries the risk of releasing the adsorbed Cr(VI) and resulting in secondary pollution [24]. Therefore, reduction Cr(VI) to stable, low-toxicity Cr(III) is the most promising method for removing Cr(VI) for engineering applications. Due to the outstanding properties in terms of reducibility, source and operation, Fe⁰ is widely used in wastewater treatment and water remediation, including the removal of Cr(VI) from aqueous solution [21].

To enhance the reduction of Cr(VI), in this work, different amounts of Cu⁰ are loaded on the surface of Fe⁰ to form Fe/Cu bimetallics for the removal Cr(VI) from aqueous solution. The influences of Fe⁰ dosage, initial pH and ratio of Cu/Fe on removal of Cr(VI) were studied. The overarching objective of this study was to investigate the role of Cu⁰ on the surface of Fe/Cu bimetallic particles in the removal of Cr(VI) from aqueous solution. In addition, the fate of chromium in Fe/Cu bimetallic system and the reutilization of Fe/Cu bimetallics were studied.

The reagents and analytical methods can be found in Supporting information.

During the experimental process, initial Cr(VI) concentration of 20 mg/L was used as the simulated contaminant to test the efficiency and mechanism of Cr(VI) removal by mFe/Cu bimetallics. Key experimental parameters affecting Cr(VI) removal by mFe/Cu bimetallics, including the Fe⁰ dosage, ratio of Cu/Fe and initial pH of Cr(VI) aqueous solution, were investigated. In each batch experiment, the weighted mFe/Cu bimetallics and 400 mL Cr(VI) aqueous solution were added into a 500 mL beaker, which was mixed by mechanical mixer with speed of 280 rpm. About 2 mL samples were withdrawn at the desired reaction time, and filtered by a PTFE syringe filter with 0.45 μm membrane for analyzing the concentration of residual Cr(VI). The used mFe/Cu bimetallics and sludge were separated from aqueous solution after reaction by magnetic suction and filtration for characterizing the properties. All experiments were performed twice.

All the spin-polarized density functional theory (DFT) calculations were performed with the Vienna *ab initio* simulation package (VASP) code [25,26] using the Perdew-Burke-Ernzerhof (PBE) functional [27], which was used to model electronic exchange and correlation. The interactions between the ionic core and the valence electrons were described by the projector-augmented wave framework [28]. A plane wave basis with an energy cutoff of 400 eV was used to describe the valence electrons. A (3 × 3 × 1) Monkhorst-Pack k-point mesh was used to sample the Brillouin zone in structural optimizations. The convergence criterion for the electronic structure and the atomic geometry was 10⁻⁴ eV and 0.05 eV/Å, respectively.

Based on the experimental methods for preparing mFe/Cu catalysts and some related references [29–31], a 3 × 3 Fe(100) slab model with four atomic layers and 12 Å of vacuum was chose to model the mFe/Cu catalysts in this study. The bottom two layers were fixed in bulk position, and all other atoms were free to relax. The binding energies E_b were defined as Eq. 1:

$$E_b = E_{M/\text{slab}} - E_M - E_{\text{slab}} \quad (1)$$

where $E_{M/\text{slab}}$, E_M , and E_{slab} are the total energies of the slab with the adsorbed Cr species, the isolated Cr species, and the slab with or without Cu atoms placed on the Fe surfaces, respectively. A neg-

ative binding energy indicates exothermic adsorption. The Bader valence (BV) was defined as: BV = valence charges – bader population [32]. Positive values mean relevant atoms contribute electrons to other atoms.

Fig. 1a shows the effect of the different dosage of Fe⁰ on Cr(VI) removal. The ratio of Cu/Fe was 1:30, the temperature was 30°C and reaction time was 30 min. The removal efficiencies of Cr(VI) increased from 47.0% to 99.8% when the amount of Fe⁰ increased from 2 g/L to 5 g/L. In light of previous studies, the removal efficiencies of targeted pollutants could increase with the increase in dosage of Fe/Cu bimetallics [17,33]. While with the dose of Fe⁰ increased from 5 g/L to 10 g/L, the removal efficiency decreased slightly. As shown in Fig. 1a, Cr(VI) removal efficiency increased to the maximum with Fe⁰ dosage of 5 g/L.

When ratio of Cu/Fe was a constant value, the increase of Fe⁰ dosage could increase the total surface area, active sites and the number of galvanic couple between Fe and Cu, and accelerate the rate of electrons release [34]. However, when enough Fe⁰ dosage was added (e.g., > 5 g/L), Cr(VI) removal efficiency would be limited by other factors, especially for the mass transportation rate of Cr(VI), intermediates, corrosion products between the surface of mFe/Cu bimetallics and water phase. It is similar to the results observed in previous work [33,35].

It has been found that reaction between Fe and the pollutant in bimetallic system might occurs primarily at the surface of the transition metal [34,35], thus the activity of Fe/Cu bimetallic system could be affected by the ratio of Cu/Fe [36,37]. In order to investigate ratio of Cu/Fe on the Cr(VI) removal by the mFe/Cu bimetallic system, the batch experiments using prepared mFe/Cu bimetallics with different ratio of Cu/Fe were set up. As shown in Fig. 1b, when the ratio of Cu/Fe increased from 1:40 to 1:30, the removal efficiency of Cr(VI) was increased from 89.1% to 99.8% after 10 min, however, when increasing ratio of Cu/Fe from 1:30 to 1:10, the removal efficiency decreased to 76.7%. In other words, with the increase of Cu/Fe ratio, removal efficiency of Cr(VI) shows a trend of increasing firstly and then decreasing. And the similar results were occurred in reduction of *p*-nitrophenol and haloacetamides [17,38].

As a comparison experiment of bare Fe⁰ (without Cu) for the removal of Cr(VI), the removal efficiency was only 2.8%. This might due to the high standard reduction potential (0.777 V) between Fe and Cu, which could promote the corrosion rate of Fe⁰ and promote the reaction between Fe⁰ and Cr(VI) [39,40]. The direct contact between the covered Cu and Fe⁰ could improve the formation of galvanic couples between Cu (cathode) and Fe⁰ (anode). However, excess Cu was easy to drop off from the surface of Fe⁰, and did not easily contact with Fe⁰. As a result, number of galvanic couples between Cu and Fe⁰, and efficient electron transfer were decreased, which led to lower activity [39].

Fig. 1c shows the effect of initial pH on Cr(VI) removal efficiency in mFe/Cu process. According to Fig. 1c, removal of Cr(VI) by mFe/Cu was a pH-dependent process, and Cr(VI) removal efficiencies decreased with the increase of pH (in the range of 3.0 to 9.0). For example, at the initial pH of 3.0, 5.8, 7.0 and 9.0, Cr(VI) removal efficiencies reached 100%, 99.8%, 89.0% and 58.0% after 10 min of reaction, respectively. When pH of aqueous solution is lower than 6.0, the main form of Cr(VI) is HCrO₄⁻, which is absorbed on the surface of mFe/Cu or mFe easily due to the lower adsorption free energy [11]. Moreover, Fe⁰ is easier to be oxidized and release electrons under acidic conditions, which is also more conducive to the reduction of Cr(VI) [41].

Fig. 2a presents the Cr(VI) removal efficiencies by mFe/Cu bimetallic and mFe⁰ processes, as can be seen, Cr(VI) removal efficiency is less than 5% by mFe⁰ process under neutral condition (pH_i of 5.8). In contrast, mFe/Cu bimetallics show excellent removal of Cr(VI) (almost 100%). The result indicates that the copper on surface of mFe⁰ is particularly critical for removing of Cr(VI) in

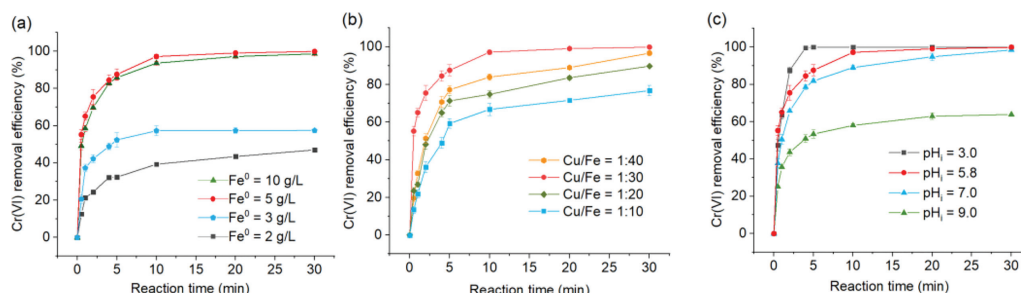


Fig. 1. Cr(VI) removal efficiencies by mFe/Cu at different Fe⁰ dosage (a), Cu/Fe ratio (b) and initial pH (c). Experiment conditions: [Cr(VI)]₀ = 20 mg/L, (a) pH_i = 5.8, Cu/Fe = 1:30, (b) pH_i = 5.8, Fe⁰ = 5 g/L, (c) Fe⁰ = 5 g/L, Cu/Fe = 1:30.

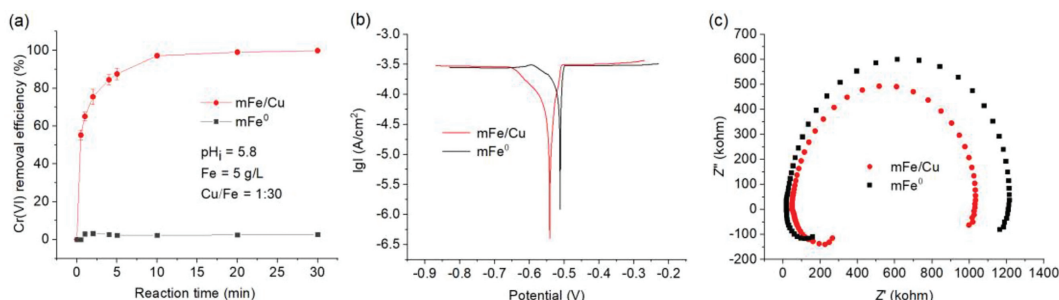


Fig. 2. Cr(VI) removal efficiencies by mFe/Cu and mFe⁰ (a), OPR curve (b) and EIS spectra (c) of mFe/Cu and mFe⁰.

mFe/Cu bimetal system. Previous studies of Fe/Cu bimetal process in the removal of nitrobenzenes and haloacetamides have shown that the role of copper is promoting the corrosion of Fe⁰ or as an electron transport carrier promoting reduction of Fe³⁺ to Fe²⁺ [15,17].

To verify the role of copper on surface of mFe⁰ for removing of Cr(VI) by mFe/Cu bimetal, OPR curves and EIS spectra were used to analyze electron release and transfer in mFe/Cu and mFe⁰ systems. Fig. 2b presents the negative corrosion of mFe/Cu and mFe⁰ is -0.54 V and -0.51 V, respectively. The greater negative corrosion potential, the easier it is to release electrons, Fig. 2b illustrates that copper can promote the release of electrons from Fe⁰, thus improving the reduction of Cr(VI) in mFe/Cu system. Additionally, EIS Nyquist plot could be used to characterize the electron transfer impedance of materials, and the smaller the radius of the ring, the lower the electron transfer impedance [42]. As can be seen in Fig. 2c, mFe/Cu bimetal has a smaller impedance ring radius, which means that mFe/Cu bimetal transfers electrons faster [26].

To clarify the experimental results deeply, we used theoretical methods to model one Cr atom binding on the Fe(100) surfaces with different Cu clusters. Different initial configurations of Cr binding on the mFe/Cu surfaces have been checked, and only the most stable (with the lowest total energy) relaxed configurations are reported, as shown in Fig. 3. The structure of the dashed square in each panel showed the theoretical slab model, *i.e.* 3×3 Fe(100) surface. To directly perceive whether the periodic structures influenced Cr binding characteristics, we mapped out the double size of the slab models and found that the Cr atoms in Fig. 3e and f would have been influenced by adjacent Cu clusters. Based on the optimized structures of Fig. 3, we also can get one message that the Cr atom was predominately adsorbed at the hollow site of the Fe surface which was close to the Cu atoms.

Table 1 showed the corresponding binding energies of the most stable configurations of Cr binding on mFe/Cu surfaces (Figs. 3a-f). We can get the information that Cr was more easily adsorbed on the mFe/Cu surfaces because of the smaller binding energy than that of the bare Fe surface, in other words, the addition of Cu

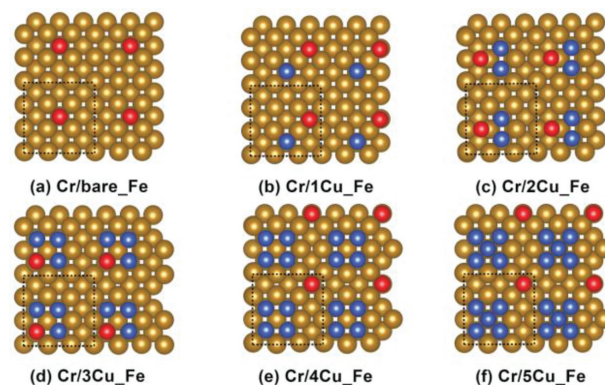


Fig. 3. Optimized structures with Cr binding on the mFe/Cu surfaces. Red, blue, and brown spheres represent Cr, Cu, and Fe atoms, respectively.

Table 1

The Bader valences (BV, e) of the most stable configurations of mFe/Cu with Cr atom or not and the corresponding binding energies (E_b , eV).

Structure	Cr_Free		Cr_Binding		E_b (eV)
	Cu_BV (e)	Fe_BV (e)	Cu_BV (e)	Fe_BV (e)	
bare_Fe	–	0.630	–	0.223	–3.251
1Cu_Fe	–0.250	0.772	–0.275	0.414	–4.388
2Cu_Fe	–0.498	0.814	–0.578	0.532	–4.187
3Cu_Fe	–0.667	0.828	–0.807	0.565	–3.833
4Cu_Fe	–0.807	0.918	–0.811	0.484	–3.505
5Cu_Fe	–0.872	0.960	–0.883	0.586	–4.261

increased the Cr adsorption ability, which could be conducive to promote the Cr removal by mFe/Cu bimetal and replenish the experiment result of Fig. 2a. Among the different mFe/Cu surfaces, the binding energies firstly increased, then decreased, along with the ratios of Cu/Fe increasing. That is to say, the ratios of Cu on the Fe surface could affect the binding energies of Cr binding on mFe/Cu surfaces, which agreed with the experimental results of

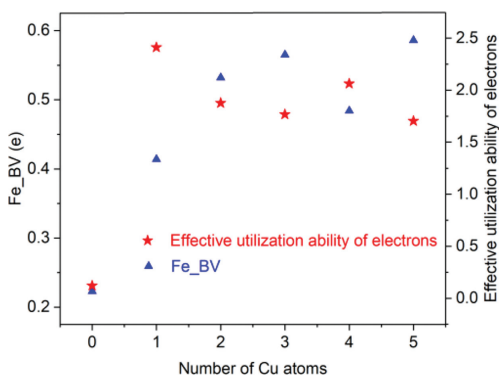


Fig. 4. The Fe_{BV} and effective utilization ability of electrons to the number of Cu atoms.

Cr(VI) removal by mFe/Cu at different Cu/Fe ratios (Fig. 1b). In addition, the binding energies of Cr binding on 4Cu₁Fe and 5Cu₁Fe surfaces didn't fit the rule which was discussed above. It was attributed to the larger size of Cu₄ and Cu₅ clusters supported on 3 × 3 Fe(100) surfaces and led to the Cr atoms more easily be adsorbed on the hollow positions of the Fe surfaces which were almost out of the model box, and the periodic structures had effects on the Cr atoms so that the binding energies of Cr binding on Cr/4Cu₁Fe and Cr/5Cu₁Fe surfaces had some fluctuations.

Table 1 also showed the corresponding Bader valences of Cu (Cu_{BV}) and Fe (Fe_{BV}). Cu_{BV} and Fe_{BV} included all Bader valences of the Cu atoms and nine Fe atoms of the 3 × 3 Fe(100) surface, respectively. Unsurprisingly, Cu_{BV} was negative and decreased as the number of Cu atoms increased no matter whether Cr was adsorbed on the surfaces or not, indicating that Cu atoms were prone to gain electrons in the Fe/Cu bimetallic system, and the electrons gained increase with the increase of the amount of Cu in the Fe/Cu bimetallic system. It is reasonable to assume that in the mFe/Cu bimetallic system for Cr(VI) removal, electrons released from mFe⁰ are transferred to Cu firstly and then from Cu to Cr(VI). Combing these with the values of Fe_{BV}, we can know that the presence of Cu atoms would accelerate Fe atoms releasing electrons and make the mFe/Cu catalysts have higher activities for the removal of Cr than bare Fe, which was in accordance with the experimental results. When the Cr atom was adsorbed on mFe/Cu surface, we also clearly found Fe_{BV} sharply decreased and Cu_{BV} had a slight downward trend, which manifested Cr would inhibit the release of electrons from iron.

In mFe/Cu bimetallic system, there are three direct ways of utilizing electrons released by Fe⁰ in the Cr(VI) removal process [24]: (i) oxygen gains electrons to produce reactive oxygen species or iron oxides; (ii) protons captures electrons to generate hydrogen; (iii) Cr(VI) captures electrons and is reduced, which can be called the electron effective utilization path. We take the ratio of Cr(VI) removal efficiency to Fe_{BV}, a parameter representing Fe electron release, as the effective utilization ability of electrons, and the calculation formula is as follows (Eq. 2):

$$\text{Effective utilization ability of electrons} = \frac{\text{Cr(VI) removal efficiency}}{\text{Fe}_{\text{BV}}} \quad (2)$$

The removal efficiencies of Cr(VI) in mFe/Cu bimetallic and mFe⁰ system were taken the data in Fig. 2a. The Fe_{BV} and effective utilization ability of electrons to the number of Cu atoms are shown in Fig. 4, as can be seen, effective utilization ability of electrons varies greatly with or without Cu. In the absence of Cu (mFe⁰), effective utilization ability of electrons is only 0.12. In the presence of Cu (mFe/Cu), however, effective utilization ability of electrons is greater than 1.5, 12.5 times higher than that of the

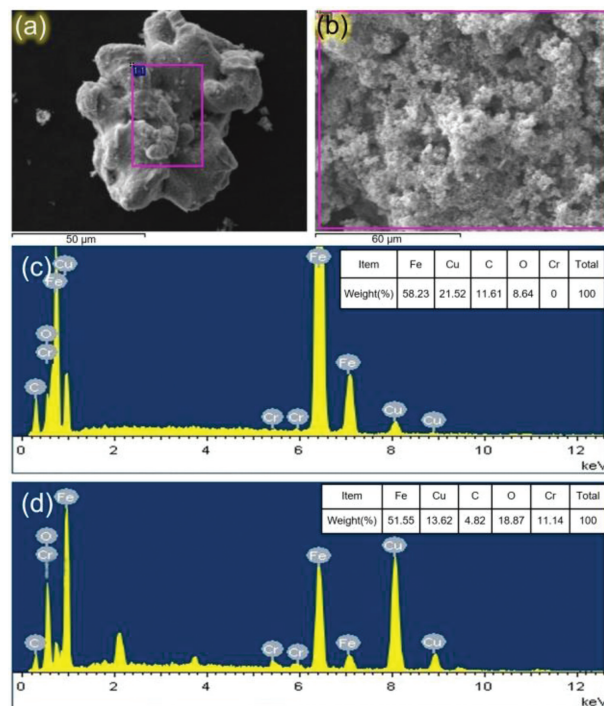


Fig. 5. SEM images of mFe/Cu bimetal (a) and floccule (b) after the reaction; EDS spectrum of the area in the purple frame of the SEM in part a (c), and EDS spectrum of the area in the purple frame of the SEM in part b (d).

mFe⁰ system. The improvement of effective utilization ability of electrons is mainly attributed to the fact that Cu can always attract Cr to the hollow position near itself of the Fe surface (as can be seen in Fig. 3), which is conducive to electron transfer. It is also confirmed that the presence of Cu in mFe⁰ system can improve the electron selectivity when removing Cr(VI).

To investigate the possible disposition of Cr(VI) in mFe/Cu system, characteristics of the reacted mFe/Cu bimetal and the sludge were observed by SEM-EDS (Fig. 5). The fresh mFe⁰ or with different ratio of Cu/Fe have been shown in our previous reports [18,19,34]. The elementary composition of the mFe⁰ particles were only three elements (i.e., Fe, C and O), and the mFe/Cu particles were four elements (i.e., Fe, Cu, O and C). Fig. 5a and c show the surface morphology and elemental composition of the reacted mFe/Cu bimetal. It is observed that main elements on the surface of mFe/Cu bimetal including Fe (58.23%, w/w), Cu (21.52%, w/w), C (11.61%, w/w) and O (8.64%, w/w), which suggest that the removal of Cr(VI) was not attribute to absorption of mFe/Cu bimetal.

Figs. 5b and d show the surface morphology and elemental composition of the floccule produced during Cr(VI) removal by mFe/Cu system. It is observed that main elements on the surface of the sludge including Fe (51.55%, w/w), Cu (13.62%, w/w), C (4.82%, w/w), O (18.87%, w/w) and Cr (11.14%, w/w). It can be seen that the removed Cr(VI) has been transferred from aqueous solution to the floccule. However, results of the only Fe²⁺/Fe³⁺ system with different pH shown that Cr(VI) was hardly removed by absorption and/or coagulation (removal efficiencies were less than 1%, and the data has not been shown). The results implied the absorption and/or coagulation does not play a pivotal role for Cr(VI) removal by mFe/Cu system, and Cr(VI) was reduced to Cr(III) which is easier to precipitate for removal [24].

In view of the excellent effect of mFe/Cu bimetal on the removal of Cr(VI), it is necessary to test the recyclability for long-term use. Fig. 6 shows the Cr(VI) removal efficiencies of recycle for 5 times with mFe/Cu bimetal, and mFe⁰ as the control mate-

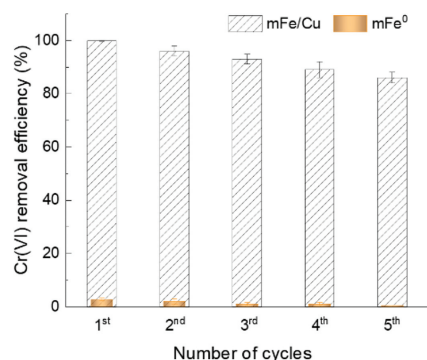
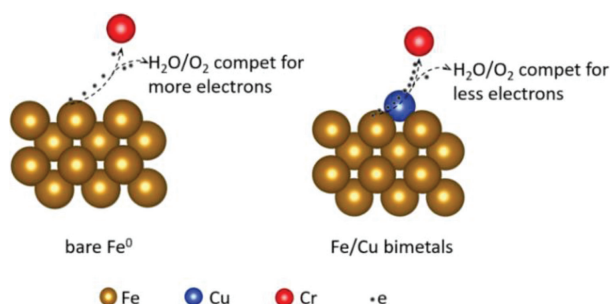


Fig. 6. Recyclability of mFe/Cu and mFe⁰ for Cr(VI). Experiment conditions: [Cr(VI)]₀ = 20 mg/L, pH_i = 5.8, Cu/Fe = 1:30, Fe⁰ = 5 g/L.



Scheme 1. Proposed mechanism for Cu improve electron utilization efficiency and Cr(VI) removal efficiency of mFe/Cu bimetallics.

rial. After five reuse, Cr(VI) removal efficiencies were 99.8%, 96.2%, 93.0%, 89.4% and 86.1% in mFe/Cu bimetal system, respectively. As shown in Fig. 6, Cr(VI) removal efficiencies obtained by mFe/Cu bimetallics had obvious advantages over mFe⁰ every time at the initial pH of 5.8 (without adjusting the initial pH of 20 mg/L Cr(VI)). Fig. 6 reveals that plating copper on the surface of mFe⁰ can effectively improve the Cr(VI) removal efficiency from aqueous solution under nearly neutral conditions. Combined with the previous analysis and the removal efficiency of Cr(VI), the excellent effect may be attributed to the addition of copper, which improves the ability of mFe⁰ to adsorb Cr(VI) and release electrons, and reduces the impedance of mFe⁰.

To conclude from the above discussion, a possible mechanism for the role of Cu for Cr(VI) removal in mFe/Cu bimetallic system is proposed in Scheme 1. Cu can improve electron utilization efficiency and Cr(VI) removal efficiency of mFe/Cu bimetallics mainly from three aspects: (1) Consistent with the classical view, the high potential between Fe⁰ and Cu⁰ (0.777 V) increases the corrosion and ability to release electrons of Fe⁰. (2) Cu can attract Cr to the hollow position near itself of the Fe surface, and can also be used as an electron transport medium, which shortens the electron transport path. (3) Cu reduces the binding energy of Cr on the surface of Fe matrix and improves the adsorption capacity of Fe to Cr, which increases the contact probability between electron donor (Fe) and electron acceptor (Cr).

In summary, Cr(VI) was reduced by mFe/Cu bimetallics in this study. In mFe/Cu bimetallic system, 20 mg/L Cr(VI) was removed in 30 min, and the removal efficiency reached more than 99% (Fe⁰ dosage of 5 g/L, Cu/Fe ratio of 1:30 and pH_i = 5.8), especially after five reuse, Cr(VI) removal efficiency could still be greater than 85% in mFe/Cu bimetallic system. The reacted mFe/Cu particle and the floccule produced by the reaction were analyzed by EDS, it was found that the removed Cr(VI) has been transferred from the aqueous solution to the floccule. Due to the addition of chromium, the

ability of iron to release electrons is inhibited, but in the presence of copper, the ability to release electrons is improved. The ability of mFe/Cu to release electrons is higher than that of mFe⁰, and the impedance of mFe/Cu is lower than that of mFe⁰, which is also confirmed by the electrochemical experiments. The effective utilization ability of electrons has increased from 0.12 in bare iron system to higher than 1.5 in mFe/Cu bimetallic system, which may be attributed to the fact that Cu can always adsorb Cr at the hollow position near itself of the Fe surface. It is hoped that our work can promote the application and popularization of mFe/Cu bimetallics in the reduction of heavy metals.

Declaration of competing interest

The authors declare no conflict of interest.

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