



Aqueous Cr(VI) reduction by electrodeposited zero-valent iron at neutral pH: Acceleration by organic matters

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ABSTRACT

This work investigated the effect of co-existing organic matters on aqueous Cr(VI) reduction by electrodeposited zero-valent iron (ED Fe⁰) at neutral pH. The ED Fe⁰ prepared in a solution containing mixture of saccharin, L-ascorbic acid and sodium dodecyl sulfate showed higher activity in reducing the aqueous Cr(VI) at neutral pH than that prepared without any organic presence. XRD and SEM indicated that the structure of ED Fe⁰ was significantly improved to nano-scale by the presence of organic mixture in the preparation solution. Further, the ED Fe⁰ activity in the Cr(VI) reduction at neutral pH was increased by the co-existence of citric acid or oxalic acid in the chromate solution. Electrochemical impedance spectroscopy (EIS) demonstrated that the corrosive current increased with the concentration of organic matter in the reaction solution. With the co-existing organic matters in the preparation solution, the ED Fe⁰ corroded more rapidly due to its nano-size, thus the Cr(VI) reduction by the ferrous iron was accelerated. With the co-existing organic matters in the reaction solution, the Cr(VI) reduction was accelerated by a Fe(II) complex as the main electron donor, and a prevention of the passivation due to the Fe(III) and Cr(III) complexes also accelerated the Cr(VI) reduction.

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1. Introduction

Chromium is widely used in metallurgical, electroplating, production of paints and pigments, tanning, wood preservation [1–3], etc., thereby commonly identified in waters. Two primary oxidation states, Cr(VI) and Cr(III) species, are present in aqueous media. The former is highly toxic and carcinogenic to human and animals, while the latter is generally non-toxic [4–6]. Consequently, the reduction of the Cr(VI) to the Cr(III) is of environmental interest. Much work has been focused on the cleanup of Cr(VI)-contaminated waters by various reducing reagents including hydrogen sulfide [7], divalent iron [8,9], Fe(II)-bearing minerals [5,10], thios and thiols [11,12], etc. Recently, zero-valent iron (Fe⁰) [13–16] has been tested for the remediation of polluted waters, and it is established that halogenated hydrocarbons such as nitro- [14,15] and chloro-compounds [13,16], toxic metals [2,17], nitrate and arsenate [18–20] are effectively transformed by the Fe⁰ to relatively more benign products.

However, the conventionally employed Fe⁰ has been observed to show a lower activity at neutral pH. The Fe⁰ activity may be enhanced through strategies working in either preparation or

application process. For example, the Fe⁰ activity can be improved by utilizing smaller sized, i.e., nano-scaled Fe⁰ [13,19]. In our previous work, we adopted an alternative Fe⁰ preparation method of electrodeposition, and observed that the ED Fe⁰ enjoyed a higher activity due to the preclusion of the surface oxides [21]. On the other hand, it was found that the ED Fe⁰ still encountered an activity loss during the subsequent application process, i.e. pollutant reduction process in aqueous solution at neutral pH. Improvement of the ED Fe⁰ reactivity still remains a challenge.

In the electrodeposition processes of metals, adding organic matters into electrolyte has been proved effective to change the surface morphology of samples. For example, saccharin is used as a reagent for grain refining, leveling, brightening, and stress-reducing in iron-group deposits [22]. Ascorbic acid is used to extend the life time of solution baths and ensure the operation at higher pH values by preventing oxidation of ferrous ions [23]. And sodium lauryl sulfate is employed to decrease the surface tension and the size of the hydrogen bubbles on the cathode surface [24]. In this study, a mixture of the three mentioned organic matters was added into the electrolyte with an attempt to adjust the morphology of Fe⁰ film.

Furthermore, it is documented that some Fe(III)-stabilizing ligands such as bi- and multidentate carboxylates and phenolates accelerate the Cr(VI) reduction by iron(II), whereas the Fe(II)-stabilizing ligands such as phenanthroline essentially stop the reaction [25]. Li et al. [26] have reported that reductive dechlorination transformation of PCP at the iron oxide–water interface

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could be promoted effectively with the co-existing polycarboxylic acids. Obviously, these iron-stabilizing ligands may be applicable to enhance the Fe^0 activity during the application process of Fe^0 system. In fact, many organic matters, such as citric acid and oxalate acid, can complex the iron ions, and abound in natural waters, so are environmentally compatible, whereas their effect on the reduction reaction of Cr(VI) by the Fe^0 has been scarcely available. In this study, the influence of organic matters, i.e. citric acid and oxalic acid, on the Cr(VI) reduction by the ED Fe^0 was investigated.

2. Materials and methods

2.1. Chemicals

All chemicals were analytical reagent and used as obtained. In all experiments, double distilled water was used.

2.2. Methodology

2.2.1. Preparation of the ED Fe^0

The ED Fe^0 was prepared by an electrodeposition on a titanium substrate as described previously [21]. The composition of the preparation solution was 0.20 M ferrous sulfate, 0.40 M boric acid, 0.50 M ammonium sulfate. A mixture of organic matters (saccharine 1.0 g/L, ascorbic acid 1.0 g/L, and sodium lauryl sulfate 0.50 g/L) was added if needed. The preparation solution was degassed by bubbling N_2 for 60 min prior to the electrodeposition. The applied current density was 10.0 mA/cm² and the bath temperature was maintained at 25 °C.

2.2.2. Surface analysis of the ED Fe^0

X-ray diffraction (XRD) and scanning electron microscope (SEM) were employed to investigate the chemical composition and surface morphology of the prepared ED Fe^0 samples, respectively. The XRD measurements were performed at 45 kV and 30 mA on a D/MAX 2200 VPC (RIGAKU, Japan) equipped with a graphite monochromator (Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$). The SEM was performed on a Philips Quanta 400 FE environment scanning electron microscope (FEI, Holand) coupled with an INCA energy dispersive X-ray spectrometer (EDS, Oxford, England) to obtain the atom composition.

2.2.3. Cr(VI) reduction by the ED Fe^0 at neutral pH

The Cr(VI) reduction by the ED Fe^0 at neutral pH were carried out in batch mode in a home-made setup that used a borosilicate glass vessel with 100 mL effective volume as the reactor. To prevent the oxidation of Fe^0 surface by air, N_2 was supplied continuously into the setup during the experimental process. In each experiment, unless stated specially, 100 mL 10.0 mg/L potassium chromate was treated by $20.0 \pm 0.2 \text{ mg Fe}^0$, and the ED Fe^0 was prepared with organic matters. To investigate the effect of the co-existing organic matters on the Cr(VI) reduction, citric acid and oxalic acid were added into the Cr(VI) solution.

Following the addition of citric acid and oxalic acid, the initial solution pH was adjusted to 7.0 by adding H_2SO_4 and $\text{NH}_3 \cdot \text{H}_2\text{O}$, then 0.1 M ammonium acetate solution was added to buffer the reaction pH. Samples of 2.0 mL were taken at preset time intervals for an immediate analysis of Cr(VI) or Fe(II) . Without the presence of co-existing organic matters in the reaction solution, precipitate emerged in the solution, and the samples were filtered to remove it before the measurement.

2.2.4. Analytic methods

The Cr(VI) concentration was quantified by the diphenyl carbazide method [27] on a UV-vis spectrophotometer (TU1810,

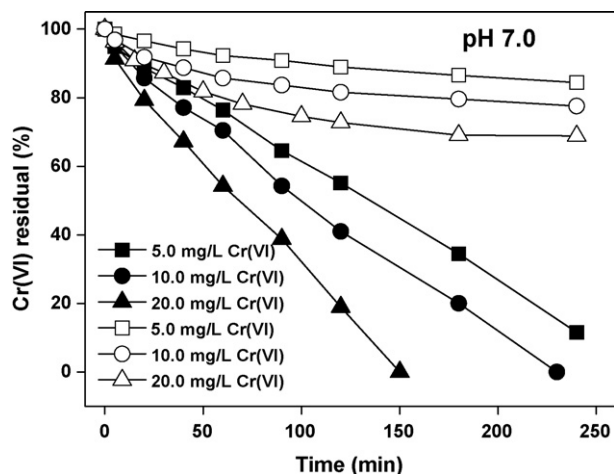


Fig. 1. Cr(VI) reduction by the ED Fe^0 sample prepared with (solid symbols) or without organic matters (hollow symbols) at 10.0 mA/cm² current density.

Universal Analysis, Beijing, China) at 540 nm, in which 1,5-diphenyl carbazide interacted with the Cr(VI) to form a pink complex in extremely acidic solution of pH <1.0. The Fe(II) concentration in the solution was determined using 1,10-phenanthroline method [28] also using the UV-vis spectrophotometer. Electrochemical impedance spectroscopy (EIS) [29] was performed on an electrochemical work station (IM6E, Germany) to record the corrosive current and corrosive voltage of the ED Fe^0 system in the chromate solution. All potentials were reported with respect to the SCE. In the EIS experiments, the amplitude of sinusoidal waveform was $\pm 5 \text{ mV}$, and the applied frequency ranged from 5×10^{-3} to 10^5 Hz .

3. Results and discussion

3.1. Effect of organic matters in preparation solution on the ED Fe^0 properties

Fig. 1 compared the Cr(VI) reduction results at neutral pH by the ED Fe^0 sample obtained with and without organic matters. For the ED Fe^0 prepared without any organic matter, 31.4%, 22.4% and 15.5% Cr(VI) concentration decayed in 240 min in 5.0, 10.0 and 20.0 mg/L Cr(VI) solution, respectively. By contrast, for the ED Fe^0 prepared with the co-existent of organic matters, the Cr(VI) reduction rate significantly increased. The Cr(VI) solution of 5.0 mg/L Cr(VI) , 10.0 mg/L and 20.0 mg/L Cr(VI) completely disappeared in 150, 230 and 280 min, respectively.

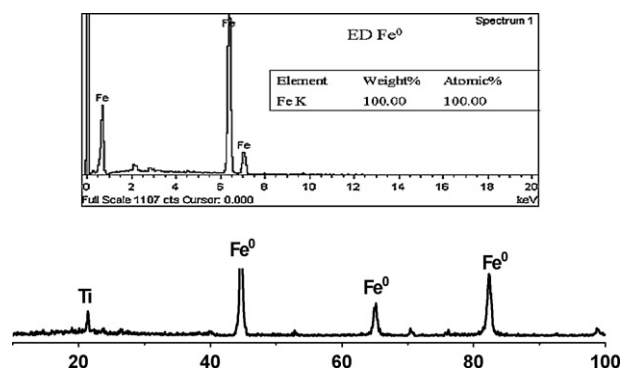


Fig. 2. XRD and EDS results of the ED Fe^0 samples prepared with organic matters in the preparation solution.

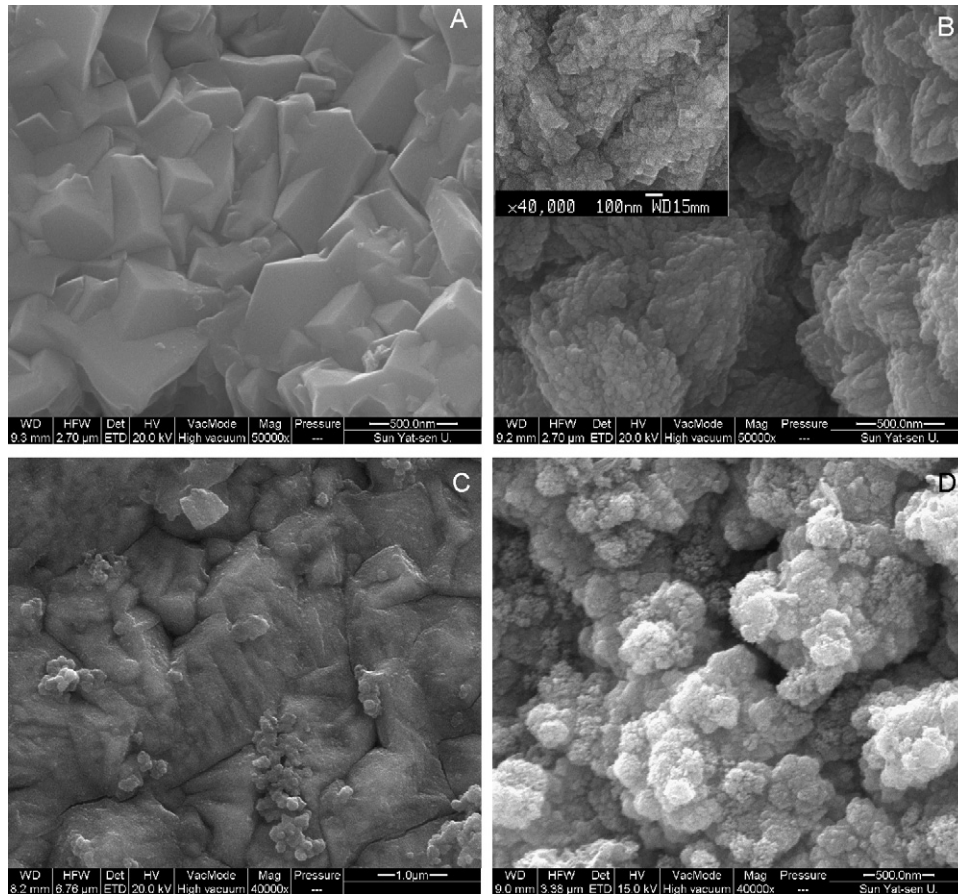


Fig. 3. SEM results of the ED Fe⁰ samples prepared without organic matters (A and C) and with organic matters (B and D) in the preparation solution. A and B were freshly ED Fe⁰, C and D were obtained from A and B after 2 h Cr(VI) reaction of reduction.

The EDS and XRD results in Fig. 2 demonstrated that no other component was present within the ED Fe⁰ sample. The SEM image of Fig. 3(A) showed that the grain diameter of the ED Fe⁰ obtained without any organic matter in the preparation solution was more than 500 nm. Fig. 3(B) showed that the grain diameter of the ED Fe⁰ prepared with the addition of the mixture of three organic matters was less than 100 nm. In the mixture, the sodium saccharin served to decrease the nuclei sizes of treated samples [22,30]. The morphology change of the ED Fe⁰ after reacting with Cr(VI) for 2 h was illustrated in Fig. 3(C and D). The results indicated that a compactly composed passivation film occurred on the ED Fe⁰ surface prepared without the organic matters. By contrast, loosely composed oxide occurred on the ED Fe⁰ surface prepared with the organic matters. The BET surface area of the ED Fe⁰ in Fig. 3(A and B) were measured to be 10.10 and 11.93 m²/g, respectively. It could be seen that there was no significant difference between the BET results. Obviously, the nano-size attributed to increase the ED Fe⁰ corrosion and to decrease the surface passivity by the reaction products.

3.2. Effect of co-existing organic matters in the reaction solution on the Cr(VI) reduction at neutral pH

Fig. 4 showed that the Cr(VI) reduction rate significantly increased with the concentration of co-existing citric acid or oxalic acid in the reaction solution. For example, at the 0.01 M concentrations of citric acid and oxalic acid, 97.7% Cr(VI) decays were obtained after reaction of 60 min. While without any organic matter, only 31.1% Cr(VI) decays were obtained. Moreover, when the organic concentrations increased to 0.1 M, the Cr(VI) reduction proceeded

more rapidly and 100% Cr(VI) decays were achieved after reaction of 10 min.

To further understand the acceleration of Cr(VI) reduction from the point view of electrochemistry, the EIS was employed to measure the electrode system with the ED Fe⁰ as the work electrode. EIS was a powerful method to disclose the reaction kinetics [29] and mechanism [31] occurring at the interface of electrolyte and electrode. Arroyo et al. [32] employed the EIS to determine the effect

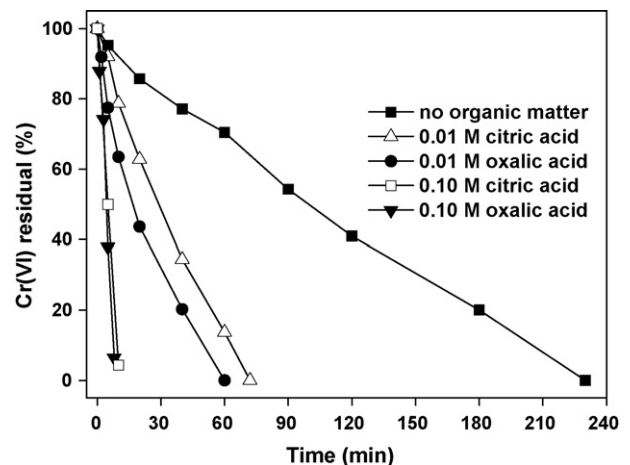


Fig. 4. Cr(VI) reduction by the ED Fe⁰ sample with and without organic matters in 10.0 mg/L Cr(VI) solution.

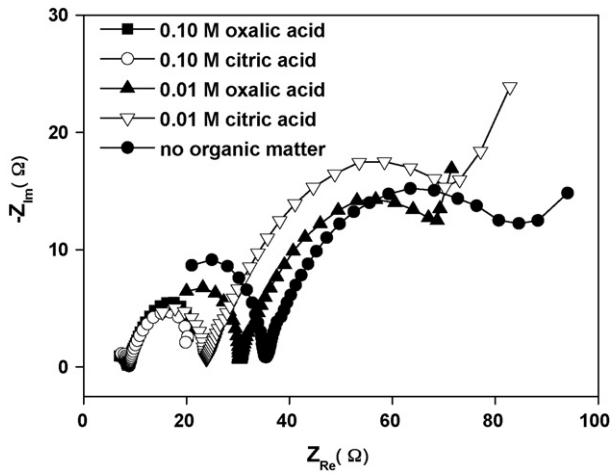


Fig. 5. EIS of the ED Fe⁰ samples with and without organic matters in 10.0 mg/L Cr(VI) solution.

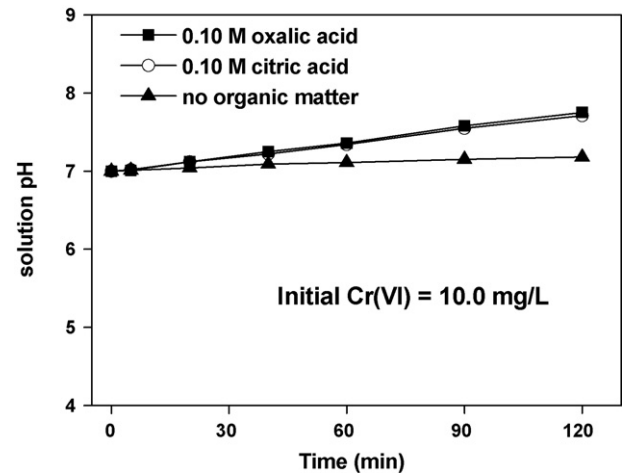


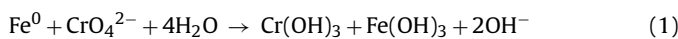
Fig. 6. pH variation during Cr(VI) reduction by the ED Fe⁰ in 10.0 mg/L Cr(VI) solution.

of pH and various binder additives on the corrosion of pure iron in aqueous solution with 0.05 M K₂SO₄.

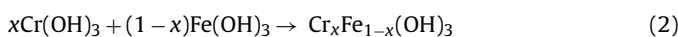
Fig. 5 displayed the EIS results obtained in the Cr(VI) reduction reaction solution with and without the co-existing organic matters at neutral pH. It could be seen that the EIS for each sample consisted of three parts. The high frequency arc was associated with the solution resistance and capacitance in the micro holes at the active pits. The medium frequency arc was associated with the electrochemical process, i.e. the relaxation process of the charge-transfer resistance in parallel with the double layer capacitance. The low frequency arc might be associated with the process from diffusion to semi-infinite diffusion. Notably, in the medium frequency arc, the charge-transfer resistance significantly decreased with the co-existence of the citric acid or oxalate acid, which indicated that the Cr(VI) reduction reaction proceeded more favorably. The decrease in the arc diameter was attributed to the increase of corrosive rate of the ED Fe⁰ immersed in the Cr(VI) solution. This result was in agreement with the variation of corrosive potential and corrosive current listed in Table 1, which showed that the corrosive potential decreased and the corrosive current increased at neutral pH with the increase of organic concentration. Therefore, the Cr(VI) reduction was accelerated by the co-existing organic matters.

3.3. Accelerating mechanism of the reduction of Cr(VI) by organic matters at neutral pH

Two mechanisms were reported to govern the Cr(VI) reduction reactions on the chemically obtained Fe⁰ at neutral pH [2,4,29,33–35]. One underlined a direct electron transfer that had the following reactions [3,4]:

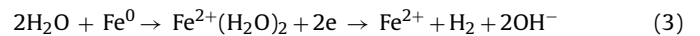


In addition to precipitation of Cr(OH)₃(s), Cr(III) may also form other types of solids with Fe(III) according to Ref. [4,8]:



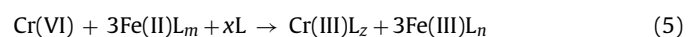
where *x* varies from 0 to 1. Thus, the Cr(VI) was first adsorbed on the Fe⁰ surface and reacted with the Fe⁰. However, the Fe⁰ surface was subject to be passivated by the precipitates of hydroxides of Fe(III) and Cr(III).

The other underlined an indirect electron transfer that had the following reactions [8,33]:



Thus, the water reduction released Fe(II) in the solution, then the Fe(II) reduced Cr(VI) to Cr(III) homogeneously.

In this study, the above mechanism of both the direct and indirect electron transfers appeared to work but tuned. On one hand, the ED Fe⁰ received the nano-size (Fig. 3) to increase its corrosive rate, thus the process through reactions (1), (3) and (4) was accelerated. As a result, the reduction rate of Cr(VI) was increased. On the other hand, the iron species was present as a complex. Fig. 6 illustrated the profile of solution pH during the reaction. It could be seen that during the reaction with the citric acid and oxalic acid, the pH increased from 7.0 to 7.7, which was in the neutral range. At neutral pH, the stability constants of Fe(II) citrate, Fe(III) citrate, Fe(II) oxalate and Fe(III) oxalate are 15.5, 25, 5.22, 20.2, respectively [36], which indicate that the organic matters can interact with the free iron ions to form complex. Also, no precipitate was observed in the solution with a neutral pH. Thus, we concluded that the iron species was present as a complex, and the formation of Fe(II)_m prevented the precipitation of ferrous iron which otherwise occurred in the solution without any organic matter. Moreover, the Fe(II)_m could also reduce the Cr(VI) homogeneously as a main electron donor. Therefore, reaction (4) changed to a process as follows [26]:



In reaction (5), the formation of soluble Cr(III)_{L_z} and Fe(III)_{L_n} was advantageous for avoiding the precipitation of Cr(III) and Fe(III) hydroxides in the Cr(VI) solution, which could efficiently prevent the surface passivation.

Table 1

Corrosive potential and corrosive current of the ED Fe⁰ with or without organic matters in 10.0 mg/L Cr(VI) solution

	Blank	0.01 M oxalic acid	0.01 M citric acid	0.10 M oxalic acid	0.10 M citric acid
Corrosive potential	-0.521 V	-0.564 V	-0.553 V	-0.594 V	-0.598 V
Corrosive current	37.377 μA	137.76 μA	97.629 μA	297.15 μA	278.18 μA

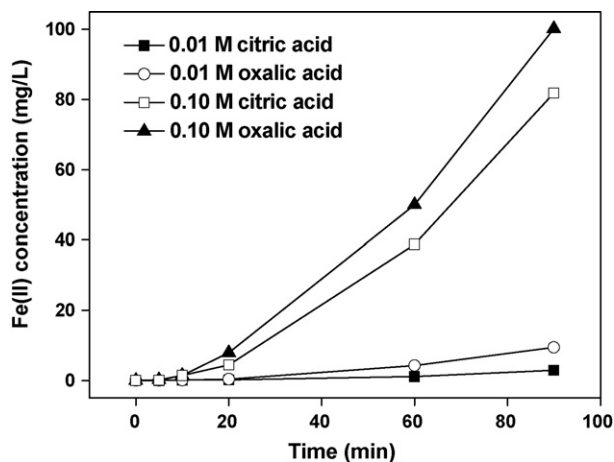


Fig. 7. Concentration of Fe(II) with co-existing citric acid or oxalic acid in 10.0 mg/L Cr(VI) reduction solution.

It should be noted that reactions (3 and 5) underlined that Fe(II) was a main electron donor for the Cr(VI) reduction to occur in the solution homogeneously. This tuned mechanism for the Cr(VI) reduction by the ED Fe⁰ with the co-existing organic matters was supported by the following results.

First, the EIS results in Fig. 5 showed that the corrosive rate of the ED Fe⁰ in the presence of citric acid and oxalic acid was more rapid in Cr(VI) solution than that without the two organic compounds. Thus, more Fe(II) should be present in the reaction solution.

Second, addition of carboxylic acids in solution accelerated the corrosion of Fe⁰. Arroyo et al. reported that the iron corrosion was enhanced by carboxylic acids. And the corrosion rate was increased by the increasing concentration and by the decreasing the chain length of carboxylic acids containing 2–10 carbons [32]. The main reason was considered to be the complex effect between the carboxylic ions and Fe(III)/Fe(II). Such formation of complexes has an important influence on the dissolution of metals, and results in small concentrations of free metal ions, thereby shifts the equilibrium potential of the related metal/metal-ion to negative values [37]. Our results in Table 1 supported the findings by Isecke et al. That was to say, the evolution of ED Fe⁰ to Fe(II/III) was enhanced by the presence of organic matters in the reaction solution. Thus, more Fe(II) should be present in the reaction solution.

At last, Fig. 7 showed the variation of the Fe(II) concentration with the co-existing citric acid or oxalic acid in the Cr(VI) reaction solution. Clearly, before the Cr(VI) was removed completely, and the Fe(II) concentration was small and almost kept constant, indicating the Fe(II) donated the electrons and evolved to Fe(III). Only after the Cr(VI) removal, did the Fe(II) concentration increase. Moreover, the increase of organic compounds led to a more rapid increase of Fe(II) concentration in the solution. The results exactly indicated that the complexed Fe(II) was the main electron donor for the Cr(VI) reduction, which allowed the Cr(VI) reduction to occur in the solution homogeneously.

4. Conclusions

The findings demonstrated that in the preparation of the ED Fe⁰, the added organic matters served to improve the Fe⁰ structure, which benefited the subsequent Cr(VI) reduction. Moreover, in the reduction reaction of Cr(VI) at neutral pH, the co-existing organic matters served to further accelerate Cr(VI) reduction rate. In the ED Fe⁰ preparation process, the co-existence of a mixture of saccharin, L-ascorbic acid and sodium dodecyl sulfate in the preparation solu-

tion allowed the ED Fe⁰ to receive a nano-size. The nano-sized Fe⁰ could corrode more rapidly, thereby showed significantly higher activity in the Cr(VI) reduction at neutral pH than the ED Fe⁰ prepared without any organic matter. In the Cr(VI) reduction process at neutral pH, the Cr(VI) reduction reaction was accelerated by the co-existing citric acid or oxalic acid, and the higher concentration of the organic matters, the more rapid Cr(VI) reduction rate. The co-existence of citric acid or oxalic acid complexed the free iron ions and chromium in the reactions solution, which prevented passivation of the ED Fe⁰. The complexed Fe(II) species functioned as a main electron donor to the Cr(VI) in the solution, thus the Cr(VI) reduction rate was accelerated.

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