

Synthesis, characterization and re-activation of a Fe⁰/Ti system for the reduction of aqueous Cr(VI)

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Abstract

The conventionally employed zero-valent iron (Fe⁰) particles suffer a formation of surface oxides to lower their activity prior to use. During their using process for contaminant remediation, such oxide formation is also encountered, while the cumbersome handling of particles impedes the Fe⁰ recovery. To conquer the drawbacks, a Fe⁰ film was synthesized by electrodepositing ferrous ion cathodically on titanium (Ti) substrate to form a new Fe⁰/Ti system. X-ray diffraction (XRD) revealed that the freshly electrodeposited (FED) Fe⁰ film was free of oxides, which was attributed to the particularity of electrodeposition procedure. Reduction results of 10.0 mg/L chromium [Cr(VI)] indicated that the FED Fe⁰ film had higher activity than the oxide-covered counterpart. Further analysis of the pH-dependent Cr(VI) reduction reaction indicated that the Fe⁰/Ti system kept its activity and could be reused for further Cr(VI) reduction at pH 3.0 and 4.0, while it was inactivated at pH 5.0 and 7.0. Due to the easy handling of Fe⁰/Ti system, the inactivated Fe⁰ was recovered significantly through a cathodic reduction.

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1. Introduction

Zero-valent iron (Fe⁰), favorably donating electrons to acceptors with relatively high redox potentials, has been intensively studied for the contaminant remediation in waters [1,2]. Along with the extensive research in laboratory, field applications using permeable reaction barrier (PRB) filled with the Fe⁰ material have emerged for groundwater remediation [3,4]. The running results have promisingly demonstrated that numerous contaminants such as nitro- [4] and chloro-compounds [2], toxic metals [5], nitrate and arsenate [6] are effectively transformed in situ to relatively more benign products.

However, the conventionally employed Fe⁰, both commercial and self-made, are particles that are covered with a surface oxide

layer [3,6,7]. For example, the commercial particles from Toda Kyogo, Japan, have a Fe⁰ core with a magnetite (Fe₃O₄) shell [8], and some pristine self-made Fe⁰ particles even include 19% zero-valent state and 81% iron oxides determined by Mössbauer spectroscopy [6]. The oxide layer greatly impedes the Fe⁰ reduction activity. Recently, Sohn et al. have reported that the reaction rate using the oxide-covered Fe⁰ decreases 50% in the nitrate reduction [7].

For the commercially obtained Fe⁰, to be effective, measures including acid washing [9], ultrasonication [10], thermal hydrogen reduction at 400 °C [11] or deposition of copper [11] have been undertaken prior to use. Such measures serve to enhance the Fe⁰ activity by removing the surface oxide layer. For example, after the thermal hydrogen reduction at 400 °C for 3 h, the reaction rate of nitrate reduction doubles [11]. However, the inconvenience and cost increase brought by those measures are of concern in the application of Fe⁰ technique.

For the self-made Fe⁰ particles, to be effective, it is desired to preclude the formation of surface oxides during the synthesis,

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although it is actually difficult to do so. The most frequently employed synthesizing method is the NaBH_4 [1,2] or KBH_4 [7] liquid reduction. Although the synthesis procedure is carefully designed to use organic solvents or degassed water or inert gas, the multi-step procedure that consists of reaction, separation, washing and drying [1] is time-consuming as well as inconvenient, thus not capable of ensuring to preclude any occasional contact of oxygen that results in the surface oxides.

Moreover, for the commercial and self-made Fe^0 particles, during the reduction process of contaminant, the formation of the surface oxides is also encountered due to the contact with surrounding electrolyte [12]. Also, the Fe^0 usually overdoses the stoichiometric requirement for a complete reduction of the contaminant [1,3,7]. As a result, once the surface oxides lower and inactivate the Fe^0 activity, the remaining Fe^0 materials become a solid waste. Clearly, it is expected to recover the remaining Fe^0 . However, any recovery operation is a cumbersome handling due to the property of particles, and no effective means has been developed to date.

This study attempts to radically preclude the adverse effect of the Fe^0 surface oxides during the synthesis process by electrodepositing a Fe^0 film on titanium substrate. Also, the film allowed that some simple measures could be adopted to further prevent the occurrence of surface oxides during storage or utilization. Although the deposition of iron has been widely studied in areas of materials and electrochemistry [13,14], it has not been employed for the contaminant remediation. Herein, taking into account the easy handling and robustness, titanium was selected as the substrate for forming a Fe^0/Ti system. Thus, developed system prevented the adverse effect of the surface oxides by (i) keeping an anaerobic atmosphere and a reducing state to obtain an oxide-free Fe^0 film during the synthesis process, (ii) providing a simple and rapid post-treatment of the as-synthesized samples, and (iii) benefiting the recovery of the oxide-inactivated Fe^0 activity during the contaminant reduction process by cathodic reduction.

In the evaluation of Fe^0 film activity, aqueous hexavalent chromium [Cr(VI)] solution was used as probe media as usual [15–17]. The chromium is widely used in chemical industry such as alloys, leather, lumber and pigment [1,3,15], and has become a commonly identified contaminant in waters including subsurface waters. In aqueous solution, the distribution of the chromium redox species relies on pH, while primarily includes the forms of Cr(VI) and trivalent Cr [Cr(III)] [16–18]. The Cr(VI) is highly toxic to human and animals as well as highly mobile in waters, thereby is of great concern for the environmental community. However, the Cr(III) is much less toxic and quite immobile. Consequently, with respect to the Cr(VI) pollution remediation, its reduction process to Cr(III), particularly by the Fe^0 [16,19], is environmentally desired. This study focused on precluding the adverse effect of the Fe^0 surface oxides during both the synthesis and the utilization of the Fe^0 film and the Fe^0 performance that was evaluated in terms of the reduction the Cr(VI) in aqueous solution.

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. Optimization of Fe^0 film synthesis

The high purity titanium sheets (10 mm × 10 mm × 0.5 mm) (Xian, China) were polished with sand paper, rinsed with double distilled water, and subsequently cleaned by ultrasonication in acetone and in double distilled water, then dried in nitrogen stream. Synthesis of the Fe^0 film was performed in a conventional three-electrode system, in which the titanium sheet was used as the cathode, a pure iron sheet (1 cm × 1 cm) as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The solution for synthesis, composed of 0.2 M ferrous sulfate, 0.5 M sodium sulfate and 0.4 M H_3BO_3 , was bubbled with nitrogen for 60 min.

During the Fe^0 synthesis, a cathodic current was applied by a Potentiostat/Galvanostat model (HDV-7C, Sanming, China). The solution pH was remained by pumping the solution for synthesis to replace the used electrolyte continuously. When the Fe^{2+} concentration was monitored to keep unchanged, the synthesis procedure was completed. Thereafter, the Fe^0 film sample was washed by nitrogen-bubbled water, rinsed by acetone and stored in acetone for characterization and Cr(VI) reduction reaction.

2.3. Methods of analysis

2.3.1. Surface morphology analysis

X-ray diffraction (XRD) and scanning electron microscope (SEM) were employed to investigate the chemical composition and surface morphology of Fe^0 film 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 $\text{K}\alpha$ 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 of samples.

2.3.2. Cr(VI) reduction by the Fe^0/Ti system

The Cr(VI) reduction experiments using the Fe^0/Ti system were carried out in a home-made setup, in which a borosilicate glass vessel with 100 mL effective volume was used as the reactor. To prevent the oxidation of Fe^0 by air, nitrogen was supplied continuously into the setup to fill with the reactor inside and outside. In each batch experiment, 10.0 mg/L potassium chromate was treated by $20.0 \pm 0.2 \text{ mg Fe}^0$. The reaction solution pH was buffered by addition of oxalic acid and sodium oxalate. Samples with 2.0 mL were taken at

defined time intervals and filtered for an immediate analysis.

2.3.3. Cathodic reduction of the used Fe⁰/Ti system

To further utilize the remaining Fe⁰ after the first run of Cr(VI) reduction reaction at pH 5.0 and 7.0, cathodic reduction was performed at 2.5 mA/cm² current density and pH 4.0 in a conventional three-electrode cell containing 0.5 M Na₂SO₄ and 0.4 M HBO₃. The used Fe⁰/Ti system was washed by distilled water and employed as the work electrode, a platinum sheet (1 cm × 1 cm) as the auxiliary electrode and an SCE as the reference electrode.

2.3.4. Analysis

The Cr(VI) concentration was quantified by the diphenyl carbazide method [20] on a UV–visible spectrophotometer (TU1810, Universal Analysis, Beijing, China), 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 concentration of Cr(VI) was calculated from the complex absorbance at 540 nm.

Electrochemical impedance spectroscopy (EIS) [21] was performed to determine the charge-transfer resistance of the used Fe⁰/Ti system before and after the cathodic reduction on an electrochemical work station (IM6E, Germany). All potentials were reported with respect to the SCE. In the EIS experiments, the amplitude of sinusoidal waveform was ±10 mV, and the applied frequency ranged from 5 × 10⁻³ to 10⁵ Hz.

3. Results and discussion

3.1. Optimization of the Fe⁰ film synthesis

To optimize the conditions of Fe⁰ film synthesis on titanium by electrodeposition, key parameters of solution pH, temperature, Fe²⁺ concentration and current density were varied. Thereafter, Cr(VI) reduction experiments were performed to evaluate the freshly electrodeposited (FED) Fe⁰ film. Each Cr(VI) reduction experiment lasted 25 min, and the results are listed in Table 1. As can be seen from Table 1, in the experimental range, the three parameters of solution pH, Fe²⁺ concentration and temperature only slightly influenced the subsequent Cr(VI) reduction efficiency, and the three factors were selected to be 2.5, 0.20 M and 25.0 °C, respectively. The current density influenced the Cr(VI) reduction remarkably and 2.5 mA/cm² was found to be optimal.

Table 1

Synthesis conditions of Fe⁰: Fe²⁺ concentration ([Fe²⁺], mol/L), pH, temperature (*T*, °C) and current density (*I*, mA/cm²)

[Fe ²⁺] at <i>T</i> = 25, pH 2.5, <i>I</i> = 2.5	Cr(VI) red. (%)	<i>T</i> at [Fe ²⁺] = 0.2, pH 2.5, <i>I</i> = 2.5	Cr(VI) red. (%)	pH at [Fe ²⁺] = 0.2, <i>T</i> = 25, <i>I</i> = 2.5	Cr(VI) red. (%)	<i>I</i> at [Fe ²⁺] = 0.2, <i>T</i> = 25, pH 2.5	Cr(VI) red. (%)
0.10	73	25.0	82	2.5	82	1.0	70
0.20	82	35.0	71	2.0	83	2.5	82
0.30	78	45.0	73	1.5	81	5.0	49

The Cr(VI) reduction efficiency (red.) was obtained at 25 min reaction of 10.0 mg/L Cr(VI) solution with reaction pH 4.0.

3.2. XRD characterization of the Fe⁰ film

The Fe⁰ film sample freshly electrodeposited on the titanium under the above optimized conditions was characterized by XRD to disclose its chemical composition, and the results are shown in Fig. 1. The FED Fe⁰ film was completely composed of Fe⁰ and free of oxides since no peak of other components such as oxides was observed.

By comparison, the Fe⁰ film on titanium after an exposure to air at room temperature (25 °C) for 168 h was observed by the XRD, and the results are also shown in Fig. 1. Distinctly, the intentionally air-exposed Fe⁰ film was covered with oxides, which embraced magnetite/maghemite (Fe₃O₄/γ-Fe₂O₃) and lepidocrocite (L: γ-FeOOH). Oxides were formed by air oxidation under the intentional exposure, and the fresh Fe⁰/Ti system was proposed to be stored in acetone.

3.3. Effect of the oxides on the Fe⁰ film activity

To further investigate the effect of the surface oxides formed under the intentional air-exposure, four sets of Cr(VI) reduction experiments were performed. In the first set, the FED Fe⁰ film was used, and in the other three sets, the 1, 12 and 168-h air-exposed Fe⁰ film samples were used, respectively. The Cr(VI) reduction results shown in Fig. 2 illustrated that the Cr(VI) concentration decayed rapidly using the FED Fe⁰ film, but significantly more slowly using the three air-exposed samples.

3.4. Preclusion of surface oxides during the Fe⁰ film synthesis

The absence of oxides enjoyed by the FED Fe⁰ film appeared to differ from the conventional Fe⁰ particles covered with an oxide layer [6,22,23]. During the process of NaBH₄ reduction to synthesize the Fe⁰ particles, inert gas of nitrogen was externally provided and co-produced hydrogen from the NaBH₄ oxidation protected the fresh Fe⁰ from the air oxidation [6]. However, in our experience, it was not easy to obtain a complete protection because any occasional air entry into the tank led to the oxidation of the Fe⁰ particles. Also, during the NaBH₄ reduction the solution pH was adjusted to 6.86 [1], and a small amount of O₂ favorably resulted in the oxide formation through the scheme below:



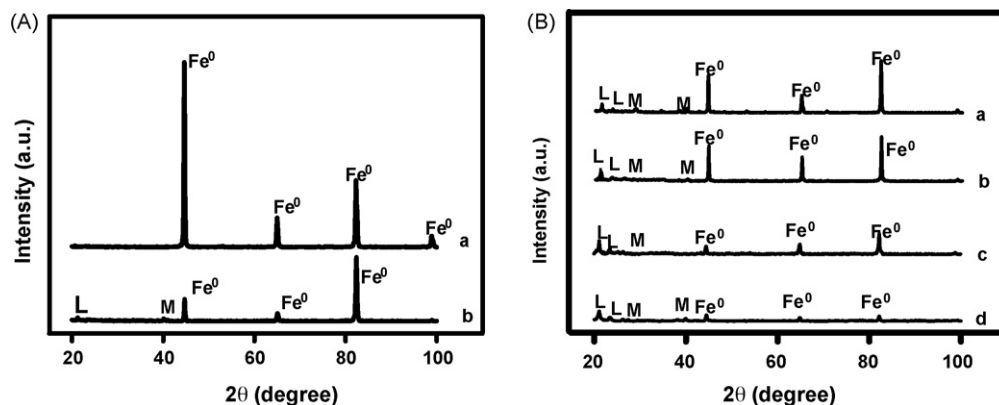


Fig. 1. XRD of the Fe⁰/Ti sample. (A) Freshly electrodeposited (FED) sample (a) and 168-h air-exposed sample (b); (B) 30-min reacted sample in Cr(VI) reduction at pH 3.0 (a), 30-min reacted sample in Cr(VI) reduction at pH 4.0 (b), 120-min reacted sample in Cr(VI) reduction at pH 5.0 (c), 120-min reacted sample in Cr(VI) reduction at pH 7.0 (d). Peak ascriptions: M for magnetite/maghemite (Fe₃O₄/γ-Fe₂O₃) and L for lepidocrocite(γ-FeOOH).



Sometimes, the solution pH could be adjusted to be lower than 6.86, while during the synthesis, the pH increased sharply because of the hydrogen evolution to enhance the above oxide formation.

By contrast, during the electrodeposition process, apart from the nitrogen supplied and the co-produced hydrogen from the acidic media under the cathodic current, the pH was as low as 2.5. Consequently, the H⁺ amount was sufficient to buffer the solution in a certain period of time. On the other hand, fresh electrolyte solution was conveniently supplemented to keep the pH, thus the process through Eq. (1) did not occur. Moreover, the externally applied cathode current protected the Fe⁰ film from oxidation, thus the process through Eq. (2) did not occur. In fact, with the cathode current, it was not favorable for the Fe⁰ to donate its electrons and any oxidation was inhibited compared to the otherwise identical case. Consequently, the as-synthesized Fe⁰ sample was initially free of surface oxides. After that the post-treatment procedure following the electrodeposition con-

sisted of washing by degassed water and acetone resin, and these treatments could be performed rapidly because the handling of Fe⁰/Ti system was much easier than that of the Fe⁰ particles. Therefore, the preclusion of the surface oxidation during both the synthesis and the post-treatment was realized.

3.5. Reuse of the FED Fe⁰ film

3.5.1. Utilization of the remaining Fe⁰ after the Cr(VI) reduction at pH 3.0 and 4.0

Fig. 3 displayed the results of Cr(VI) reduction by the FED Fe⁰ film at buffered pH 3.0, 4.0, 5.0 and 7.0. Obviously, the H⁺ accelerated the Cr(VI) reduction rate, and the pH-dependence of Cr(VI) reduction efficiency was consistent with other reports [17,19,24,25].

On the other hand, the Fe⁰ content was determined to be 20.0 ± 0.2 mg by weighing, which was excessive to react with the 10.0 mg/L Cr(VI) in 100 mL solution according to the stoichiometry [3,20,25,26]. That is to say, the Fe⁰ was remained and its activity would be kept after the first run, so the remaining Fe⁰ content could be further utilized directly. To confirm this impli-

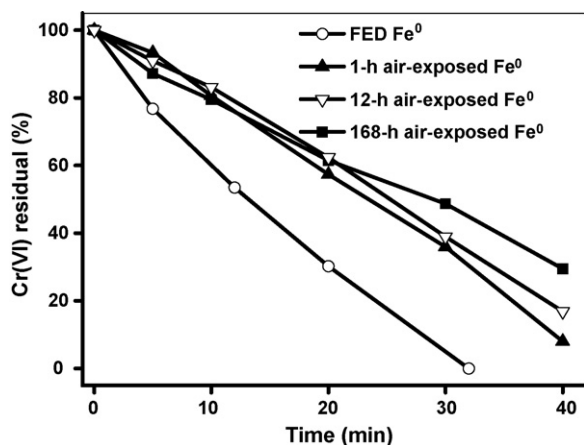


Fig. 2. Cr(VI) reduction by FED Fe⁰/Ti sample and air-exposed Fe⁰ samples in 10.0 mg/L Cr(VI) solution at pH 4.0.

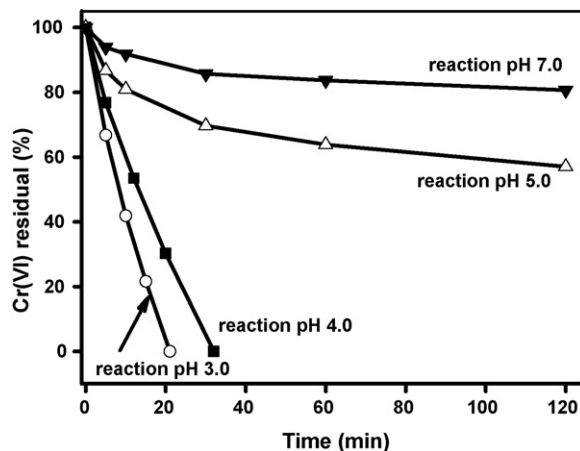


Fig. 3. Cr(VI) reduction by the FED Fe⁰/Ti sample in 10.0 mg/L Cr(VI) solution at different pH.

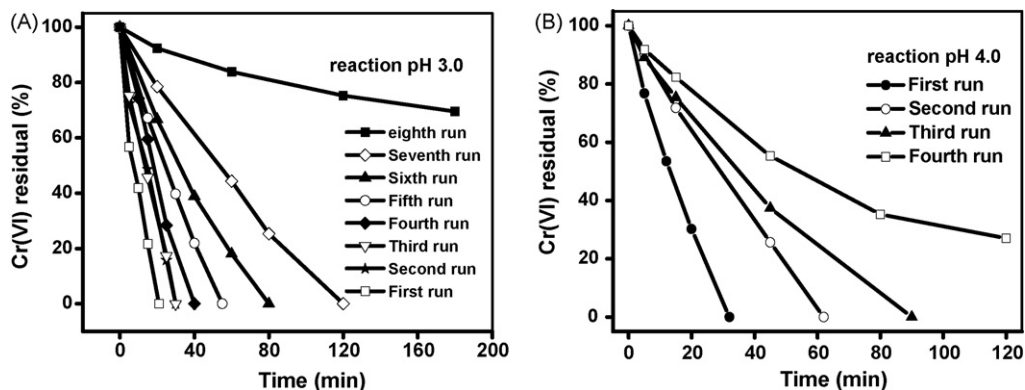


Fig. 4. Cr(VI) reduction by the recycled Fe⁰/Ti samples in 10.0 mg/L Cr(VI) solution at pH 3.0 and 4.0.

cation, after the first run of Cr(VI) reduction at pH 3.0 and 4.0, the Fe⁰/Ti system was reused to treat the fresh Cr(VI) solution with 10.0 mg/L concentration. The results given in Fig. 4 confirmed that the remaining Fe⁰ content could be directly utilized in the reduction of fresh Cr(VI) solution. Furthermore, after the eighth run at pH 3.0 and fourth run at pH 4.0, the EDS results

in Fig. 5 revealed that the Fe atom percentages were small and the oxygen percentages were as large as 66.89 and 58.30% at pH 3.0 and 4.0, respectively, indicating the exhaustion of Fe⁰ content through the direct reutilization.

Furthermore, Figs. 4 and 5 displayed that after the first run, the remaining Fe⁰ could be reused for seven runs in the reduction of Cr(VI) at pH 3.0, while at pH 4.0 after the three reused runs the Fe⁰ content appeared to be used up. To disclose this difference, XRD means was employed to investigate the chemical composition of the Fe⁰ film during the Cr(VI) reduction, and the results are shown in Fig. 1B. Fig. 1B revealed that some oxides of magnetite/maghemite (M: Fe₃O₄/γ-Fe₂O₃) and lepidocrocite (L: γ-eOOH) were formed on the Fe⁰ surface after the reactions at both pH 3.0 and 4.0, whereas at pH 4.0 the oxide peak were more mature than at pH 3.0, suggesting that the amount of the oxides was larger. Therefore, the runs of the reutilization of the Fe⁰/Ti system at pH 4.0 were fewer than at pH 3.0.

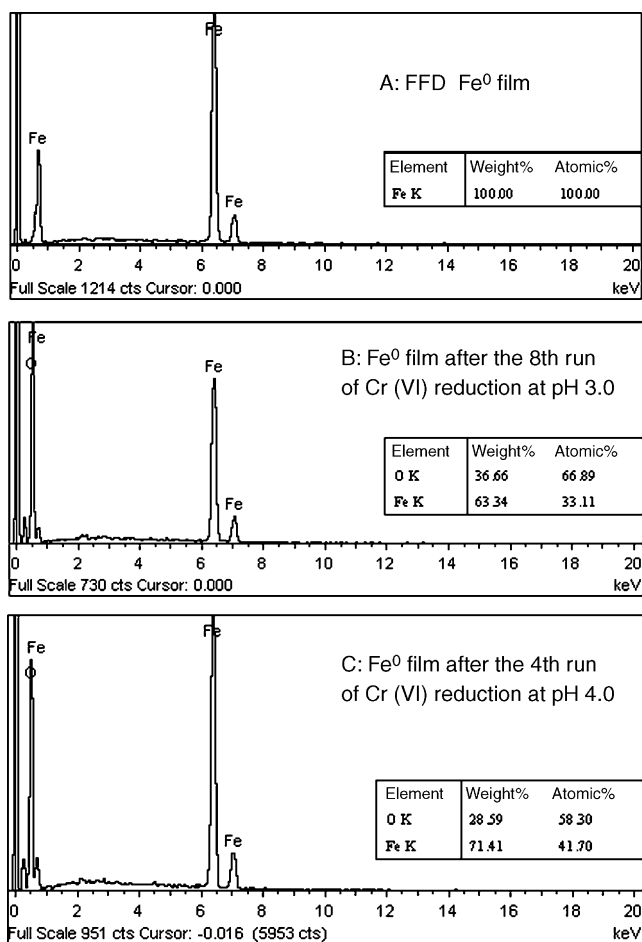


Fig. 5. EDS results of Fe⁰ film samples. (A) The Fe atom occupied 100% atomic percentage, indicating that no oxygen species was present on the Fe⁰ film. (B and C) The Fe atom occupied 33.11% and 41.70%, respectively, while O atom occupied 66.89% and 58.30%, respectively, indicating that the O atom mainly existed in the form of oxides after the Cr(VI) reduction.

3.5.2. Inactivation of the remaining Fe⁰ content during the Cr(VI) reduction at pH 5.0 and 7.0

Fig. 3 showed that contrast to the activity keeping after the first run at pH 3.0 and 4.0, the reaction slowed down significantly after 60 min at pH 5.0 and 7.0. During the subsequent time span from 60 to 120 min, only further 6.8 and 3.0% Cr(VI) reduction were obtained, respectively. The XRD results shown in Fig. 1B illustrated that both Fe⁰ and oxides were present on the Ti substrate. We failed to utilize the remaining Fe⁰ content directly to treat fresh Cr(VI) solution as in the cases at pH 3.0 and 4.0 (not shown). At pH 5.0 and 7.0, it appeared that the remaining Fe⁰ was inactivated by the oxides formed after the first run of Cr(VI) reduction.

It would also be interesting to compare the four SEM images of the Fe/Ti samples after 2-h reaction with the SEM image of the freshly electrodeposited Fe⁰ film (uncovered by oxides). The results shown in Fig. 6 indicated that at pH 5.0 and 7.0, the oxides were compactly composed, but loosely composed at pH 3.0 and 4.0. The oxides were considered passivated film which was formed by oxidation of chromate at neutral pH (pH 5.0 and 7.0). Obviously, the compactly composed passivated film formed at pH 5.0 and 7.0 inactivated the remaining Fe⁰.

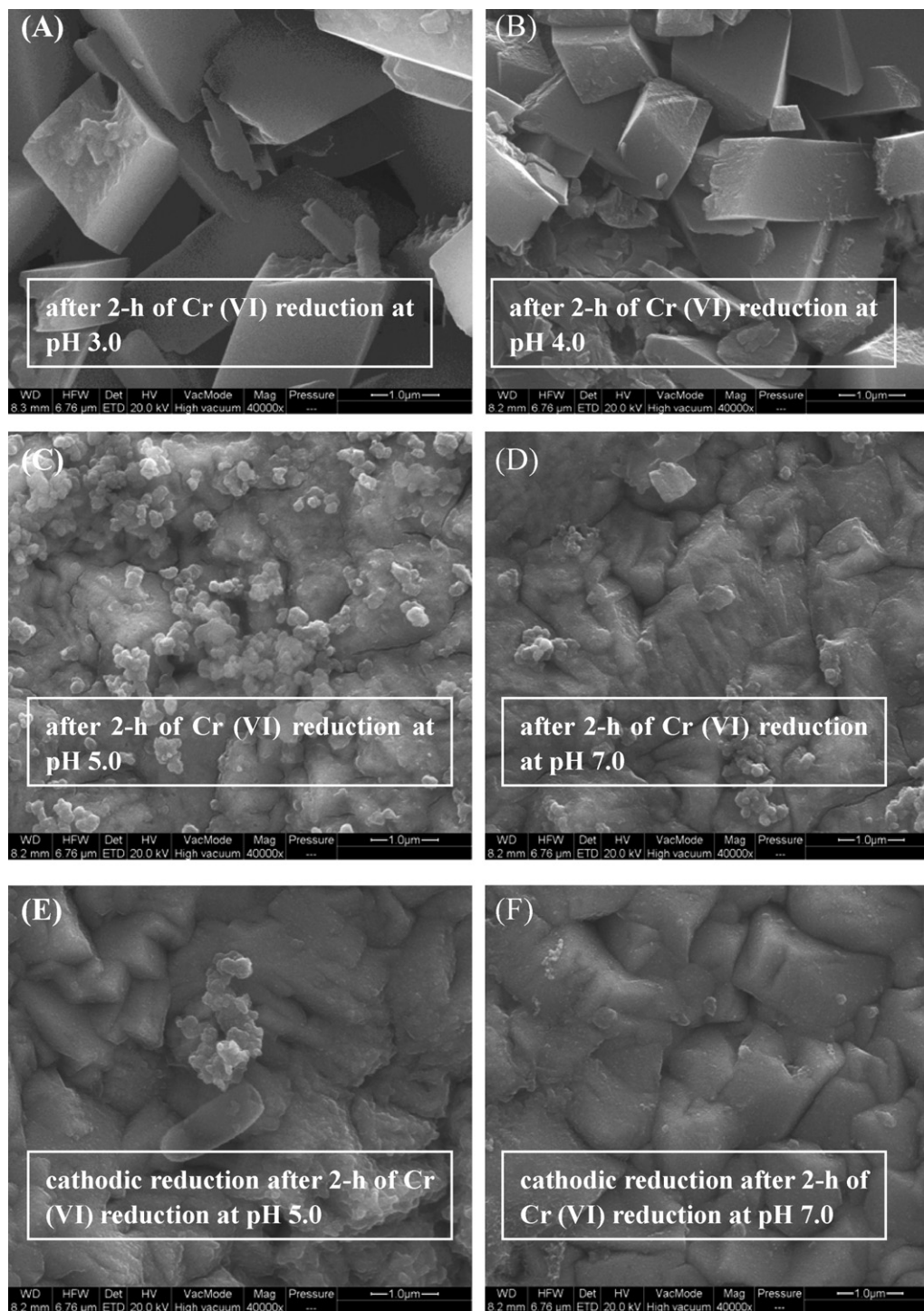


Fig. 6. SEM images of the Fe⁰/Ti samples. The Fe⁰ film samples were obtained after 2-h Cr(VI) reduction reaction at pH 3.0 (A), pH 4.0 (B), pH 5.0 (C) and pH 7.0 (D), (E and F) were obtained from (C and D) after the cathodic reduction at pH 4.0, respectively.

3.5.3. Utilization of the inactivated Fe⁰ content after the Cr(VI) reduction at pH 5.0 and 7.0 by cathodic reduction

The Fe⁰ could be directly reused after the Cr(VI) reductions at pH 3.0 and 4.0, however, most water systems including the subsurface water are at neutral pH. Thus, it appeared more desirable to recover the inactivated Fe⁰ during the Cr(VI) reductions at pH 5.0 and 7.0. Consequently, two methods were tested after the first run of Cr(VI) reduction at pH 5.0 and 7.0. One was acid

immersion and the other was cathodic reduction. The results of Cr(VI) reduction were shown in Fig. 7. Fig. 7 displayed that the cathodic reduction at pH 4.0 was more effective to recover the Fe⁰ than the acid immersion and the cathodic reduction at pH 2.5. The surface oxides might be removed by immersion into the more extremely acidic solution with pH lower than 2.5, while the Fe⁰ could also be destroyed through a fast acidic corrosion.

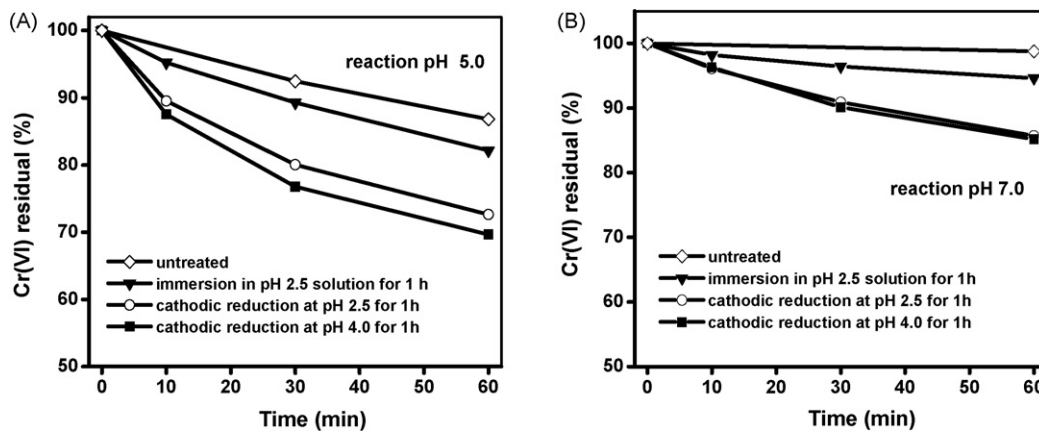


Fig. 7. Comparison of Cr(VI) reduction at pH 5.0 (A) and at 7.0 (B) using differently treated Fe⁰/Ti system.

To assess the cathodically reduced Fe⁰/Ti system, Cr(VI) reduction experiments using thus treated Fe⁰/Ti system continued in the residual Cr(VI) solution, and the results are shown in Fig. 8. Fig. 8 displayed that after the cathodic reduction, a faster Cr(VI) reduction compared to the inactivated Fe⁰ film sample (see Fig. 3) was achieved, and that after 60 min reaction, the Cr(VI) concentration decreased from 6.36 to 4.43 mg/L at pH 5.0 and decreased from 8.58 to 7.26 mg/L at pH 7.0, respectively. Thereafter, the Fe⁰/Ti system was cathodically reduced repeatedly for further three runs, and similarly each cathodical reduction led to a significant Cr(VI) reduction.

The SEM results in Fig. 6E and F illustrated that after the cathodic reduction, the content of iron increased, and the content of oxygen decreased, indicating that the oxides were removed partially, thus the inactivated Fe⁰ was recovered significantly through the cathodic reduction.

To further understand the removal of surface oxides by the cathodical reduction, electrochemical impedance spectroscopy was employed to measure the used Fe⁰/Ti system with and without the cathodic reduction, respectively. The EIS was such a powerful method to disclose the Fe⁰ reaction kinetics [21] and mechanism [25] to reduce contaminants. During the EIS measurement, a sinusoidal signal of small amplitude was superimposed onto the system, thus barely disturbing the charac-

teristics of electrode surface. Melitas and Farrell [21] employed the EIS to determine the corrosion rates and charge-transfer resistances associated with the Cr(VI) removal by iron wires. They found that the iron coated with an air-formed oxide was significantly less effective than the initially oxide-free iron.

Fig. 9 displayed the EIS results of the used Fe⁰/Ti samples before and after the cathodic reduction. It could be seen that the EIS for each sample included one arc and the arc diameter corresponded to the charge-transfer resistance reduction [21]. Clearly, after the cathodic reduction, the charge-transfer resistance significantly decreased, confirming the removal of the surface oxides by the cathodic reduction. The decrease in the arc diameters was attributed to the increase in the Fe⁰ corrosion rate on the Ti substrate. Because the surface oxides protected the Fe⁰ from corrosion, so less surface oxides caused a faster Fe⁰ corrosion rate.

It was documented that a two-stage electrochemical dissolution mechanism governed the galvanostatic reduction of passive film on Fe⁰ [27]. The first stage included a potential that was ascribed to the Fe^{II} dissolution from Fe₃O₄, and the second stage included a potential plateau that corresponded to the equilibrium potential of bare Fe⁰ with minor amount of a surface-trapped Fe^{II}. Obviously, the cathodic reduction could make the compact passivated layer more loosely by destroying its structure due to a

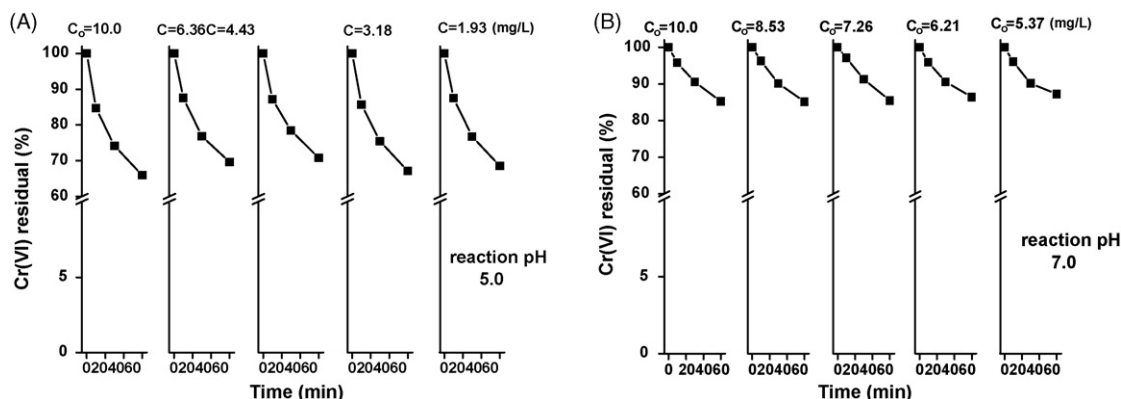


Fig. 8. Comparison of Cr(VI) reduction between using the fresh Fe⁰/Ti sample and the cathodically treated Fe⁰/Ti sample at pH 5.0 (A) and at 7.0 (B): the first curve from left in A or B is for the fresh Fe⁰/Ti system.

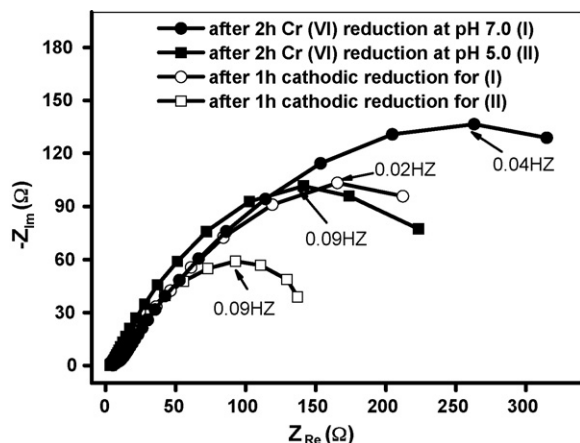


Fig. 9. EIS of used Fe⁰/Ti samples before and after the cathodic reduction at pH 5.0 and 7.0. Before the cathodic reduction, the samples were obtained after the 2 h Cr(VI) reduction reaction in 10.0 mL⁻¹ Cr(VI) solution at pH 5.0 and 7.0, respectively.

reduction of the oxides, thus the oxide layer was partially flaked off as indicated by the SEM (see Fig. 6). Also, these changes left the remaining Fe⁰ exposed to the Cr(VI), then the inactivated Fe⁰ was recovered.

4. Conclusions

A new Fe⁰ film free of surface oxide layer could be synthesized by electrodeposition on titanium substrate, and the freshly electrodeposited Fe⁰ film enjoyed a higher activity than that with an oxide layer. During the Cr(VI) reduction, a pH-dependant growth of the surface (hydro)oxide layer was encountered. At pH 3.0 and 4.0, the loose oxide layer on the Fe⁰ surface allowed to keep a sustainable activity, so the remaining Fe⁰ content on the Ti substrate was used in the further reactions. By contrast, at pH 5.0 and 7.0, the compact oxide layer on Fe⁰ film led to an activity loss, while the remaining Fe⁰ could still be used after a cathodic reduction of the Fe⁰ film system. The removal of surface oxides by the cathodic reduction to recover the inactivated Fe⁰ enhanced the applicability of the Fe⁰ technique for the Cr(VI) reduction at neutral pH. Interestingly, the Fe⁰/Ti system developed herein embraced not only a high activity initially due to the oxide-free surface, but an easy handling that readily allowed the cathodic reduction to recover the inactivated Fe⁰.

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