

Simultaneous removal of chromium and arsenate from contaminated groundwater by ferrous sulfate: Batch uptake behavior

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Abstract

Chromium and/or arsenate removal by Fe(II) as a function of pH, Fe(II) dosage and initial Cr(VI)/As(V) ratio were examined in batch tests. The presence of arsenate reduced the removal efficiency of chromium by Fe(II), while the presence of chromate significantly increased the removal efficiency of arsenate by Fe(II) at pH 6–8. In the absence of arsenate, chromium removal by Fe(II) increased to a maximum with increasing pH from 4 to 7 and then decreased with a further increase in pH. The increment in Fe(II) dosage resulted in an improvement in chromium removal and the improvement was more remarkable under alkaline conditions than that under acidic conditions. Chromium removal by Fe(II) was reduced to a larger extent under neutral and alkaline conditions than that under acidic conditions due to the presence of 10 $\mu\text{mol/L}$ arsenate. The presence of 20 $\mu\text{mol/L}$ arsenate slightly improved chromium removal by Fe(II) at pH 3.9–5.8, but had detrimental effects at pH 6.7–9.8. Arsenate removal was improved significantly at pH 4–9 due to the presence of 10 $\mu\text{mol/L}$ chromate at Fe(II) dosages of 20–60 $\mu\text{mol/L}$. Elevating the chromate concentration from 10 to 20 $\mu\text{mol/L}$ resulted in a further improvement in arsenate removal at pH 4.0–4.6 when Fe(II) was dosed at 30–60 $\mu\text{mol/L}$.

Key words: chromium removal; arsenate removal; ferrous iron; groundwater treatment

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Introduction

Chromium is found in wastewaters originated from metal etching and plating operations, wood preservative manufactures, leather tanning industries, paint and pigments, dyeing, steel fabrication and industrial operations involving the processing of ferrous and nonferrous metals (Raji and Anirudhan, 1997; Parga et al., 2005). Sources of arsenic include petroleum refineries, fossil fuel power plants, nonferrous smelting activities and ceramics, semiconductors, pesticides, and fertilizer production (Pierce and Moore, 1980). Chromium and arsenic have been identified as co-contaminants in wastes from wood preservative manufacture, paint and ink manufactures, and petroleum refineries, as well as some municipal wastewaters (Jha et al., 2006). Inadequate storage and improper disposal practices of chromium and arsenic have caused many incidences of soil and groundwater contamination in industrialized areas (Aceto and Fedele, 1994; Qin et al., 2005; Greven et al., 2007; Liu et al., 2009). Both arsenic and chromium represent potential threats to the environment, human health, and animal health due to their carcinogenic and toxicological effects (Guan et al., 2008; Buerge and

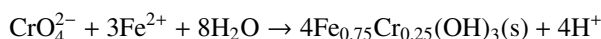
Hug, 1999). Arsenic and hexavalent chromium have been considered as important priority pollutants worldwide owing to numerous health problems arising from groundwater contaminated by these two pollutants (Parga et al., 2005; Oliveira et al., 2008). Therefore, the World Health Organization (WHO) and the Ministry of Health of China have established a provisional guideline of 10 $\mu\text{g/L}$ for As and 50 $\mu\text{g/L}$ for Cr(VI) in drinking water (MHPRC, 2007; WHO, 1993). Recent public concern regarding As and Cr(VI) in drinking water has promoted the investigation of treatment technologies with the potential to remove them simultaneously to levels well below the drinking water maximum contaminant level.

Limited research has explored methods to remove As(V) and Cr(VI) simultaneously from water. Jha et al. (2006) employed a hybrid field-gradient magnetic separation device filled with magnetic iron exchange resin for simultaneous removal of As(V) and Cr(VI). However, the removal efficiency of As(V) and Cr(VI) in their system was only 33.3% and 53%, respectively, in the mixed metal solution. Khaodhiar et al. (2000) studied the adsorption of copper, chromium and arsenic on iron-oxide-coated sand and reported that As(V) adsorption was not affected by the presence of Cr(VI) but the presence of As(V)

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greatly decreased Cr(VI) adsorption due to competition for adsorption sites and electrostatic effects. The removal of co-present chromate and arsenate by zero-valent iron was investigated by Liu et al. (2009) and the results showed that chromium removal, a reduction-dominated process, was not affected by the presence of arsenate but arsenate removal was dramatically inhibited by co-present chromate. These results indicated that both adsorption or ion exchange and application of zero-valent iron were not effective for simultaneous removal of chromate and arsenate. Therefore, more effective methods for simultaneous removal of chromate and arsenate from contaminated groundwater should be explored.

Chromium exists in natural waters in two main oxidation states, Cr(VI) and Cr(III). Cr(III) occurs primarily as a cation in solution and can be easily adsorbed onto the surface of iron oxides and oxyhydroxides at pH higher than 4.0 by forming strongly bound inner-sphere complexes or precipitates (Charlet and Manceau, 1992; Pettine et al., 1998). Cr(III) hydroxide ($\text{Cr}(\text{OH})_3$) exhibits a low solubility in the neutral pH range (Rai et al., 1987). Furthermore, Cr(III) is generally considered to be benign and an essential trace nutrient for animals and humans (Qin et al., 2005). Therefore, Cr(VI) removal by reduction to Cr(III) with ferrous iron and subsequent precipitation, coprecipitation, or coagulation is well documented (Qin et al., 2005; Pettine et al., 1998; Eary and Rai, 1988; Fendorf and Li, 1996; Buerge and Hug, 1997; Brown et al., 1998; Lee and Hering, 2003; Sharma et al., 2008; Schlautman and Han, 2001). In the reaction between Cr(VI) and Fe(II), Cr(VI) is reduced to Cr(III) by Fe(II), while Fe(II) is oxidized to Fe(III), which forms ferric hydroxide rapidly. The reduced Cr(III) can be easily sorbed and/or coprecipitated with the ferric hydroxide as the following reaction (Lee and Hering, 2003):



Our previous study had demonstrated that Fe(III) formed *in-situ* by oxidizing Fe(II) with permanganate was very powerful for removing As(V) (Guan et al., 2009). Moreover, Namasivayam and Senthilkumar (1998) showed that Fe(III)/Cr(III) hydroxide could be effectively used for the removal of arsenate from solution. Thus, it is expected that the precipitates formed in the process of Cr(VI) reduction by Fe(II), $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_3(\text{s})$, have great capacity to entrap or coprecipitate As(V). Additionally, Cr(III) form complexes with inorganic and organic ligands present in the environment, leading to higher solubility (Rai et al., 1987, 2004). It was reported that at increasing concentrations, Cr(III) also can cause adverse effects on living organisms (Anirudhan and Radhakrishnan, 2007). Since the soluble complexes of Cr(III) can be re-oxidized to Cr(VI) either by the naturally occurring oxidants (Eary and Rai, 1988; Fendorf and Li, 1996; Buerge and Hug, 1997; Brown et al., 1998; Lee and Hering, 2003) or by chlorine or other strong oxidizing disinfectants during drinking water treatment (Schlautman and Han, 2001), removal of both Cr(VI) and Cr(III) (i.e., total Cr) is vital to a successful Cr treatment technology (Qin et al., 2005). Therefore, the

overall purpose of this study is to investigate chromium and arsenate removal from contaminated groundwater by Fe(II) in single-solute and bi-solute systems. The effects of pH, Fe(II) dosage, and Cr(VI)/As(V) molar ratio on the removal of chromium or/and arsenate by Fe(II) were also discussed.

1 Experimental section

1.1 Chemicals and reagents

All chemicals used in the experiments were reagent grade and all solutions were prepared with distilled water. The stock solutions of As(V) and Cr(VI) were prepared weekly from $\text{Na}_3\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$, respectively. FeSO_4 solution was prepared freshly for each set of experiments using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and acidified (to avoid Fe(II) oxygenation) by adding concentrated HCl to the solution. Background electrolyte solutions were prepared from the reagent-grade salts NaCl and NaHCO_3 . Samples containing As(V) and/or Cr(VI) were prepared by diluting stock solutions to target concentrations, with a constant ionic strength and alkalinity provided by 0.01 mol/L NaCl and 0.001 mol/L NaHCO_3 , respectively.

1.2 Batch experiments

The batch experiments were carried out by preparing a series of 100 mL samples containing As(V) and/or Cr(VI) of predetermined concentrations in conical flasks. The pH values were adjusted to 4–10 with HCl or NaOH, and then the flasks were capped and placed in a reciprocating shaker immediately after dosing certain amount of ferrous iron. The concentrations of both Cr(VI) and As(V) were relevant to their levels in groundwater, Cr(VI) 0–22 mg/L and As 0.0005–5 mg/L (Liu et al., 2009; Smedley and Kinniburgh, 2002; Gonzalez et al., 2005).

A shaking rate of 130 r/min was used and all experiments were carried out at 22°C in a water bath. Given that it is very difficult to purge oxygen from the process stream during full scale drinking water treatment, the experiments were carried out without any attempt to control dissolved oxygen (DO) concentrations. The initial DO concentration was in the range of 5.46–5.82 mg/L. The preliminary study indicated that both chromium and arsenate removal by Fe(II) could approach equilibrium in 2 hr under common environmental conditions (pH 6–8) when they coexisted in solution. Although prolonged reaction time could improve chromium and arsenate removal significantly at pH < 6, it had limited influence on chromium and arsenate removal at pH > 6 (data not shown). Considering the practical retention time in groundwater treatment, a reaction time of 2 hr was employed in this study. Each experiment was carried out at least in duplicates with reproducible results. All points in the figures are the mean values and error bars represent standard deviation of the means.

The kinetics of chromium and/or arsenate removal by Fe(II) was investigated at pH 6, 7, 8 by shaking vials of samples containing 10 $\mu\text{mol/L}$ Cr(VI) or/and 10 $\mu\text{mol/L}$ As(V) immediately after dosing 45 $\mu\text{mol/L}$ of Fe(II). One

vial of sample was taken at certain time intervals up to 120 min for equilibrium pH measurement and total Cr and/or As analysis. To investigate the removal of chromium and/or arsenate, various concentrations of ferrous iron ranging from 20 to 60 $\mu\text{mol/L}$ were applied to react with the samples containing Cr(VI) and/or As(V) at desired pH values for 2 hr.

1.3 Chemical analysis.

After each test, the supernatant was sampled and filtered immediately through a cellulose acetate membrane (MFS) of 0.45 μm pore size for the determination of total As, Cr and Fe by inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer Optima 5300 DV, USA) with detection limits for As, Cr and Fe are and 7, 1, and 0.1 $\mu\text{g/L}$, respectively. All samples and standards were acidified according to the standard methods (APHA, 1995) before subject to ICP-OES analysis.

2 Results

2.1 Kinetics of chromium and arsenate removal by Fe(II)

Kinetics of chromium removal by Fe(II) in the absence or presence of arsenate was investigated at pH 6–8, as demonstrated in Fig. 1. In the absence of arsenate, chromium removal by Fe(II) reached equilibrium at 120, 10, and 5 min, respectively, at pH 6, 7 and 8. At equilibrium, 99.1% and approximately 100% of chromium was removed at pH

6 and pH 7–8, respectively. The presence of 10 $\mu\text{mol/L}$ arsenate had negligible effects on the removal rate of chromium at pH 7, however, it showed slight inhibitory effects at pH 6 and 8. The removal efficiency of chromium was reduced by 2.8% and 6.5%, respectively, at pH 6 and 8 due to the presence of arsenate.

Arsenate removal by Fe(II) was very slow at pH 6–8 and did not achieve equilibrium in 120 min in the absence of chromate. As shown in Fig. 1d, only 6.4%–23.8% of arsenate was removed by 45 $\mu\text{mol/L}$ Fe(II). The presence of 10 $\mu\text{mol/L}$ chromate remarkably enhanced the removal rate of arsenate at pH 6–8. In the presence of chromate, arsenate removal increased rapidly in the first 45 min and then increased gradually. The removal rate of arsenate at pH 7 and 8 was greater than that at pH 6 in the first 20 min and 10 min, respectively, which may be attributable to the more rapid oxidation of Fe(II) by chromate at pH 7–8 than that at pH 6. As both chromium and arsenate removal by Fe(II) could approach equilibrium in 2 hr at pH 6–8 when they were coexisted in solution, a reaction time of 2 hr was employed in the following experiments.

2.2 Chromium removal by Fe(II) in the absence of arsenate

Chromium removal by Fe(II) in the absence of arsenate as a function of pH and Fe(II) dosage was determined and illustrated in Fig. 2. Chromium removal was strongly influenced by pH and Fe(II) dosage. At various Fe(II) dosages, chromium removal increased to the maximum

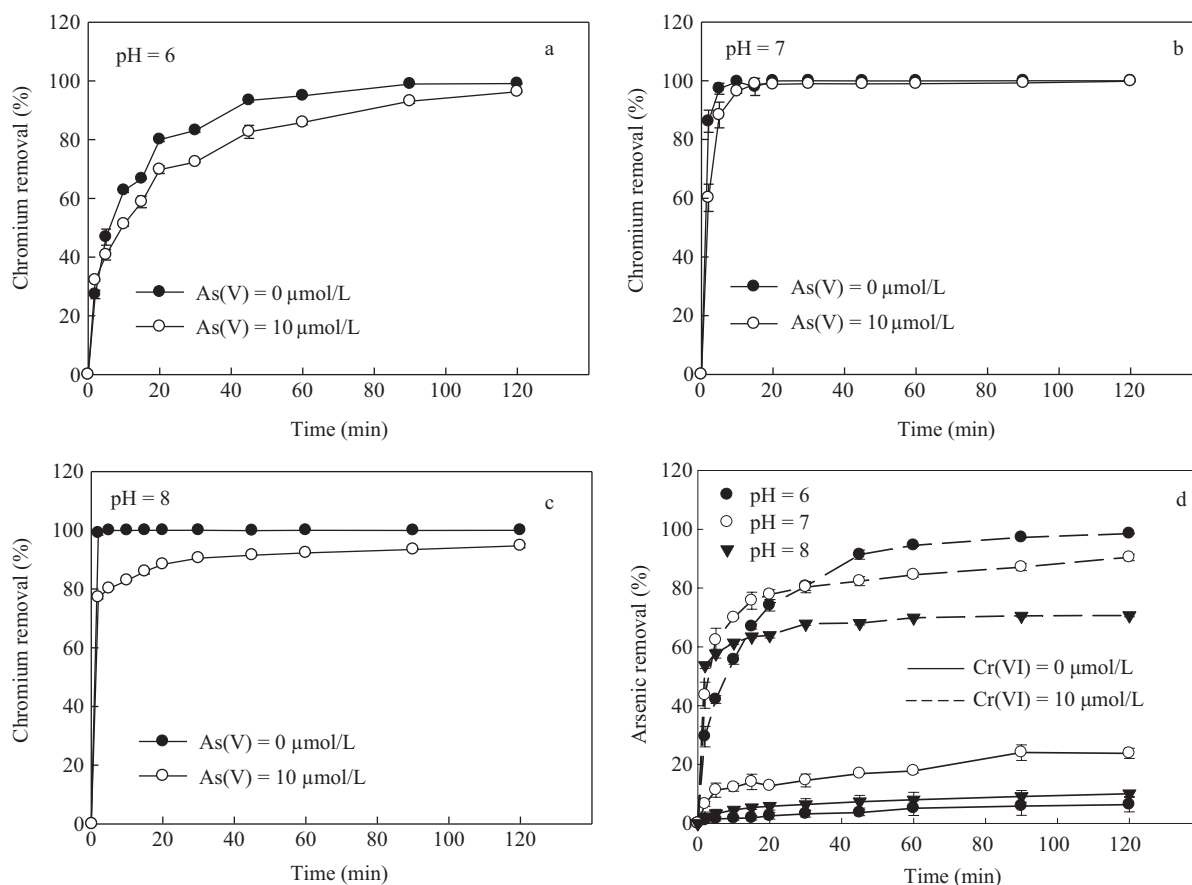


Fig. 1 Kinetics of chromium removal and arsenate removal by Fe(II) under various conditions (Fe(II): 45 $\mu\text{mol/L}$).

with increasing pH and then decreased with further increase in pH. When Fe(II) was dosed at 20 $\mu\text{mol/L}$, maximum removal of chromium was 68.6% which was achieved at pH 6. When the dosage of Fe(II) was increased to 30 $\mu\text{mol/L}$, 97.5% of chromium was removed at pH 7. The chromium removal of 99%–100% was observed over the pH range of 5.9–7.7 and 5.8–7.8, respectively, when Fe(II) was dosed at 45 $\mu\text{mol/L}$ and 60 $\mu\text{mol/L}$. Decrease in pH or increment in pH out of this range resulted in a decline in chromium removal. The increase in Fe(II) dosage resulted in an improvement in chromium removal and the improvement was more remarkable under alkaline conditions than that under acidic conditions. Chromium removal was enhanced over pH 5–10 by increasing Fe(II) dosage from 20 to 45 $\mu\text{mol/L}$ and a further rise in Fe(II) dosage from 45 to 60 $\mu\text{mol/L}$ only resulted in an improvement in chromium removal at pH 8–10.

2.3 Chromium removal by Fe(II) in the presence of arsenate

The effects of arsenate on chromium removal by Fe(II) (initial Cr(VI)/As(V) molar ratio was 1) were strongly dependent on pH and Fe(II) dosages, as illustrated in Fig. 2. The presence of arsenate had more drastic effects on chromium removal by Fe(II) under alkaline conditions

than that under acidic and neutral conditions. For instance, chromium removal was decreased by 5.4%–11.2% at pH 4–7 and by 12.4%–33.9% at pH 7.5–10 due to the presence of 10 $\mu\text{mol/L}$ arsenate when Fe(II) was 20 $\mu\text{mol/L}$. Increasing Fe(II) dosage could alleviate the inhibitive effects from arsenate for chromium removal by Fe(II). When Fe(II) was dosed at 45 $\mu\text{mol/L}$, the presence of 10 $\mu\text{mol/L}$ arsenate had negligible effects on chromium removal at pH 4–7 but reduced chromium removal under alkaline condition. When Fe(II) was applied at 60 $\mu\text{mol/L}$, chromium removal was only slightly affected by the presence of arsenate at pH 8–9. Over 99% of chromium was removed at pH 6.8 even in the presence of arsenate when Fe(II) was dosed at 45 or 60 $\mu\text{mol/L}$.

2.4 Arsenate removal by Fe(II) in the absence of chromate

It was expected that arsenate could be removed by ferric hydroxide derived from oxidation of Fe(II) by dissolved oxygen in the solution. Accordingly, arsenate removal by Fe(II) at various pH levels and Fe(II) dosages was investigated, as shown in Fig. 3. When Fe(II) was dosed at 20–45 $\mu\text{mol/L}$, arsenate removal varied from 2.2% to 14.7% at pH 4–6 and reached maximum at pH 6.7–6.9. With further increment in pH, arsenate removal experienced a

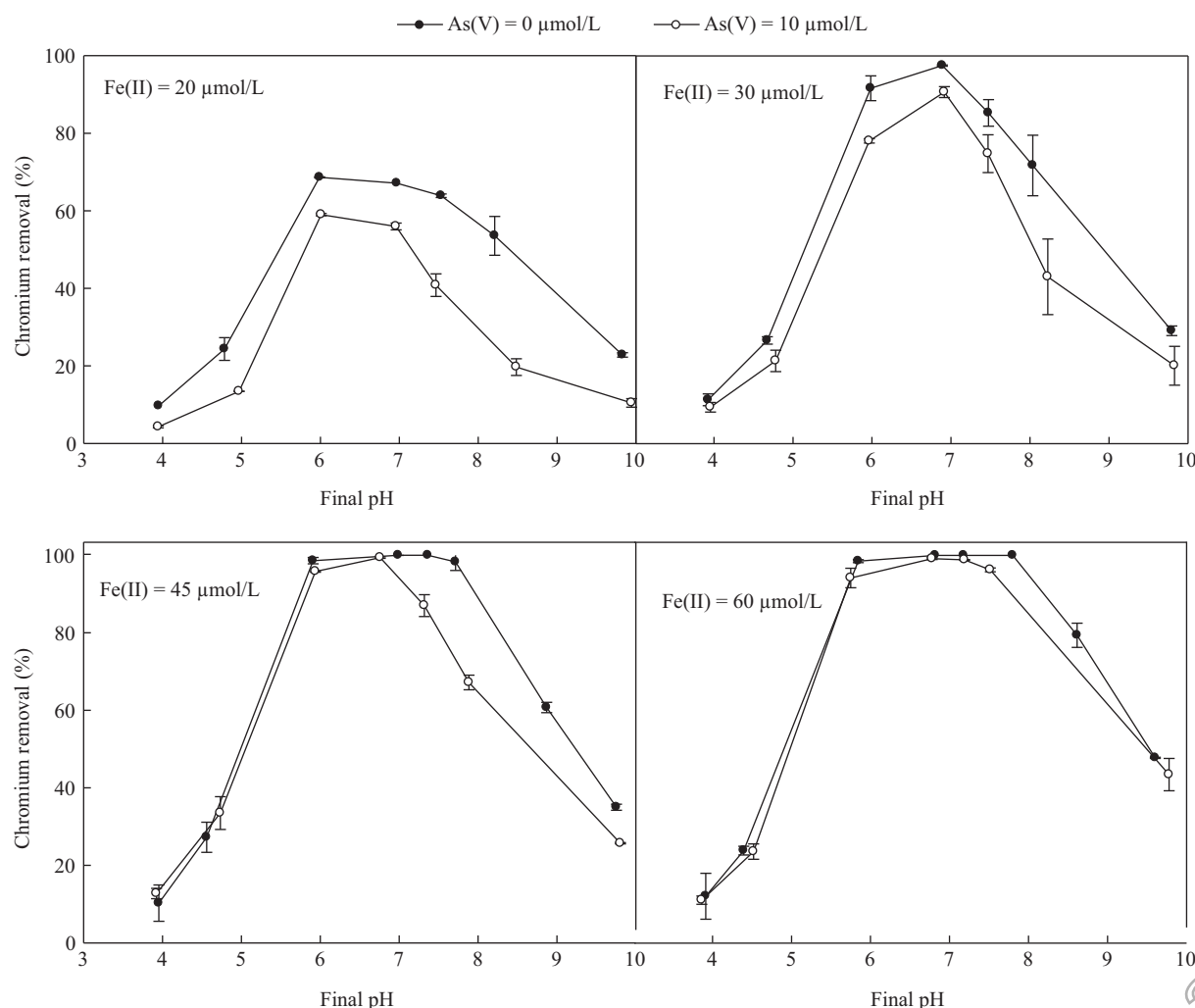


Fig. 2 Chromium removal by Fe(II) in the absence and presence of arsenate as a function of pH and Fe(II) dosage at Cr(VI) of 10 $\mu\text{mol/L}$.

reduction and then a slight increase. However, a different removal edge for arsenate was observed when Fe(II) was 60 $\mu\text{mol/L}$. Arsenate removal rose slowly from pH 4.0 to pH 6.0 but increased sharply to 92.7% over the pH range of 6.0–7.1. Under the alkaline conditions, arsenate removal was lowered sharply from pH 7.1 to pH 7.4 but decreased gradually at pH 7.4–9.7.

2.5 Arsenate removal by Fe(II) in the presence of chromate

The presence of 10 $\mu\text{mol/L}$ chromate (initial Cr(VI)/As(V) molar ratio 1) dramatically improved arsenate removal by Fe(II) under most conditions investigated in this study, as shown in Fig. 3. At various Fe(II) dosages, the optimal arsenate removal was achieved at pH 5.8–6.0 and the increase or reduction in pH resulted in a decline in arsenate removal. When Fe(II) was dosed at 20 $\mu\text{mol/L}$, arsenate removal rose gradually from 28.1% to 71.1% as pH increased from 4.0 to 6.0 and then reduced gradually from 71.1% to 9.5% as pH varied from 6.0 to 8.5. The variation of arsenate removal with pH at Fe(II) dosage of 30 or 45 $\mu\text{mol/L}$ was very similar to that at Fe(II) dosage of 20 $\mu\text{mol/L}$, except that higher Fe(II) dosage resulted in a higher arsenate removal at pH 3.9–9.8. In particular, when Fe(II) was applied at 60 $\mu\text{mol/L}$, arsenate removal over the pH range of 3.8–9.6 can be divided into

three stages: a slow increase from 74.0% to 99.2% at pH 3.9–5.8, a very slow decline from 99.2% to 94.4% at pH 5.8–7.2, and a sharp decrease from 94.4% to 22.1% over the pH range of 7.2–9.8. Arsenate removal was improved by 9.3%–68.7%, 26.0%–86.0%, 44.7%–83.6% and 1.7%–84.9%, respectively, at pH 4–9 due to the presence of 10 $\mu\text{mol/L}$ chromate at Fe(II) dosages of 20, 30, 45, and 60 $\mu\text{mol/L}$. In addition, arsenate removal by Fe(II) in the presence of chromate was enhanced by the increase of Fe(II) dosages over the pH range of 4–10.

2.6 Effects of initial Cr(VI)/As(V) molar ratios on chromium and arsenate removal by Fe(II).

The removal of chromium and arsenate by Fe(II) was examined when the initial concentrations of chromate and arsenate were 20 $\mu\text{mol/L}$ and 10 $\mu\text{mol/L}$ (initial Cr(VI)/As(V) molar ratio 2:1), respectively, and the results are illustrated in Fig. 4. In the presence of 10 $\mu\text{mol/L}$ arsenate, chromium removal by Fe(II) increased with increasing pH from 3.9 to 5.9 and remained almost constant over pH 5.9–7.4 before a decline with further increase in pH. The maximum chromium removal was achieved at pH 6.9 at various Fe(II) dosages. The increment in Fe(II) dosage from 30 to 60 $\mu\text{mol/L}$ resulted in a drastic enhancement in optimum chromium removal from 50.7% to 97.1%.

In the presence of 20 $\mu\text{mol/L}$ chromate (Fig. 5), arsenate

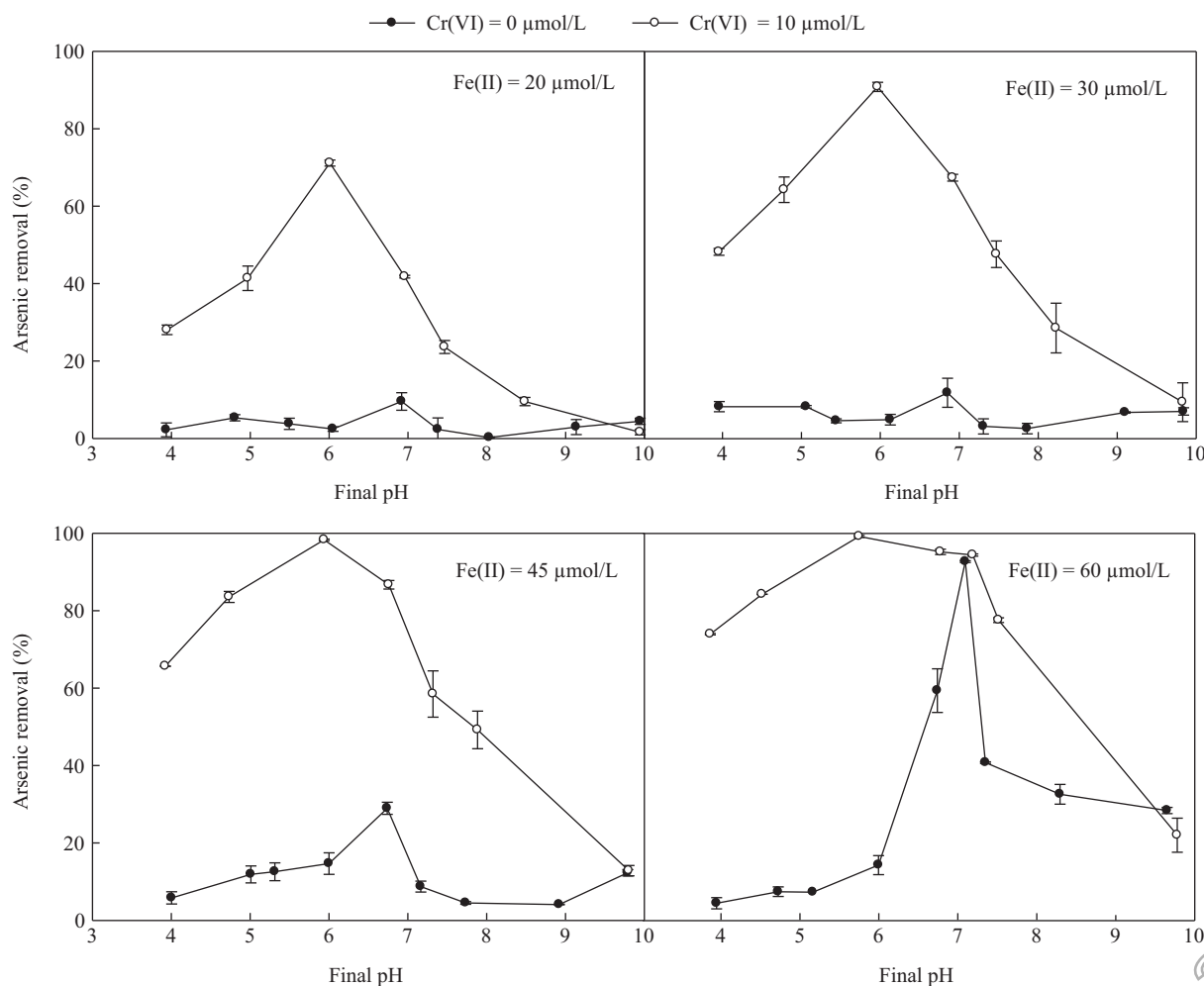


Fig. 3 Arsenic removal by Fe(II) in the absence and presence of chromate as a function of pH and Fe(II) dosages (As(V): 10 $\mu\text{mol/L}$).

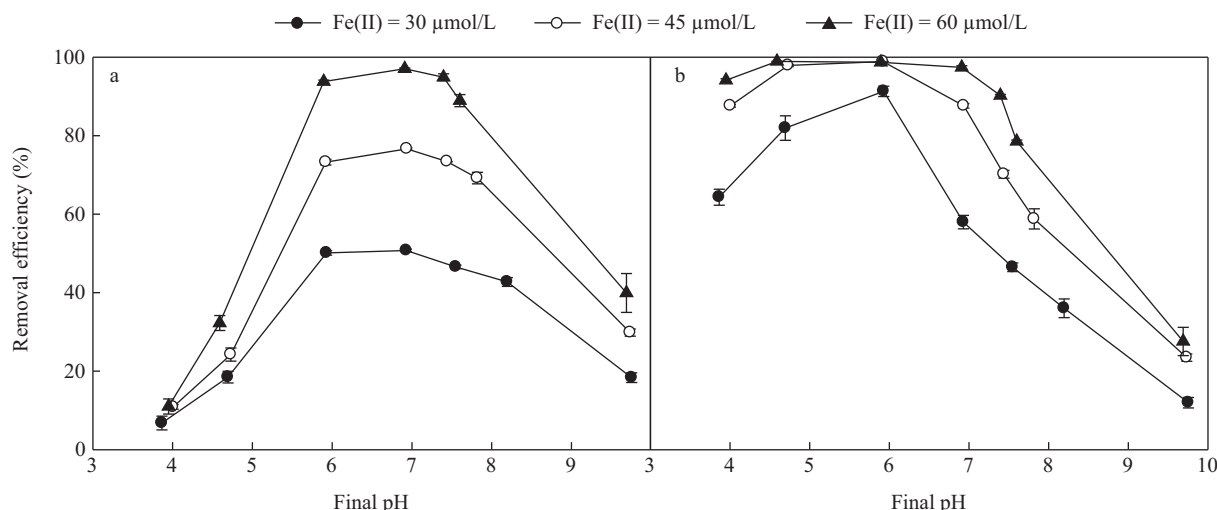


Fig. 4 Simultaneous removal of chromium (a) and arsenate (b) as a function of pH and Fe(II) dosage at Cr(VI)/As(V) molar ratio of 2:1 (Cr(VI) 20 µmol/L, As(V) 10 µmol/L).

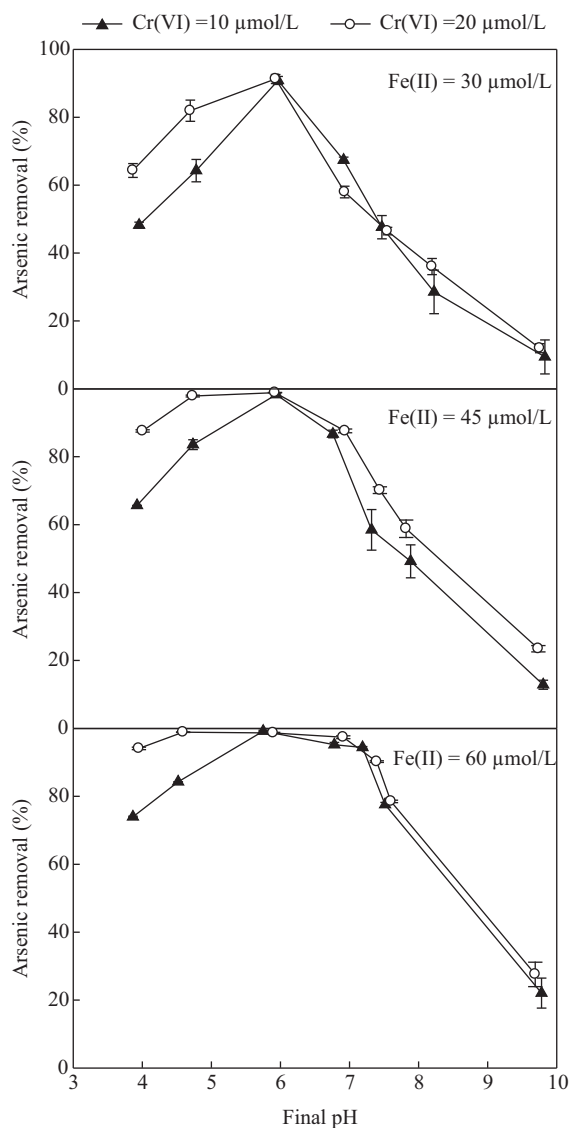


Fig. 5 Effects of concentration of co-existing chromate on arsenate removal as a function of pH and Fe(II) dosages (As(V): 10 µmol/L).

removal rose gradually from 64.3% to 91.3% as pH increased from 3.9 to 5.9 and then reduced gradually from 91.3% to 12.0% as pH varied from 6.0 to 9.8, when Fe(II) was dosed at 30 µmol/L. As Fe(II) dosage was applied at 45 or 60 µmol/L, a broad removal maximum was achieved for arsenate, with 97.4%–98.9% arsenate uptake at pH 4.7–5.9 and pH 4.6–6.9, respectively. Interestingly, it was found that increasing chromate concentration from 10 to 20 µmol/L resulted in an improvement in arsenate removal by 16.1%–20% and 14.3%–17.7%, respectively, at pH 4.0 and pH 4.6 when Fe(II) was dosed at 30–60 µmol/L.

This study also examined chromium and arsenate uptake by Fe(II) dosed at 30–60 µmol/L when the initial concentrations of chromate was 10 µmol/L and arsenate was 20 µmol/L (initial Cr(VI)/As(V) molar ratio 1:2). As shown in Fig. 6, in the presence of 20 µmol/L arsenate, optimum chromium removal was achieved at pH 5.8 at various Fe(II) dosages and increase or decrease in pH resulted in a sharp decrease in chromium removal (Fig. 6a). Chromium removal in the presence of 20 µmol/L arsenate was not greatly affected by Fe(II) dosages, especially under neutral and alkaline conditions. The increase in Fe(II) dosage from 30 to 60 µmol/L only led to a slight improvement in chromium uptake at pH 5.8 from 84.0%–97.7%. Arsenate removal by Fe(II) in the presence of chromate was strongly dependent on pH but moderately dependent on Fe(II) dosage when the initial Cr(VI)/As(V) molar ratio was 1:2, as illustrated in Fig. 6b. Arsenate removal improved gradually as pH increased from 3.9 to 5.8 but reduced sharply with further increase in pH. Arsenate removal was enhanced by only 12.1%–26.7% at pH 3.9–6.8 when the Fe(II) dosage was increased from 30 to 60 µmol/L; however, there was almost no improvement under neutral and alkaline conditions. It was found that chromium removal by Fe(II) was increased by 1.2%–19.6% at pH 3.9–5.8 due to the presence of 20 µmol/L arsenate, compared to the case where arsenate was 10 µmol/L, as shown in Fig. 7. On the other hand, the presence of 20 µmol/L arsenate dramatically decreased chromium removal by Fe(II) over the pH range of 6.7–9.8, as illustrated in Figs. 6a and 7.

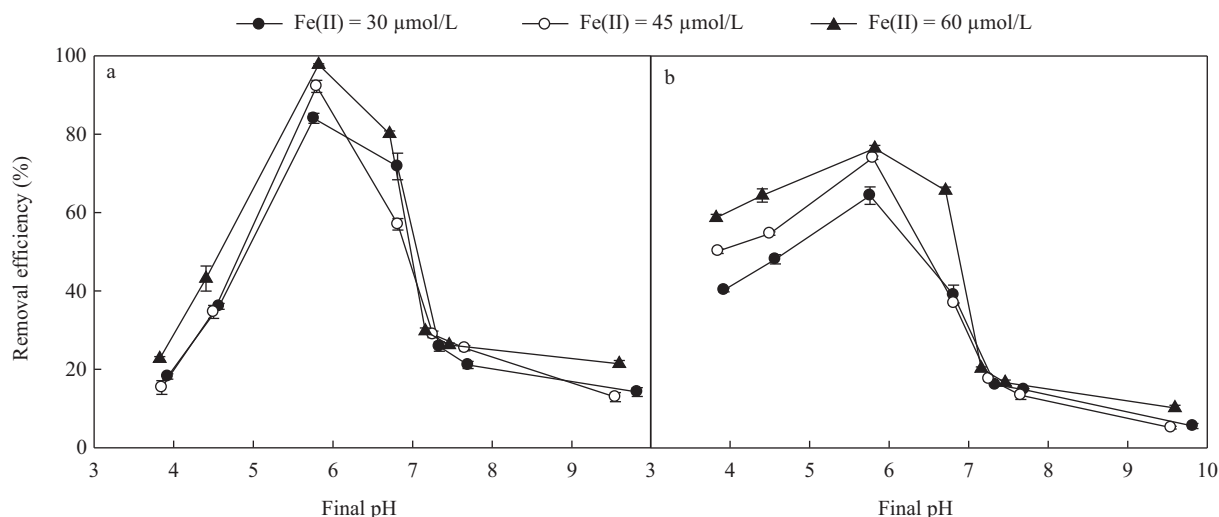


Fig. 6 Simultaneous removal of chromium (a) and arsenate (b) as a function of pH and Fe(II) dosages at Cr(VI)/As(V) molar ratio of 1:2 (Cr(VI): 10 $\mu\text{mol/L}$, As(V): 20 $\mu\text{mol/L}$).

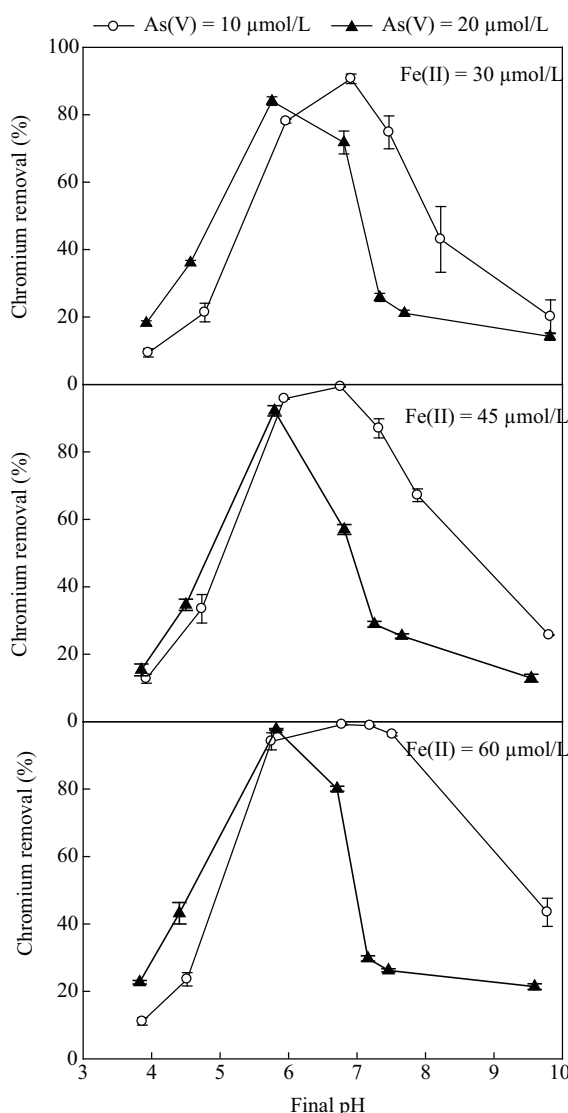


Fig. 7 Effects of concentration of co-existing arsenate on chromium removal as a function of pH and Fe(II) dosage (Cr(VI): 10 $\mu\text{mol/L}$).

Under neutral and alkaline conditions, increasing Fe(II) dosage could not mediate the detrimental effects from

arsenate of 20 $\mu\text{mol/L}$ on chromium removal by Fe(II).

3 Discussion

Batch experiments showed that Fe(II) is effective in removing chromium from water under neutral conditions, even in the presence of arsenate when the initial molar ratio of As(V)/Cr(VI) ≤ 1 . However, in the case of groundwater containing arsenate and chromate with molar ratio of As(V)/Cr(VI) ≥ 2 , some cations, e.g., Ca^{2+} or Mg^{2+} , should be applied together with Fe(II) to the contaminated groundwater to improve the precipitation of Fe-Cr hydroxides as well as the removal of both chromium and arsenate. In this method, Fe(II) may have to be dosed at a higher concentration than the theoretical requirement to remove both chromium and arsenate in order to meet the drinking water standard. Nonetheless, the residual Fe(II) can be easily removed by aeration and filtration.

In addition, as all of our experiments were performed in solutions without deoxygenation, more efficient removal of chromium and arsenate by Fe(II) would be anticipated in groundwater containing little dissolved oxygen since the competing side reaction with oxygen would not be a concern. Therefore, *in-situ* remediation of groundwater contaminated by both chromium and arsenate by addition of soluble Fe(II) salts may be an economic alternative to pump and treat remediation or to permeable reactive Fe(0) barriers which might become less reactive with time because of surface passivation (Liu et al., 2009).

4 Conclusions

Effects of pH, Fe(II) dosage, Cr(VI)/As(V) molar ratio on the removal of chromium or/and arsenate by Fe(II) were investigated in single-solute and bi-solute systems. In the absence of arsenate, chromium removal by Fe(II) reached a maximum at pH 7 and declined with either further decrease or rise in pH. The increment in Fe(II) dosage resulted in an improvement in chromium removal. The presence of 10 $\mu\text{mol/L}$ arsenate caused more significant decrease in

chromium removal under neutral and alkaline conditions than that under acidic conditions, but the decrease could be alleviated by increasing Fe(II) dosage. Over 99% of chromium was removed at pH 6.8 even in the presence of 10 $\mu\text{mol/L}$ arsenate when Fe(II) was dosed at 45 or 60 $\mu\text{mol/L}$. However, in the case of Cr(VI)/As(V) molar ratio 1:2, increasing Fe(II) dosage could not mediate the detrimental effects from arsenate on chromium removal by Fe(II) under neutral and alkaline conditions. Arsenate removal by Fe(II) alone was trivial except at extremely high dosage of Fe(II), but was significantly improved at pH 4–9 due to the presence of 10 $\mu\text{mol/L}$ chromate at various Fe(II) dosages. Increasing chromate concentration from 10 to 20 $\mu\text{mol/L}$ resulted in further improvement in arsenate removal at pH 4.0–4.6 when Fe(II) was dosed at 30–60 $\mu\text{mol/L}$.

This study implies that Fe(II) is feasible for the treatment of groundwater contaminated by both chromate and arsenate. This method is very appealing because of its relatively low cost, ease of handling and effectiveness. In addition, Fe(II) is most effective for chromium and arsenate removal at pH 7, suggesting that it is not necessary to adjust pH for most waters.

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References

- Aceto M, Fedele A, 1994. Rain water effect on the release of arsenic, chromium and copper from treated wood. *Fresenius Environmental Bulletin*, 3: 389–394.
- APHA (American Public Health Association), 1995. Standard Methods for the Examination of Water and Wastewater (19th ed.). Washington DC, USA.
- Anirudhan T S, Radhakrishnan P G, 2007. Chromium(III) removal from water and wastewater using a carboxylate-functionalized cation exchanger prepared from a lignocellulosic residue. *Journal of Colloid and Interface Science*, 316: 268–276.
- Buerge I J, Hug S J, 1997. Kinetics and pH dependence of chromium(VI) reduction by iron(II). *Environmental Science & Technology*, 31: 1426–1432.
- Buerge I J, Hug S J, 1999. Influence of mineral surfaces on chromium(VI) reduction by iron(II). *Environmental Science & Technology*, 33: 4285–4291.
- Brown R A, Leahy M C, Pyrih R Z, 1998. *In situ* remediation of metals comes of age. *Remediation*, 8: 81–96.
- Charlet L, Manceau A A, 1992. X-ray absorption spectroscopic study of the sorption of Cr(III) at the oxide-water interface, II. Adsorption, coprecipitation, and surface precipitation on hydrous ferric oxide. *Journal of Colloid and Interface Science*, 148: 443–458.
- Eary L E, Rai D, 1988. Chromium removal from aqueous wastes by reduction with ferrous ion. *Environmental Science & Technology*, 22(8): 972–977.
- Fendorf S E, Li G C, 1996. Kinetics of chromate reduction by ferrous ion. *Environmental Science & Technology*, 30: 1614–1617.
- Gonzalez A R, Ndung 'U K, Flegal A R, 2005. Natural occurrence of hexavalent chromium in the aromas red sands aquifer, California. *Environmental Science & Technology*, 39(15): 5505–5511.
- Greven M, Green S, Robinson B, Clothier B, Vogeler I, Agnew R et al., 2007. The impact of CCA-treated posts in vineyards on soil and ground water. *Water Science and Technology*, 56(2): 161–168.
- Guan X H, Ma J, Dong H R, Jiang L, 2009. Removal of arsenic from water: Effect of Ca^{2+} on As(III) removal in KMnO_4^- Fe(II) process. *Water Research*, 43: 5119–5128.
- Guan X H, Su T Z, Wang J M, 2008. Removal of arsenic from water using granular ferric hydroxide: Macroscopic and microscopic studies. *Journal of Hazardous Materials*, 156: 178–185.
- Jha A K, Bose A, Downey J P, 2006. Removal of As(V) and Cr(VI) from aqueous solution using a continuous hybrid field-gradient magnetic separation device. *Separation Science and Technology*, 41: 3297–3312.
- Khaodhiar S, Azizian M F, Osathaphan K, Nelson P O, 2000. Copper, chromium, and arsenic adsorption and equilibrium modeling in an iron-oxide coated sand, background electrolyte system. *Water, Air, & Soil Pollution*, 119: 105–120.
- Lee G, Hering J G, 2003. Removal of chromium(VI) from drinking water by redox-assisted coagulation with iron(II). *Journal of Water Supply: Research & Technology-Aqua*, 52(5): 319–332.
- Liu T Z, Rao P H, Mak M S H, Wang P, Lo I M C, 2009. Removal of co-present chromate and arsenate by zero-valent iron in groundwater with humic acid and bicarbonate. *Water Research*, 43(9): 2540–2548.
- MHPRC (Ministry of Health of the People's Republic of China), 2007. http://www.moh.gov.cn/open/db_query/new/20070628143525.pdf.
- Namasivayam C, Senthilkumar S, 1998. Removal of arsenic(V) from aqueous solution using industrial solid waste: Adsorption rates and equilibrium studies. *Industrial & Engineering Chemistry Research*, 37: 4816–4822.
- Oliveira D Q L, Goncalves M, Oliveira L C A, Guilherme L R G, 2008. Removal of As(V) and Cr(VI) from aqueous solutions using solid waste from leather industry. *Journal of Hazardous Materials*, 151: 280–284.
- Parga J R, Cocke D L, Valverde V, Gomes J A G, Kesmez M, Moreno H et al., 2005. Characterization of electrocoagulation for removal of chromium and arsenic. *Chemical Engineering & Technology*, 28(5): 605–612.
- Pettine M, D'Ottone L, Campanella L, Millero F J, Passino R, 1998. The reduction of chromium(VI) by iron(II) in aqueous solutions. *Geochimica et Cosmochimica Acta*, 62(9): 1509–1519.
- Pierce M L, Moore C B, 1980. Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. *Environmental Science & Technology*, 14(2): 214–216.
- Qin G, McGuire M J, Blute N K, Seidel C, Fong L, 2005. Hexavalent chromium removal by reduction with ferrous sulfate, coagulation, and filtration: A pilot-scale study. *Environmental Science & Technology*, 39: 6321–6327.
- Raji C, Anirudhan T S, 1997. Chromium (VI) adsorption by sawdust: Kinetics and equilibrium. *Indian Journal of Chemical Technology*, 4(5): 228–236.
- Rai D, Sass B M, Moore D A, 1987. Chromium(III) hydrolysis constants and solubility of chromium(III) hydroxide. *Inorganic Chemistry*, 26(3): 345–349.

- Rai D, Moore D A, Hess N J, Rao L, Clark S B, 2004. Chromium(III) hydroxide solubility in the aqueous Na^+ - OH^- - H_2PO_4^- - HPO_4^{2-} - PO_4^{3-} - H_2O system: A thermodynamic model. *Journal of Solution Chemistry*, 33: 1213–1242.
- Schlautman M A, Han I, 2001. Effect of pH and dissolved oxygen on the reduction of hexavalent chromium by dissolved ferrous iron in poorly buffered aqueous systems. *Water Research*, 35(6): 1534–1546.
- Sharma S K, Petrusevski B, Amy G, 2008. Chromium removal from water: a review. *Journal of Water Supply Research and Technology*, 57(8): 541–553.
- Smedley P L, Kinniburgh D G, 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17(5): 517–568.
- WHO, 1993. Guidelines for Drinking Water Quality: 1. Recommendations, World Health Organization, Geneva.