

# Arsenic and chromate removal from water by iron chips —Effects of anions

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**Abstract** The purpose of this study is to estimate the removal efficiency of As and Cr (VI) by one kind of industrial waste – iron chips, as well as to estimate the effects of typical inorganic anions (sulfate, phosphate, and nitrate), and typical organic anions (citrate, oxalate, and humate) on As or Cr (VI) removal. The results showed that 98% of As (V) and 92% of As (III) could be removed from aqueous phase by the iron chips within 60 min. Compared with As species, Cr (VI) was removed much more rapidly and efficiently with 97% of Cr (VI) being removed within 25 min. The removal efficiency for arsenic was in the order: As (III) (sulfate), As (III) (nitrate) or As (III), As (III) (humate), As (III) (oxalate), As (III) (citrate), As (III) (phosphate), and for chromate was in the order: Cr (VI) (sulfate), Cr (VI) (phosphate) or Cr (VI) (nitrate) or Cr (VI) (oxalate), Cr (VI), Cr (VI) (citrate), Cr (VI) (humate). In all the treatments, pH level increased with time except for As (III), the removal of which was either without anions or in the presence of humate or nitrate.

**Keywords** arsenic, chromate, iron chips, permeable reactive barrier, remediation, groundwater

## 1 Introduction

Arsenic (As) and chromium (Cr) compounds are often found in contaminated soils and groundwater as a result of industrial waste discharges such as from chrome plating, metallurgy, timber protection, leather tanning, and agricultural use of arsenical herbicides and pesticides. Much attention has been paid to the contamination of As and Cr since some of their species such as arsenate [As(V)], arsenite [As(III)], and chromate [Cr(VI)], are known to be carcinogenic, mutagenic, and teratogenic [1,2]. Both As and Cr have been ranked as the top 20

hazardous substances by the Agency for Toxic Substances and Disease Registry (ATSDR). Hence, it is necessary to develop simple, efficient and cost effective methods for the removal of As and Cr from the environment.

Many methods have been used to remove As and Cr from contaminated waters, including anion exchange, reverse osmosis, precipitation, and adsorption. However, each has some serious drawbacks. For example, the ion exchange process becomes inefficient due to the competition for exchange sites by background electrolytes, which may be present at considerably greater levels than the contaminant. Reverse osmosis is expensive and often requires pretreatment of the water to remove compounds that may contaminate the membrane.

Permeable reactive barrier (PRB) of zero-valent iron ( $\text{Fe}^0$ ) is a new technology for the remediation of contaminated groundwater streams [3,4]. *In-situ* barriers have shown the advantages of passive, continuous treatment of the plume without requiring ongoing maintenance and a pump-and-treat physical plant. Successful implementation of a PRB requires a thorough understanding of the effects of geochemical variables such as chemical compositions of the plume, pH, and redox potential, on the behavior of the PRB. Simple aliphatic organic acids with one to three carboxylic groups such as oxalate and citrate, which occur frequently in soil and subsurface environments due to biological activities, alter chemical processes in soils through complexation with metal ions in solution and ligand exchange at soil surfaces [5,6]. Natural organic materials (NOMs) are ubiquitous in natural environments and affect the adsorption and mobility of As and Cr species [7,8]. Consequently, they may play an important role in As and Cr removal by  $\text{Fe}^0$  via adsorption and complexation reaction on the surface of  $\text{Fe}^0$  and iron corrosion products, or via influence on the speciation of As and Cr. However, the influence of these organic anions and NOMs on As and Cr removal by  $\text{Fe}^0$  has not been systematically studied. Some major inorganic

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anions such as sulfate, nitrate, and phosphate, have been reported to decrease the removal rate of As by Peerless Fe<sup>0</sup> in both batch and column tests [9,10]. Our previous study [11] found that sulfate had different effects on arsenate removal by Fe<sup>0</sup> under different concentrations. In another study [12], sulfate was found to decrease both As (V) and As (III) adsorption on hydrous ferric oxide in a pH range of 4–7. Thus, these inorganic anions may give different influences on As and Cr removal by Fe<sup>0</sup> under different conditions. Hence, the objective of this study was to evaluate the effects of some organic (oxalate, citrate, and humate) and inorganic (sulfate, nitrate, and phosphate) anions on As and Cr removal by iron chips.

## 2 Materials and methods

### 2.1 Materials and chemicals

Iron chips (<20 mesh) as the waste from Guangxin Factory, Tianjin, China, were washed by 10% hydrochloric acid to remove the surface oil, and dried under slight N<sub>2</sub> stream to avoid oxidation by air. Chemical composition of the iron chips was analyzed by an X-ray fluorescence spectrometer (PW1404, Philip Co., Holland) and mineral phase was characterized by X-ray diffraction (XRD) with a diffractometer (D/Max-2500, Rigakudmax, Japan). The results show that more than 95% of the chips are Fe and its compounds, among which 75% is Fe<sup>0</sup>, 22% Fe<sub>3</sub>O<sub>4</sub>, and 3% FeO while the other components are Mn, Cu, Zn, Ca, and Si. BET surface of this material is 0.31 m<sup>2</sup>/g (determined by NOVA 2000, Quantachrom Co., USA).

Stock solutions (100 mg/L of As, and 100 mg/L of Cr (VI)) were prepared from analytical grade of Na<sub>3</sub>AsO<sub>4</sub> for As (V), As<sub>2</sub>O<sub>3</sub> for As (III), and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for Cr (VI). Working solutions were prepared just before they were used.

### 2.2 Experiments

Batch experiments were conducted using 50 mL aqueous solution containing 500 µg/L of As or 5 mg/L of Cr, and 1.0 g of iron chips in 100-mL capped glass flasks. In order to evaluate the effects of different anions on As or Cr removal, the experiments were carried out in the presence of certain levels of phosphate (NaH<sub>2</sub>PO<sub>4</sub>, 15 mg/L of PO<sub>4</sub><sup>3-</sup>), sulfate (Na<sub>2</sub>SO<sub>4</sub>, 500 mg/L of SO<sub>4</sub><sup>2-</sup>), nitrate (NaNO<sub>3</sub>, 100 mg/L of NO<sub>3</sub><sup>-</sup>), oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 50 mg/L of C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 15 mg/L of C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup>) and sodium humate (10 mg/L), respectively. The flasks were shaken regularly at 200 r/min at 20 ± 1°C. No attempt was made to adjust the pH once the reaction was initiated. All experiments were conducted twice.

At designated intervals, the suspension was taken out, and centrifuged for 10 min at 4000 r/min. 10 mL of the

supernatant solution was used for the analysis of total As, As (III) and As (V) or total Cr and Cr (VI), respectively. pH was measured using the remaining supernatant solution with a pH meter (Orion 868, Orion Research Inc., China).

### 2.3 Analytical methods

The standard methods for analysis of As and Cr recommended by the State Environmental Protection Administration of China were adopted to determine As and Cr concentration [13]. Total As and its speciation in aqueous phase were determined with hydride generation-atomic fluorescence absorption spectroscopy (AFS 2201, Haiguang Co., China), in which total As was determined in aqueous solution containing 10% of HCl, 1% of sulphurea, 0.5% of ascorbic acid, and As (III) was determined in a buffer solution with pH of 5–6, As (V) was calculated by subtracting As (III) from the total As. Cr (VI) concentration was determined by diphenylcarbazide colorimetric method at 540 nm (SP-2000 UV Spectrum, Shanghai Spectrum Instruments Co., China). Total Cr was determined using the same method as Cr (VI) after oxidizing Cr (III) to Cr (VI) by KMnO<sub>4</sub>.

## 3 Results and discussion

### 3.1 Removal kinetics of As and Cr

The time-dependent removal of As (III), As (V), and Cr (VI) by iron chips are illustrated in Fig. 1. Both As (III) and As (V), and Cr (VI) could be removed from the aqueous phase rapidly and efficiently by the iron chips. As (V) showed a slightly higher removal efficiency compared with As (III), with 98% of As (V) and 92% of As (III) lost within 60 min. The mechanisms of adsorption and coprecipitation of As species on Fe corrosion products (Fe(II/III) oxides) have been proposed for the removal of arsenic by Fe<sup>0</sup> [14]. The oxides of iron are electropositive, whereas H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> for As (V) and H<sub>3</sub>AsO<sub>3</sub> for As (III) are predominant species in aqueous phase under the neutral condition. Hence it is easy to understand that the

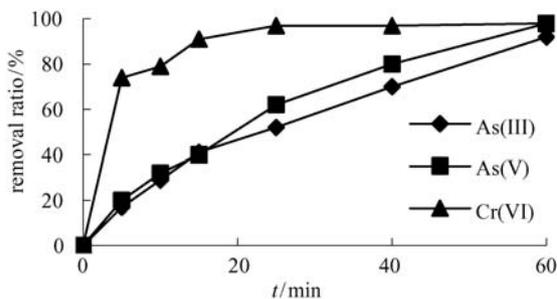
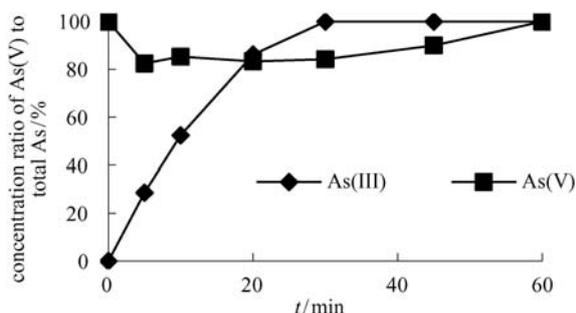


Fig. 1 Time-dependent removal of 500 µg·L<sup>-1</sup> of As(III) and As(V), and 5 mg·L<sup>-1</sup> of Cr by iron chips

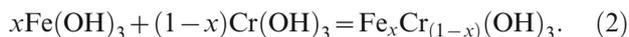
electronegative As (V) has greater affinity to the surface of iron oxides than the electroneutral As (III).

In order to explain the high efficiency of As (III) removal, we tested the change of As valence during the reaction (Fig. 2). When only As (III) was added initially, As (V) occurred and its fraction in the total As increased continuously with time, which indicates that oxidation of As (III) to As (V) happened in the system. Hence, it can be concluded that As (III) was removed by adsorption and coprecipitation on Fe corrosion products through oxidized As (V). The transformation from As (V) to As (III) was at a negligible level when only As (V) was initially added (Fig. 2). Some previous studies have reported that As (V) species may be reduced by  $\text{Fe}^0$  to As (III), and As (III) is oxidized to As (V) during the  $\text{Fe}^0$  corrosion reaction [11,14,15]. In the present study, which uses the waste iron chips, only oxidation of As (III) to As (V) was significant.



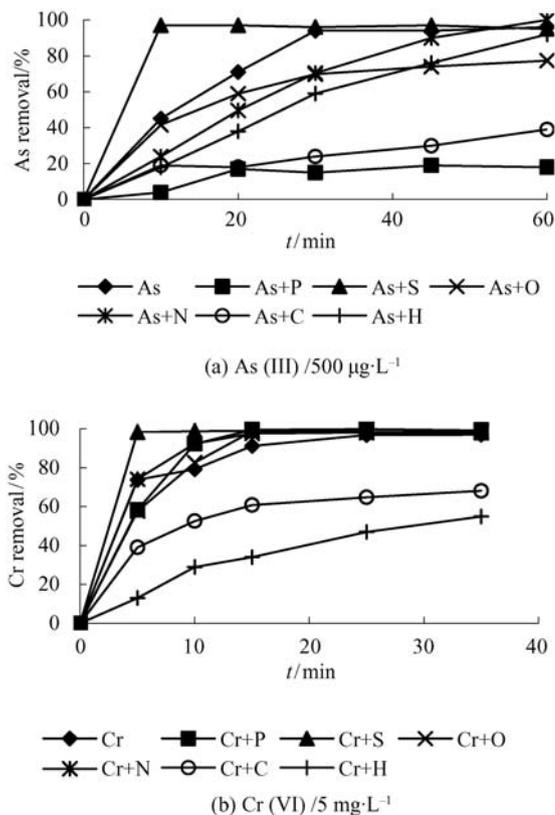
**Fig. 2** Change in concentration ratio of As(V) to total As during different As speciation removing by iron chips

Compared with As, Cr (VI) was removed at a greater rate though its concentration was 9 times higher (Fig. 1), with 97% of Cr (VI) being removed within 25 min. Previous investigators have found that highly water soluble Cr (VI) may be removed from solution via being reduced to Cr (III) by  $\text{Fe}^0$  through the following reactions [4,16]:



### 3.2 Influence of anions on removal of As(III) and Cr (VI)

With the addition of 500 mg/L of  $\text{SO}_4^{2-}$ , the removal rate of As (III) was accelerated significantly (Fig. 3a). 100 mg/L of  $\text{NO}_3^-$  caused a slight enhancement, whereas 15 mg/L of  $\text{PO}_4^{3-}$  caused a significant reduction in As (III) removal. Therefore, the three inorganic anions had different effects on As (III) removal by the iron chips. All the three organic anions, i.e., oxalate, citrate, and humate, decreased the removal efficiency of As (III), but only citrate to a significant extent.



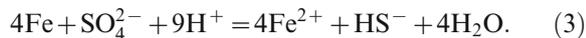
**Fig. 3** Contaminants removal by iron chips in the presence of  $\text{SO}_4^{2-}$  (S, 500  $\text{mg}\cdot\text{L}^{-1}$ ),  $\text{PO}_4^{3-}$  (P, 15  $\text{mg}\cdot\text{L}^{-1}$ ),  $\text{C}_2\text{O}_4^{2-}$  (O, 50  $\text{mg}\cdot\text{L}^{-1}$ ),  $\text{C}_6\text{H}_5\text{O}_7^{3-}$  (C, 15  $\text{mg}\cdot\text{L}^{-1}$ ), humate (H, 10  $\text{mg}\cdot\text{L}^{-1}$ ), and  $\text{NO}_3^-$  (N, 100  $\text{mg}\cdot\text{L}^{-1}$ )

The first-order reaction kinetics was found to describe the data well (Table 1) with  $r^2$  values ranging from 0.85 to 1.00. The first order rate constant ( $k_1$ ) for As (III) removal by the iron chips followed the sequence: As (III) (sulfate), As (III) (nitrate) or As (III), As (III) (humate), As (III) (oxalate), As (III) (citrate), As (III) (phosphate), and Cr (VI) removal followed the sequence: Cr (VI) (sulfate), Cr (VI) (phosphate) or Cr (VI) (nitrate) or Cr (VI) (oxalate), Cr (VI), Cr (VI) (citrate), Cr (VI) (humate).

### 3.3 Effect mechanisms of inorganic ions

The addition of sulfate was found to promote the removal of As (III), which is contrary to Su and Puls [9], who reported a reduction in arsenic removal by Peerless  $\text{Fe}^0$  with the addition of sulfate compared with chloride in batch tests. The disagreement in the effect of sulfate on As (III) removal may have been derived from different experimental conditions. First, sulfate concentration in the present study is higher than that used by Su and Puls (1.0 mmol/L of  $\text{Na}_2\text{SO}_4$ ). Our previous study also found that the removal of As slightly slackened at lower sulfate concentration [11]. Secondly, chloride acts as a corrosion promoter, and its presence could thus enhance

iron reactivity, which in turn leads to an enhancement for arsenic removal. Accordingly, compared with chloride, the removal of arsenic may be comparably slower in the presence of sulfate. Moreover, Cr (VI) removal was also accelerated with the addition of sulfate. All these could be explained by the interaction between sulfate and Fe<sup>0</sup> (Eq. 3), which could consume Fe<sup>0</sup> approximately 50 times more rapidly than by the reduction and precipitation of Cr (VI) (Eq. 1) [17]:



At the end of the test, more obvious precipitation on iron surface in the presence of sulfate was observed, which could also prove the above reaction and Eq. 4. Hence, it could be concluded that the enhancement of As (III) removal with the addition of SO<sub>4</sub><sup>2-</sup> is due to the promotion of Fe<sup>0</sup> corrosion by SO<sub>4</sub><sup>2-</sup>, and the following enhancement of As (III) removal by the production of the corrosion products [18]. The generated Fe<sup>2+</sup> may also enhance Cr (VI) removal by reacting with Cr (VI):



NO<sub>3</sub><sup>-</sup> can also be reduced by Fe<sup>0</sup>, but the reaction rate seems to be much slower than that of SO<sub>4</sub><sup>2-</sup> [19]:



Accordingly, in the presence of NO<sub>3</sub><sup>-</sup>, As (III) removal rate was reduced slightly at the initial time (Fig. 3a) as a result of the competition for the active sites on iron chips by NO<sub>3</sub><sup>-</sup>. With the formation of Fe<sup>2+</sup>, As (III) removal rate was accelerated to a little extent. On the whole, NO<sub>3</sub><sup>-</sup> has a slight effect on As (III) removal. Su and Puls [9] reported that NO<sub>3</sub><sup>-</sup> reduced arsenic removal significantly compared to chloride. The reason for the different result has been discussed above. Cr (VI) removal rate was also accelerated slightly in the presence of NO<sub>3</sub><sup>-</sup> (Fig. 3b), and it can be attributed to the redox and precipitation reactions (Eqs. 1, 4, and 5).

The enhancement of Cr (VI) removal by PO<sub>4</sub><sup>3-</sup> could be ascribed to its reaction with Fe<sup>2+</sup>/Fe<sup>3+</sup>, the product of redox reaction between Cr (VI) and Fe<sup>0</sup>, and consequently the reaction (Eq. 1) might be sped up. Since PO<sub>4</sub><sup>3-</sup> has a higher affinity to iron hydroxide surface [20], the restraining effect of PO<sub>4</sub><sup>3-</sup> for As (III) removal was significant due to the competition with As (III) for the active sites, which is consistent with the previous studies [9,10].

### 3.4 Effect mechanisms of organic ions

We attribute the reduction of As (III) removal by the addition of citrate and oxalate to the competition of these anions for the active sites on the surface of iron chips with As (III). The sequence of reduction extent of oxalate and citrate on As (III) removal may be explained by the relative stability of the complexes between Fe<sup>2+</sup>/Fe<sup>3+</sup> and these anions, whose critical stability constants (log *K*) are 3.05 and 7.58 for oxalate, and 4.8 and 10.25 for citrate [21], respectively. Humate is a stronger complexant with a lot of complex groups such as carboxylic, phenolic, amino, nitroso, sulfhydryl, and hydroxyl, however, its reduction effect was the least among the three organic anions. It has been presumed by Ko et al. [8] that humic acid could act as a bridge between the positively charged iron oxides and neutral As (III) or negative As (V). Consequently, in the presence of humate, As (III) removal rate decreased only to a little extent, with *k*<sub>1</sub> changing from 5.7 × 10<sup>-2</sup> to 4.1 × 10<sup>-2</sup> min<sup>-1</sup>.

Contrary to As (III), oxalate accelerated Cr (VI) removal rate slightly (Table 1 and Fig. 3b). This can be explained by that oxalate can also reduce Cr (VI) [22], which accelerated the removal of Cr (VI). Both citrate and humate retarded Cr (VI) removal, which is similar to As (III) removal. The mechanism, however, might be quite different. As for citrate, the reduction of Cr (VI) removal is primarily due to the interaction of Cr (VI) with citrate. In order to prove our hypothesis, Cr (VI) removal efficiency was observed under different experimental

**Table 1** Kinetics of arsenite and chromate removal by iron chips in presence of organic or inorganic anions<sup>a</sup>

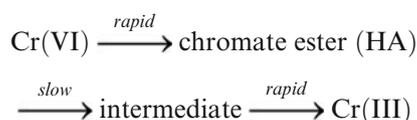
anion	As(III)	As+S <sup>b</sup>	As+N	As+P	As+O	As+C	As+H
concentration/mg·L <sup>-1</sup>	0.500	500 <sup>c</sup>	100	15	50	15	10
<i>k</i> <sub>1</sub> /min <sup>-1</sup>	5.7 × 10 <sup>-2</sup>	3.4 × 10 <sup>-1</sup>	6.4 × 10 <sup>-2</sup>	3.9 × 10 <sup>-3</sup>	2.4 × 10 <sup>-2</sup>	6.7 × 10 <sup>-3</sup>	4.1 × 10 <sup>-2</sup>
<i>r</i> <sup>2</sup>	0.9714	1.000	0.9547	0.9325	0.8831	0.9498	0.9592
<i>t</i> <sub>1/2</sub> /min	12.1	2.0	3.5	177.7	29.2	103.5	17.1
anion	Cr	Cr+S	Cr+N	Cr+P	Cr+O	Cr+C	Cr+H
concentration/mg·L <sup>-1</sup>	5.00	500	100	15	50	15	10
<i>k</i> <sub>1</sub> /min <sup>-1</sup>	1.3 × 10 <sup>-1</sup>	9.8 × 10 <sup>-1</sup>	2.5 × 10 <sup>-1</sup>	2.8 × 10 <sup>-1</sup>	2.2 × 10 <sup>-1</sup>	4.0 × 10 <sup>-2</sup>	1.7 × 10 <sup>-2</sup>
<i>r</i> <sup>2</sup>	0.9569	1.000	0.9987	0.9386	0.9496	0.8365	0.9636
<i>t</i> <sub>1/2</sub> /min	5.1	0.7	2.8	2.5	3.1	17.5	39.8

a. *r*<sup>2</sup> represents for correlation coefficients of first-order equation, *k*<sub>1</sub> is the first order rate constant and *t*<sub>1/2</sub> was the calculated half-live time, all data are reported as the mean value (*n* = 2).

b. S for sulfate (SO<sub>4</sub><sup>2-</sup>), N for nitrate (NO<sub>3</sub><sup>-</sup>), P for phosphate (PO<sub>4</sub><sup>3-</sup>), O for oxalate (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), C for citrate (C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup>), and H for humate.

c. The data represent the concentration of organic or inorganic anions.

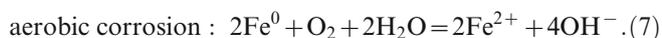
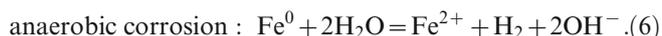
manipulations: (1) citrate and iron chips were first mixed, and Cr (VI) was added 30 min later; (2) citrate and Cr (VI) were first mixed, and iron chips were added 30 min later; (3) citrate, Cr (VI), and iron chips were mixed simultaneously. Cr (VI) removal efficiency for the three tests was 88%, 69%, and 67%, respectively. These data suggest that citrate affects the removal of Cr (VI) mainly through interacting with Cr (VI). In the case of humate, the interaction with Cr (VI) might occur either by complexation through ester formation or reduction of Cr (VI) to Cr (III). The reduction of Cr (VI) by humic substances is a slow process which can only be achieved under certain experimental conditions, such as high temperature and low pH, which is illustrated by the equation below [23]:



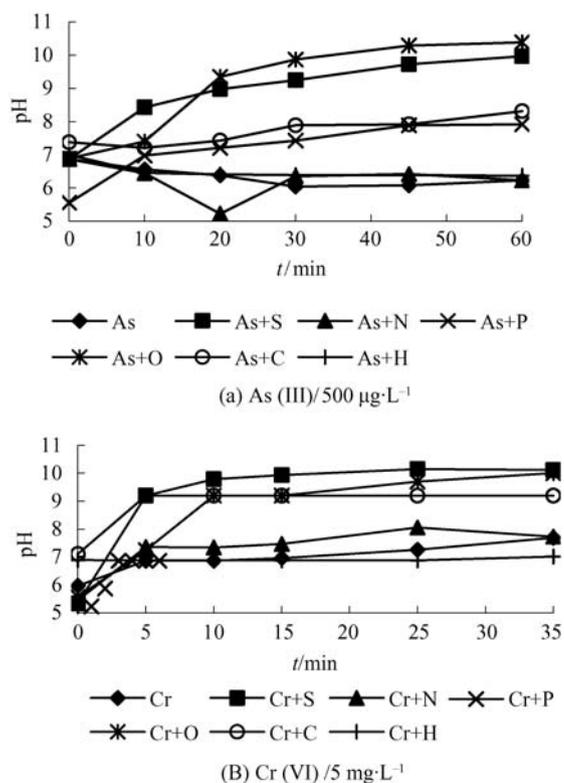
Considering the short reaction time (40 min), the neutral pH of the solution and the low concentrations of the reactants in the present study, the reduction of Cr (VI) to Cr (III) by humate is thought to be negligible. Therefore, humate is thought to retard Cr (VI) removal by iron chips mainly through ester formation.

### 3.5 pH variation during reaction

In all treatments, except for As (III) removal either singly or in the presence of humate or nitrate, pH of the solution increased with the reaction, especially for the treatments with sulfate and oxalate (Fig. 4a and 4b), where  $\Delta\text{pH}$  was 3.10 and 3.50 for As, and 4.78 and 4.44 for Cr. The change of pH was likely caused by a number of chemical processes. First, iron corrosion releases hydroxyl ions:



Secondly, the adsorption of organic or inorganic anions to the iron corrosion products through ligand exchange releases  $\text{OH}^-$  into the solution. Thirdly, Cr (VI) removal by  $\text{Fe}^0$  (Eq. 1), the interaction between sulfate and  $\text{Fe}^0$  (Eq. 3), and the interaction between oxalate and Cr (VI) also release  $\text{OH}^-$ . Finally, As (III) adsorption onto the surface of iron and its corrosion products will release  $\text{H}^+$  into the solution. Apparently, in most cases, the net result of these different chemical processes is an increase in solution pH. Whereas for the system that contains As (III) without other anions, the primary process seems to be  $\text{H}^+$  release by As (III) [24]. Accordingly, the pH decreased in the solution. As a result of slight effect on As (III) removal and buffer action, pH also decreased slightly in the presence of humate. As for nitrate, the decrease of pH at the initial time can be attributed to  $\text{H}^+$  release by As



**Fig. 4** Change of pH during contaminants removal (S for 500 mg·L<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup>, N for 100 mg·L<sup>-1</sup> of NO<sub>3</sub><sup>-</sup>, P for 15 mg·L<sup>-1</sup> of PO<sub>4</sub><sup>3-</sup>, O for 50 mg·L<sup>-1</sup> of C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, C for 15 mg·L<sup>-1</sup> of C<sub>6</sub>H<sub>5</sub>O<sub>7</sub><sup>3-</sup>, H for 10 mg·L<sup>-1</sup> of humate)

(III) adsorption, and the increase of pH at the following time seems to be the result of Eq. 5 and the iron corrosion.

## 4 Conclusions

As and Cr (VI) can be removed efficiently from aqueous solution by waste iron chips, Cr (VI) removal was much more rapid and efficient compared to As species. During the removal of As by iron chips, oxidation of As (III) to As (V) occurred, which is thought to be the path for As (III) removal. In the presence of sulfate, As (III) and Cr (VI) removals were accelerated, whereas in the presence of citrate, As (III) and Cr (VI) removals were decreased. Other anions (nitrate, phosphate, oxalate, and humate) had different effects on As (III) and Cr (VI) removal. These complex effects are the results of interactions of the anions both with the surface of iron and its corrosion products, and with As or Cr in the solution, which has been discussed in the paper in detail. With the removal of As (III) and Cr (VI) from the aqueous solution, the pH of the solution increased to different extent except for As (III) removal either without anions or in the presence of humate or nitrate, which is also a comprehensive result of several reactions. The removal of As or Cr by PRB of iron in real environment can be influenced by lots of factors.

Hence, the efficiency of Fe-PRB highly depends on the hydrochemical conditions of the field environment.

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