



# Electrochemical depassivation for recovering Fe<sup>0</sup> reactivity by Cr(VI) removal with a permeable reactive barrier system

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## ABSTRACT

A new electrochemical permeable reactive barrier (Electro-PRB) system for removal of hexavalent chromium [Cr(VI)] using Fe<sup>0</sup> meshes was developed. Electro-PRB was found to be effective for electrochemical depassivation of Fe<sup>0</sup> to remove Cr(VI) during treatment. During initial treatment, Cr(VI) removal rates decreased with time, due to loss of Fe<sup>0</sup> reactivity by mineral fouling. After Fe<sup>0</sup> was passivated, electrochemical depassivation was introduced for different electrolysis times to recover Fe<sup>0</sup> reactivity. It was found that there was approximately 100.4–131.3% initial removal rate recovery, due to the electrochemical break down of precipitates on the Fe<sup>0</sup> surfaces. During the treatment, the decreasing pH and increasing oxidation–reduction Potential (ORP) of the effluent implied the passivation of Fe<sup>0</sup> surfaces. Scanning electron microscope analysis of acid-washed, electrochemically depassivated, and passivated Fe<sup>0</sup> confirmed the efficiency of Electro-PRB in the recovery Fe<sup>0</sup> reactivity. The results indicate that the Electro-PRB system proposed here is capable of recovering the reactivity of Fe<sup>0</sup>, which may prolong the operation of Cr(VI) removal processes.

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## 1. Introduction

Chromium is a common contaminant of groundwater in numerous worldwide industrial regions [1–3]. Sources of chromium are metal plating, leather tanning, and pigment production [4]. Chromium exists in the forms of Cr(III) and Cr(VI) [5]. Cr(III) is an essential human nutrient, whereas Cr(VI) is extremely toxic and carcinogenic when the content exceeds the permissible drinking water limit [6–8]. The conventional treatment processes for Cr(VI)-polluted groundwater are pump-and-treat technologies [9], including adsorption [10], coagulation [11], ion exchange [12] and biological treatment methods [13]. These methods have disadvantages that limit their application, including the problem of subsequent disposal of toxic products or byproducts, treatment effectiveness, and high costs of operation [14]. In comparison to other pump-and-treat technologies, permeable reactive barriers (PRBs) have become more competitive and economical. PRBs have advantages in operation and maintenance costs, external power inputs, and above ground structures [15]. They can simultaneously remove various contaminants, such as metals [16], organics [17], radionuclides [18], and nutrients [19]. The most commonly used

reactive media is zero-valent iron (Fe<sup>0</sup>) [20] because of its low cost, high reductive potential and high reactivity.

According to previous studies, Cr(VI) is reduced to Cr(III) with the oxidation of Fe<sup>0</sup> to Fe(II) and Fe(III), and then precipitates in the form of Cr(III) hydroxides or Fe(III)/Cr(III) (oxy)hydroxides in the PRB system [4,21,22]. The high effectiveness of Cr(VI)-polluted groundwater removal by Fe<sup>0</sup>-PRBs in the laboratory and field has been reported by many researchers [23]. However, passivation of Fe<sup>0</sup> is the main problem for long-term effectiveness [24,25]. Depending upon the thickness and composition of precipitates, which mask the redox active sites, electrical resistance arises and Fe<sup>0</sup> reactivity is decreased to varying extent. Henderson and Demond [26] gathered operational data from several in situ PRBs from many pollution sites and identified the factors that influence PRB performance, determining that Fe<sup>0</sup> reactivity was the main factor limiting PRB longevity compared with permeability reduction. After four years of monitoring a full-scale PRB designed to remediate a Cr-polluted aquifer in Switzerland, Flurry et al. [27] found that thick layers of Fe-hydroxides resulted in diminished Fe<sup>0</sup> reductive capacity, which impacted long-term effectiveness, while pore space reduction was a minor factor. It was reported that geochemical changes in reactive media, which depend on the inorganic characteristics of water, can lead to the formation of different kinds of minerals [28]. Cr(III)–Fe(III) (oxy)hydroxide solids resulting from coprecipitation of Fe(III) and Cr(III), various Fe oxides, Fe

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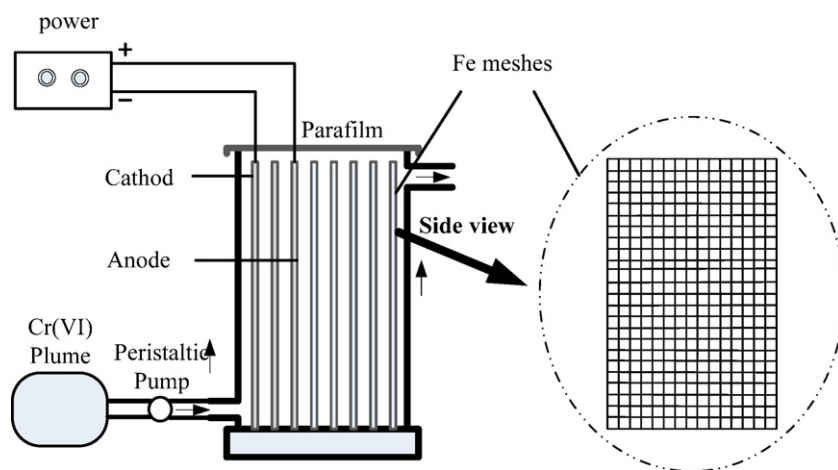


Fig. 1. Schematic of the Electro-PRB apparatus.

hydroxides, Fe oxyhydroxides, and carbonate precipitates were all identified in field and laboratory-simulated  $\text{Fe}^0$ -PRBs [28–30].

It is clear that  $\text{Fe}^0$  reactivity must be restored for continuous processing. Treatments reported to enhance  $\text{Fe}^0$  activity include acid-washing [31] and sonication [32] but they are inappropriate for field remediation due to high costs, significant work-load, and complex operations [33]. Electrochemical methods have been widely used for wastewater treatment [34–36]. Periodic application of electrochemical depassivation after  $\text{Fe}^0$  passivation may restore PRB performance. The electrochemical depassivation process refers to an electrolysis system in which an electric field is applied, comprising an entry point (cathode) and an exit point (anode). When  $\text{Fe}^0$  is the cathode, at a certain electric potential, hydrogen is produced, which has the function of peeling off  $\text{Fe}^0$  passivation layers. When the  $\text{Fe}^0$  is the anode, dissolution of  $\text{Fe}^0$  ions [37] promotes the cleaning of the iron surface.

To the best of our knowledge, the utilization of an electrochemical method to recover  $\text{Fe}^0$  reactivity and promote the longevity of PRB has not been reported previously. The main objective of this study was to evaluate the possibility of electrochemical depassivation with an Electro-PRB system for Cr(VI) removal. Column experiments were conducted to simulate the operation of  $\text{Fe}^0$ -PRBs. The experiments lasted up to hours and Cr(VI) removal efficiencies obtained by the Electro-PRB systems were then compared with traditional PRB systems to investigate the suitability of the electrochemical method for depassivation in  $\text{Fe}^0$ -PRBs. The influence of electrolysis time and the processes of pH, ORP, and dissolved oxygen (DO) variation were investigated and analyzed. Scanning electron microscopy (SEM) was used for surface characterization.

## 2. Materials and methods

### 2.1. Materials, chemicals and analytical methods

$\text{Fe}^0$  filings used in this study were from  $\text{Fe}^0$  meshes obtained from Huiyuanweiyee Co., Ltd., China, in which the mesh size was  $2.0 \text{ mm} \times 2.0 \text{ mm}$ , with total mass 9.50 g. The  $\text{Fe}^0$  meshes were pre-treated by soaking in 0.1 mol/L HCl for 20 min (Acid-washed  $\text{Fe}^0$ , AW- $\text{Fe}^0$ ). Synthetic solutions containing Cr(VI) were prepared by dissolving reagent grade  $\text{K}_2\text{Cr}_2\text{O}_7$  into deionized water, and analytical grade anhydrous  $\text{Na}_2\text{SO}_4$  was added as a supporting electrolyte. The pH, ORP, and DO of influents were  $6.40 \pm 0.30$ ,  $300.0 \pm 15.0 \text{ mV}$  and  $7.45 \pm 0.35 \text{ mg/L}$ , respectively.

### 2.2. Electro-PRB column experiments

To assess the effectiveness of electrochemical depassivation operations for recovering  $\text{Fe}^0$  reactivity under dynamic flow conditions, column experiments were conducted at room temperature, of around  $26^\circ\text{C}$ . The column reactor (Fig. 1) used in this study was made of polyvinyl butyral (PVB) with effective volume 316.9 mL. Eight pieces of AW- $\text{Fe}^0$  mesh were homogeneous packed in the radial direction. The immersed areas of each piece of  $\text{Fe}^0$  mesh were similar, at about  $22.4 \text{ cm}^2$  ( $11.50 \text{ cm} \times 1.95 \text{ cm}$ ), and the top of column was sealed with Parafilm<sup>TM</sup>. The influent solutions were fed continuously into the column from the bottom in up-flow mode at a flux of  $0.5 \text{ mL/min}$  and concentration  $2.5 \text{ mg/L}$ . A sampling port was located at the top of column, which was the effluent end. Samples of the column flow were periodically collected in duplicate for Cr(VI) analysis. Measurements of pH, ORP and DO were taken during the experiments.

Electrochemical depassivation operations were begun when the removal rate of Cr(VI) was  $<10\%$ . The Cr(VI)-removal reactor also served as an electrochemical cell. Every alternate two pieces of passivated mesh (Passivation- $\text{Fe}^0$ ) were used as anode and cathode during the electrochemical depassivation operations. When the operation was complete, solutions within the reactor were discarded, and fresh influent solutions subsequently fed into column. “Electro- $\text{Fe}^0$ ” refers to Passivation- $\text{Fe}^0$  material treated by electrochemical depassivation. To evaluate the effect of electrolysis time, different electrolysis times of 10, 2, 5, and 4 min were successively tested, with a voltage of 10 V. A DC potentiostat (Yaguang, HY1792) with a voltage range of 0–50 V and a current range of 0–5 A was applied as the power supply.

## 3. Results and discussion

### 3.1. Process of Cr(VI) removal and role of passivation

Results for Cr(VI) removal in the column reactor as a function of elapsed time are shown in Fig. 2. Substantial amounts of Cr(VI) were continuously removed by  $\text{Fe}^0$  in the Electro-PRB system. AW- $\text{Fe}^0$  was used first, and the initial removal rate was 26.85%, which served as a control condition. The removal rate of Cr(VI) depends on many factors. The surface characteristics of  $\text{Fe}^0$  are important [21] but the  $\text{Fe}^0$  meshes used here have no advantages in this respect. However, Passivation- $\text{Fe}^0$  meshes were easily obtained. It should be noted that this study focused on the processes of passivation and depassivation. Although the initial removal rate was not as good as

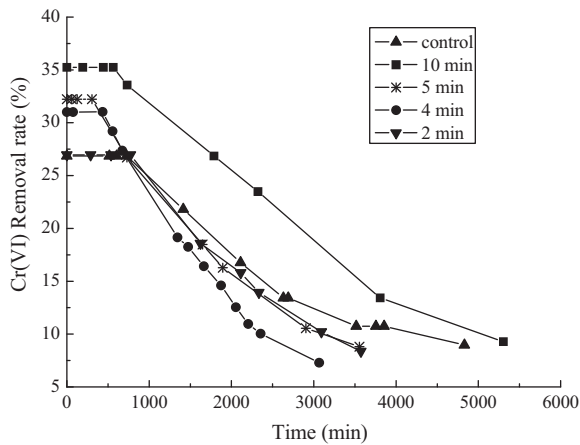


Fig. 2. Cr(VI) concentration as a function of elapsed time.

that when Fe<sup>0</sup> was used in other studies, the Fe<sup>0</sup> meshes used in the present study were easily passivated, which is favorable for electrochemical depassivation operations. Moreover, the initial removal rate of AW-Fe<sup>0</sup> was not considered important in this study. Pretreatment was another factor, and the AW-Fe<sup>0</sup> used was pretreated with 0.1 mol/L HCl for only 20 min. Furthermore, the removal rate is also related to influent solution conditions, such as the Cr(VI) concentration [22], pH [38], and flux rate [39]. The factors mentioned above also influenced the longevity of PRB, together with the dimensions, porosity of the barrier [40].

Previous studies showed that removal of Cr(VI) was a reductive precipitation process, and the precipitation step was the rate-limiting step [41]. In this study, no Cr(III) was detected in the effluent solutions, which can probably be explained by most of Cr(III) precipitating on the Fe<sup>0</sup> surfaces, which would contribute to Fe<sup>0</sup> passivation and subsequently inhibit further Cr(VI) reduction.

A decline in Cr(VI) removal rates in accordance with kinetic constants were observed with elapsed time. At less than 4500 min elapsed time, the observed removal rate of the control experiment decreased to <10%. This limited operational time may be explained as a result of mineral precipitation in the Electro-PRB system, consistent with the SEM analysis, which will be discussed later. A similar phenomenon was found in the column experiments conducted by Blowes et al. [42]. After 4.5 pore volumes had passed through columns containing iron chips used for the removal of Cr(VI), brown coatings were observed and Cr(VI) breakthrough. Passivation layers caused by mineral precipitation may block reactive sites of Fe<sup>0</sup> and influence the penetration of Cr(VI) into the passivation layers and transport of Fe<sup>2+</sup> release, resulting in a decrease of removal capacity. Mineral precipitation was also the cause of permeability reduction, with fouling of the pore space reducing the porosity and hydraulic conductivity, which may lead to preferential flow, and a shorter residence time. However, in this study, Fe<sup>0</sup> meshes were used so a reduction of pore volume could not affect the removal process to the extent observed. An absorption process should be involved in the explanation. The absorption of Cr(VI) to nonreactive sites of Fe<sup>0</sup> may lead to larger values of the removal rate and kinetic constants in the initial phase, before reaching steady state.

### 3.2. Fe<sup>0</sup> reactivity recovery by electrochemical depassivation

Significant recovery of Fe<sup>0</sup> reactivity through the electrochemical depassivation operation was observed. As described above, electrochemical depassivation experiments were introduced when the removal rate fell below 10%. As shown in Fig. 2, after the electrochemical depassivation, the initial removal rate of 10-min

Electro-Fe<sup>0</sup> (Passivation-Fe<sup>0</sup> with electrochemical depassivation operation for 10 min) increased to 35.24%. In a previous study [31], acid washing was used to break down passivation layers. Although the initial reactivity of Fe<sup>0</sup> was increased compared with unwashed Fe<sup>0</sup>, it was reported that long-term efficiency of AW-Fe<sup>0</sup> was poorer, with the explanation that acid washing resulting in more severe mineral precipitation on the Fe<sup>0</sup> surface. In the present study, the removal rate of 10-min Electro-Fe<sup>0</sup> was <10% after 5000 min, which was longer than that of the AW-Fe<sup>0</sup> initially used. Fe<sup>0</sup> reactivity recovery can be attributed to the electrochemical process. Minerals were partly or completely broken down, with the reactive sites of Fe<sup>0</sup> increased by electrochemical depassivation.

During the electrochemical depassivation process, when Fe<sup>0</sup> is used as a cathode at a certain electric potential, hydrogen is produced at the cathode via the following reactions:

Anode:



Cathode:



When Fe<sup>0</sup> is used as anode, dissolution of iron occurs at the anode via the following reactions:

Anode:



Cathode:



Two-, five-, and four-min electrochemical depassivation operations were successively carried out. In all experiments, each Fe<sup>0</sup> type had a comparable initial removal rate with AW-Fe<sup>0</sup>, and there were approximately 100.4–131.3% initial removal rate recoveries compared with the control experiment. These results suggest that Electro-PRB system may be suitable for removing Cr(VI) and that electrochemical depassivation is valid for recovery of Fe<sup>0</sup> reactivity. It can be concluded that Electro-PRB for Cr(VI) removal is a promising technology that deserves further investigation to better understand the mechanisms so as to improve the efficiency of the electrochemical depassivation operation.

### 3.3. Effect of electrolysis time on Cr(VI) removal process

The effect of electrolysis time on the Cr(VI) removal process was studied. There were no discernible differences between the initial removal rates of 2-min Electro-Fe<sup>0</sup> (26.95%) and AW-Fe<sup>0</sup> (26.85%). The longevity of 2-min Electro-Fe<sup>0</sup> was similar to 5-min Electro-Fe<sup>0</sup> experiment, which were all >3000 min. In the reactor containing 5-min Electro-Fe<sup>0</sup>, 32.23% of Cr(VI) was removed initially. For the reactor filled with 4-min Electro-Fe<sup>0</sup>, an initial rate of 31.02% was achieved, and rapid Cr(VI) break through occurred. Removal rate fell below 10% within 2500 min.

The initial removal rate for all types Fe<sup>0</sup> followed the order 10-min Electro-Fe<sup>0</sup> > 5-min Electro-Fe<sup>0</sup> > 4-min Electro-Fe<sup>0</sup> > 2-min Electro-Fe<sup>0</sup> ≈ AW-Fe<sup>0</sup>. A previous study has shown that the spatial relationship between Fe<sup>0</sup> surfaces and corrosion products determines the reactivity of Fe<sup>0</sup> [43]. The results in Fig. 2 show that the longer electrolysis took, the higher the initial removal rate was. This illustrates that initial removal rate was affected by the electrolysis process, which was related to the extent of precipitate breakdown.

As reported in a previous study, the number and activity of the reactive sites is not fixed and depends on both the Fe<sup>0</sup> and

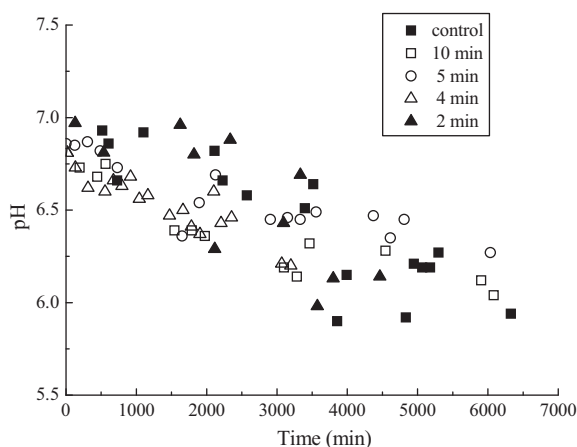


Fig. 3. pH of column effluents as a function of elapsed time.

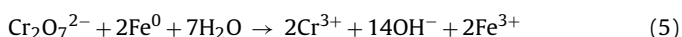
solution potentials [22]. Different types of  $\text{Fe}^0$  utilized in column experiments may lead to different longevities. In the present study, the longevity of 10-min Electro- $\text{Fe}^0$  was the highest, followed by AW- $\text{Fe}^0$ , 5-min Electro- $\text{Fe}^0$  and 2-min Electro- $\text{Fe}^0$ , while 4-min Electro- $\text{Fe}^0$  had the highest deterioration rate. The 4-min Electro- $\text{Fe}^0$  used underwent several recovery operation cycles. Too many cycles may influence the  $\text{Fe}^0$  characteristics, leading to more rapid loss of reactivity. In the future, the electrochemical depassivation operation still requires study to further improve the initial rate and long-term performance of Cr(VI) removal.

### 3.4. Process of pH, ORP, DO variation

The pH values of column effluents as a function of elapsed time during experiments are plotted in Fig. 3. In all the cases, there were no significant differences in pH between these experiments, although there was some scatter in the pH data. It is known that the reduction of Cr(VI) to Cr(III) and  $\text{Fe}^0$  corrosion result in the release of  $\text{OH}^-$ , and the precipitation of Cr(III) and Fe(III) consumes  $\text{OH}^-$ . As time increased, passivation of  $\text{Fe}^0$  may lead to the occurrence of mineral precipitation, resulting in less  $\text{OH}^-$  release, and the pH to become slightly acidic.

According to previous studies [22,31,42], the process of Cr(VI) reduction was listed as follows:

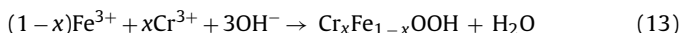
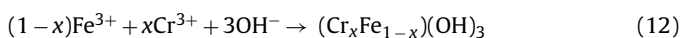
First, Cr(VI) is reduced to Cr(III) through the oxidation of  $\text{Fe}^0$ ,



Cr(III) may then be removed through precipitation of  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}(\text{OH})_3$  or  $\text{CrOOH}$ ,



The precipitates may be also be in the form of mixed Fe(III)–Cr(III) (oxy)hydroxide solids below, where  $x$  can range from 0 to 1:



The column effluent DO and difference in DO between influents and effluents are displayed in Fig. 4. The concentrations of DO were

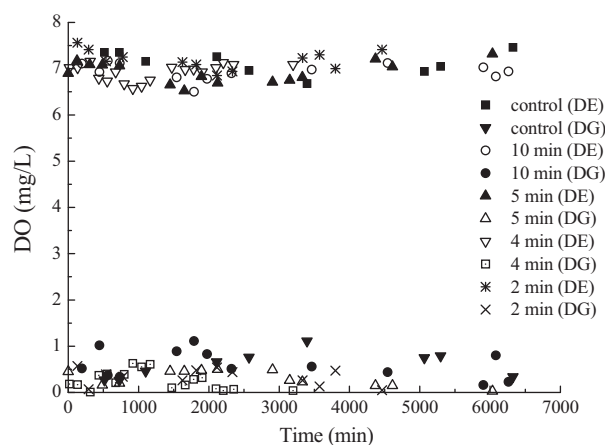


Fig. 4. DO of column effluents (DE) and DO gaps between influents and effluents (DG) with different electrochemical depassivation time as a function of elapsed time.

between 6.50 and 7.56 mg/L, which indicates aerobic conditions. DO differences were  $>0$ , indicating that the consumption of oxygen may occur during the experiments through  $\text{Fe}^0$  corrosion (Eq. (14)).



However, the equations cited above (Eqs. (5)–(14)) cannot exactly represent the reactions in the Electro-PRB system conducted in this study. The contributions of Cr(VI) removal and  $\text{Fe}^0$  corrosion to  $\text{OH}^-$  generation are not included, which is worthy of further study.

Results for ORP are shown in Fig. 5, with the level of ORP values being related to the high DO content in this study. The 10-min Electro- $\text{Fe}^0$  experiment showed the greatest decrease in the ORP value, of around 200 mV initially. After approximately 300 min, the ORP values of the 4-min and 5-min electrochemical depassivation experiments reached steady state. Once column influent contacted  $\text{Fe}^0$ , the ORP decreased as the reductive precipitation process of Cr(VI) removal occurred. With further operation time, the changes became less obvious. The explanation for this change could be the continuous precipitation of passivation layers on the  $\text{Fe}^0$  surface during the removal process.

### 3.5. SEM characterization of $\text{Fe}^0$ surfaces

An SEM image of AW- $\text{Fe}^0$  is shown in Fig. 6(a), and the surface roughness reveals that AW- $\text{Fe}^0$  had a high removal capacity.

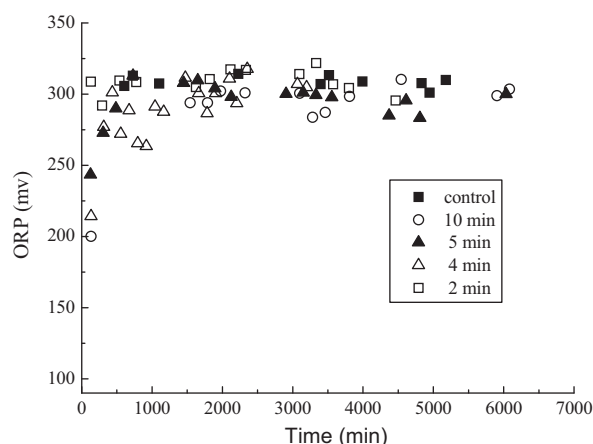


Fig. 5. ORP of column effluent as a function of elapsed time.



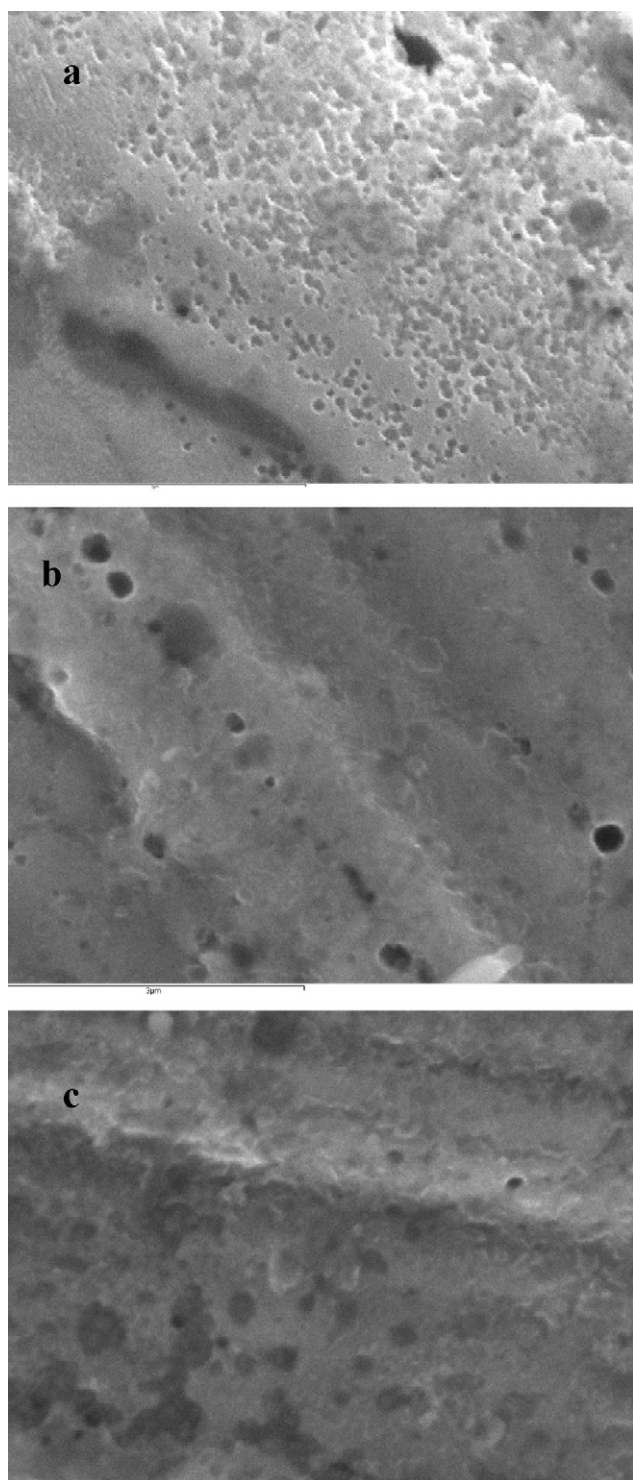


Fig. 6. SEM analysis (a) Acid-washed Fe<sup>0</sup>, (b) Passivation-Fe<sup>0</sup>, and (c) Electro-Fe<sup>0</sup>.

The loss in reactivity was consistent with changes in the surface morphology of Fe<sup>0</sup>. In Fig. 6(b), the surface of Fe<sup>0</sup> had become smooth after removal of Cr(VI) for 2.5 days. This can be explained by the occurrence of mineral fouling. Fig. 6(c) shows the surface area of Electro-Fe<sup>0</sup> was rougher than that of Passivation-Fe<sup>0</sup>, due to electrolysis operation for 5 min with a voltage of 10V, implying that Electro-Fe<sup>0</sup> was a more reactive media, compared with Passivation-Fe<sup>0</sup>.

#### 4. Conclusions

An innovative Electro-PRB system, filled with Fe<sup>0</sup> meshes for Cr(VI) remediation was proposed in this study. The efficiency of Fe<sup>0</sup> reactivity recovery using the electrochemical depassivation method was investigated. Column experiments utilizing different types of Fe<sup>0</sup> were conducted to observe removal rates and longevities as a function of elapsed time. The Cr(VI) removal rates and observed kinetic constants were initially high and then showed a continuous decrease with time, due to the variable reactivity of Fe<sup>0</sup> caused by mineral fouling. After AW-Fe<sup>0</sup> passivation, electrochemical depassivation was introduced with different electrolysis times for recovery of Fe<sup>0</sup> reactivity, resulting in approximately 100.4–131.3% initial removal rate recoveries, through the electrochemical breakdown of precipitates on Fe<sup>0</sup> surfaces. Initial removal rates of all types Fe<sup>0</sup> followed the order 10-min Electro-Fe<sup>0</sup> > 5-min Electro-Fe<sup>0</sup> > 4-min Electro-Fe<sup>0</sup> > 2-min Electro-Fe<sup>0</sup> ≈ AW-Fe<sup>0</sup>, which indicates that the initial removal rate was affected by the electrochemical depassivation process, which was in turn related to the extent of precipitate breakdown. With regard to longevity, 10-min Electro-Fe<sup>0</sup> was the longest, followed by AW-Fe<sup>0</sup>, 5-min Electro-Fe<sup>0</sup> and 2-min Electro-Fe<sup>0</sup>, while 4-min Electro-Fe<sup>0</sup> had the highest deterioration rate. This reveals that longevities were influenced not only by electrochemical depassivation but also the characteristics of Fe<sup>0</sup>. pH and ORP of column effluents were related to the DO difference between influents and effluents, which were consistent with the process of Cr(VI) removal. The DO differences between influents and effluents were >0 and may have resulted from Fe<sup>0</sup> corrosion. As time increased, passivation layers on Fe<sup>0</sup> surfaces caused slight decreases in pH and less obvious increases in ORP. SEM analyses of AW-Fe<sup>0</sup>, Electro-Fe<sup>0</sup> and Passivation-Fe<sup>0</sup> confirmed the efficiency of Electro-PRB in the process of loss and recovery of Fe<sup>0</sup> reactivity. All the results show that Electro-Fe<sup>0</sup> is suitable for Cr(VI) removal and that electrochemical depassivation experiments are valid for recovery of Fe<sup>0</sup> reactivity. Therefore, we conclude that Electro-PRB is a promising technology. Further study is required to improve the Electro-PRB system.

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