Influence of pH on hexavalent chromium reduction by Fe(II) and sulfide compounds

Juan Chen, Ri Chen and Mei Hong

ABSTRACT

Batch experiments were conducted to investigate the influence of pH on Cr(VI) reduction with Fe(II), sulfide and mixtures of Fe(II) and sulfide at pH 3.0–12.0. The results showed that Fe(II) could reduce Cr(VI) with a high removal of nearly 100% in the pH range of 3.0–9.0, while the reduction of Cr(VI) decreased to approximately 60% considering the oxygenation of Fe(II) at pH 12.0. The reaction between Cr(VI) and sulfide, however, was largely pH dependent. H2S was the main sulfide species with the Cr(VI) removal of ~80% at pH < 7.0, while sulfide mainly existed in the forms as HS− or S2− at pH ≥ 7.0, which had very limited removal of Cr(VI) (no more than 10%). The Cr(VI) removal by the mixtures of Fe(II) and sulfide was also compared with the sum of separate ones at different pH values. The sum of Cr(VI) removal by single Fe(II) and S(−II) was similar to that by the mixtures at pH 3.0–5.0 and pH 12.0, while the removal of Cr(VI) by the mixtures was observed to be more effective than the sum of the single-species removals at pH 7.0–9.0; the promoting effect was primarily attributed to the catalysis of ferric ion generated during the reduction process.

Key words | catalysis, ferrous ions, hexavalent chromium, reduction, sulfide

INTRODUCTION

Chromium is a vital industrial material which is widely used in ore processing, surface treatment of heavy metal, electroplating, wood preservation, leathering tanning, pigments etc.; thus a large quantity of chromium-contaminated wastewater, gas and residue are produced during these procedures (Nriagu & Nieboer 1988; Palmer & Wittbrodt 1994; Li et al. 2009). Inadequate storage and improper disposal practices for these chromium-contaminated wastes have caused incidents of soil and groundwater contamination in many areas. Chromium is found in two stable oxidation states, Cr(VI) and Cr(III), in the environment, which have contrasting toxicities, mobilities, and bioavailabilities. Moreover it is generally considered that the toxicity of Cr(VI) is 100 times than that of Cr(III) (Norseth 1981; Fendorf & Li 1996; Qin et al. 2005). Remediation of chromium-contaminated soil and groundwater has largely followed the two important pathways of reduction and precipitation/immobilization (Mullet et al. 2004; Xu et al. 2005; Cao & Zhang 2006; Richard et al. 2011). FeS can sequester Cr(VI) by a single step combining reduction and precipitation, shown in the following equation (Mullet et al. 2004):

\[ \text{Cr}_2\text{O}_7^{2−} + 2\text{FeS} + 7\text{H}_2\text{O} \rightarrow \text{Cr(OH)}_3 + \text{Fe(OH)}_3 + 2\text{S} + 2\text{OH}^- \] (1)

A number of studies on Cr(VI) reduction by aqueous iron(II) or iron-bearing minerals have been carried out (Buerge & Hug 1997; Batchelor et al. 1998; Hwang et al. 2002; Qin et al. 2005). In contrast, Cr(VI) reduction by sulfur species, in particularly hydrogen sulfide, has also been less widely studied (Pettine et al. 1994; Pettine et al. 1998; Kim et al. 2001; Mullet et al. 2004; Lan et al. 2007). Ferrous sulfide (mackinawite), which contains two strong reducing agents, iron(II) and sulfide(−II), could form precipitate with Cr(VI) directly and inhibit the re-oxidation of Cr(III) in the underground environment; hence many researchers have employed FeS as a reductant to remove Cr(VI) (Butler & Hayes 2000; Erdem et al. 2001; Wu & Deng 2004). But studies on the pH influences of chromium reduction by FeS, Fe(II) and S(−II) are relatively limited.

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Key words | catalysis, ferrous ions, hexavalent chromium, reduction, sulfide

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Buerge & Hug (1997) investigated the reaction kinetics of Cr(VI) reduction by Fe(II) in the pH range of 2.0–7.2, and reported that the removal increased with the decreasing of pH at pH < 4.0, while at pH 4.0–7.2, the reduction improved as pH increased, following a second-order reaction kinetics. Results obtained under oxic and anoxic conditions showed that pH could significantly affect the rates of Cr(VI) reduction, with more rapid reduction rates occurring at higher pH values (Schlautman & Han 2001). Karale et al. (2007) exploited ferrous sulfate as the reductant of Cr(VI); when the dose of ferrous sulfate was 2000 mg/L, the removal of Cr(VI) increased from 55 to 99% as pH decreased from 2.0 to 1.0. Lan et al. (2010) showed that the reduction of Cr(VI) by sulfide compounds increased dramatically as pH decreased from 9.07 to 7.67. Kim et al. (2004) also demonstrated an internal relevance between pH and Cr(VI) removal; their experimental results indicated that the rates of Cr(VI) reduction increased as pH decreased, meanwhile H2S was the main effective reductant in sulfide species for Cr(VI) reduction.

In this study, the effect of pH on Cr(VI) removal by Fe(II), S(-II) and mixed solutions of Fe(II) and S(-II) was investigated. And the interaction mechanism of Fe(II), S(-II) and Cr(VI) in the mixed solutions was also discussed.

MATERIALS AND METHODS

Materials

In this study, deionized water was thoroughly purged using high-purity nitrogen gas (99.999%) for at least 30 min to remove dissolved oxygen prior to use. Cr(VI) stock solutions (100 mg/L) were prepared by dissolving 0.2829 g dried K2Cr2O7 (ACS grade) in a 1000 mL volumetric flask with deionized water, and diluted to the desired concentration of 20 mg/L. Fe(II) and S(-II) solutions were freshly prepared in 100 mL volumetric flasks with deionized water using FeSO4·7H2O and Na2S·9H2O (both ACS grade). The pH of Cr(VI) solutions was adjusted prior to the reduction experiments by 1 mol/L H2SO4 or 0.5 mol/L NaOH, and the pH range was from 3.0 to 12.0. The temperature of the reaction system was controlled at 20 ± 0.2 °C by a SPX-150B-D concussion incubator.

Analytical methods

Aqueous Cr(VI) concentrations were determined at an absorbance wavelength of 540 nm by diphenylcarbazide method using a UNIC 7200 VIS spectrophotometer. The pH of solutions was measured by a YSI pH/ORP pH meter.

EXPERIMENTAL SETUPS

The distribution coefficients of sulfide species (H2S, HS−, S2−) in different pH conditions

Sulfide ions in water mainly exist in the forms of H2S, HS− or S2−; the dissociation equilibrium of the three sulfide species can be described as follows:

\[
H_2S \rightleftharpoons H^+ + HS^- \quad K_1 = 9.1 \times 10^{-8}
\]

\[
HS^- \rightleftharpoons H^+ + S^{2-} \quad K_2 = 1.1 \times 10^{-12}
\]

where K is the dissociation constant.

Based on mathematical mass balance, we could derive the sulfide species (H2S, HS−, S2−) distribution coefficients in different pH conditions (Wu Han University 2006). Specific calculation results are shown in Figure 1.

Influence of pH on Cr(VI) reduction by Fe(II), S(-II) and the mixtures of Fe(II) and S(-II)

All reactions were conducted in 100 mL serum bottles filled with 50 mL Cr(VI) solutions of 20 mg/L, separately. The reduction experiments with Fe(II) were conducted by adding 1 mL of dissolved FeSO4·7H2O solution with 1 mL Figure 1 | The distribution coefficient of sulfide species (H2S, HS− and S2−) in different pH conditions.
pipette to Cr(VI) solutions with five different pHs (3.0, 5.0, 7.0, 9.0 and 12.0) (concentrations of Cr(VI) and Fe(II) after mixing are listed in Table 1); the molar ratios of Fe$^{2+}$/Cr(VI) were 0, 0.3, 0.9, 1.5, 2.1 and 3.0, respectively. The reduction experiments with sulfide compounds were conducted by adding 1 mL of dissolved Na$_2$S·9H$_2$O solution with a 1 mL pipette to Cr(VI) solutions with five different pHs (3.0, 5.0, 7.0, 9.0) (concentrations of Cr(VI) and S(-II) after mixing are listed in Table 2); the molar ratios of S$^{2-}$/Cr(VI) were 0, 0.15, 0.45, 0.75, 1.05 and 1.50, respectively. The reduction experiments with the mixtures of Fe(II) and sulfide compounds were conducted by adding 1 mL dissolved FeSO$_4$·7H$_2$O solution and 1 mL Na$_2$S·9H$_2$O solution with a 1 mL pipette to Cr(VI) solution with five different pHs (3.0, 5.0, 7.0, 9.0 and 12.0) (concentrations of Cr(VI), Fe(II) and S(-II) after mixing are listed in Table 3); the molar ratios of Fe$^{2+}$/S$^{2-}$/Cr(VI) were 0, 0.1, 0.3, 0.5, 0.7 and 1.0, respectively. The bottles were shaken at 150 rpm in an SPX-150B-D concussion incubator. After the 60 min reaction period, 2 mL samples were withdrawn from the bottles by a 5 mL syringe and filtered through a 0.22 μm pore membrane filter for residual Cr(VI) concentration determination.

RESULTS AND DISCUSSION

Influence of pH on Cr(VI) reduction by Fe(II)

Figure 2 shows that when the stoichiometry of Fe(II) and Cr(VI) reaches 3:1, the reduction of Cr(VI) is close to 100% at pH 3.0–9.0, whereas the removal decreases to approximately 60% at pH higher than 12.0. In acid conditions (pH < 7.0), the reduction of Cr(VI) by Fe(II) could be described as (Buerge & Hug 1997):

$$3\text{Fe}^{2+} + \text{HCrO}_4^- + 7\text{H}^+ = \text{Cr}^{3+} + 3\text{Fe}^{3+} + 4\text{H}_2\text{O} \quad (4)$$

The standard electrode potential of Equation (4) $E = E_{\text{HCrO}_4^-/Cr^{3+}} - E_{\text{Fe}^{3+}/Fe^{2+}} = 1.35 - 0.771 = 0.561$, while in neutral or alkaline conditions (pH ≥ 7.0), the reaction pathways could be hypothesized as (Fendorf & Li 1996):

$$3\text{Fe}^{2+} + \text{CrO}_4^{2-} + 8\text{H}_2\text{O} = \text{Cr(OH)}_3 + 3\text{Fe(OH)}_3 + 4\text{H}^+ \quad (5)$$

$$3\text{Fe(OH)}^+ + \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + \text{OH}^- = \text{Cr(OH)}_3 + 3\text{Fe(OH)}_3 \quad (6)$$

Under these pH conditions, $E = E_{\text{CrO}_4^{2-/Cr}^{3+}} - E_{\text{Fe}^{3+}/Fe^{2+}} = -0.12 - (-0.56) = 0.44$ V. The difference in standard electrode potentials between acid and alkaline conditions is slight, which results in the high reduction of Cr(VI) by Fe(II) irrespective of pH from pH 3.0 to 9.0; at pH ≥ 12.0, the decline in removal could probably be attributed to the oxidation of Fe(II) by O$_2$ being larger than that of Cr(VI) (Fendorf & Li 1996; Buerge & Hug 1997).

### Table 1 | Concentrations of Cr(VI) and Fe(II) after mixing

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<th>Cr(VI) (mg/L)</th>
<th>Fe(II) (mg/L)</th>
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### Table 2 | Concentrations of Cr(VI) and S(-II) after mixing

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### Table 3 | Concentrations of Cr(VI), Fe(II) and S(-II) after mixing

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Influence of pH on Cr(VI) reduction by sulfide compounds

Figure 3 illustrates that pH obviously affects the reduction of Cr(VI) by sulfide, with the reduction decreasing rapidly as pH increases. According to Figure 1, H₂S is the main sulfide species at pH < 7.0, and the reduction of Cr(VI) by S(-II) could be expressed by (Kim et al. 2001)

\[
2\text{HCrO}_4^- + 3\text{H}_2\text{S} + 8\text{H}^+ = 2\text{Cr}^{3+} + 3\text{S} + 8\text{H}_2\text{O} \quad (8)
\]

At pH ≥ 7.0, HS\(^-\) or S\(^{2-}\) is the main sulfide species in solution; therefore the reaction pathways could be described as follows (Lan et al. 2005):

\[
2\text{CrO}_4^{2-} + 3\text{S}^{2-} + 8\text{H}_2\text{O} = 2\text{Cr(OH)}_3 + 3\text{S} + 10\text{OH}^- \quad (9)
\]

\[
2\text{CrO}_4^{2-} + 5\text{HS}^- + 5\text{H}_2\text{O} = 2\text{Cr(OH)}_3 + 3\text{S} + 7\text{OH}^- \quad (10)
\]

At pH < 7.0, the standard electrode potential \(E = E_{\text{HCrO}_4^- /2\text{Cr}^{3+}} - E_{\text{S}_2\text{H}_2\text{S}} = 1.35 - 0.141 = 1.209 \text{ V}\) in Equation (8), which is largely in excess of the standard electrode potential \(E = E_{\text{CrO}_4^{2-} /\text{Cr}^{3+}} - E_{\text{S}_2\text{H}_2\text{S}} = (-0.12) - (-0.48) = 0.36 \text{ V}\) at pH ≥ 7.0, so acid conditions (pH < 7.0) are much in favor of Cr(VI) reduction by sulfide, and H₂S is a much stronger reductant of Cr(VI) compared to HS\(^-\) or S\(^{2-}\). However, hexavalent chromium and sulfide exist mainly in the forms of CrO\(_4^{2-}\), HS\(^-\) and S\(^{2-}\) at pH ≥ 7, and electrostatic repulsion may take place between the negatively charged ions (Lee 2009; Essandoh et al. 2015; Gao et al. 2015). The two facts above could clearly explain the dynamic retardation with the reduction reaction of Cr(VI) by sulfide in neutral or alkaline conditions (Han et al. 1991).

Influence of pH on Cr(VI) reduction by the mixtures of Fe(II) and sulfide compounds

Figure 4 shows that when the molar ratio of Fe(II) (or S(-II))/Cr(VI) reaches 1.0, the removal of Cr(VI) by the mixtures of Fe(II) and sulfide compounds decreases from 100% to nearly 80% when the initial pH increases from 3.0 to 9.0, whereas it quickly drops to less than 40% at pH 12.0. Combined with the above research work, the removal of Cr(VI) by Fe(II) is almost irrespective of pH at pH 3.0–9.0; so the decline in removal is probably due to the changing of sulfide species which possess varied reduction ability with increasing pH; however, the rapid decrease of removal at pH 12.0 could probably be attributed to the oxidation of Fe(II) by O\(_2\) and electronegativity of HS\(^-\) or S\(^{2-}\).

Contrast the sum of Cr(VI) removal by single Fe(II) and S(-II) with the mixtures

As Figure 5 shows, the removal of Cr(VI) by the mixtures of Fe(II) and S(-II) and the sum of single Fe(II) and S(-II) is in close agreement at pH < 7.0 or pH = 12.0; nevertheless at pH 7.0–9.0, the removal of Cr(VI) by the mixtures of Fe(II) and S(-II) obviously exceeds the sum of sole Fe(II) and S(-II). This suggests that certain interactions might exist in the reaction of Fe(II), S(-II) and Cr(VI). In acid
conditions (pH < 7.0), Fe(II) and S(II) both could act as strong reductants to react with Cr(VI), which results in the removal of Cr(VI) by the mixtures of Fe(II) and S(II), consistent with the sum of the removals by sole Fe(II) and S(II). In the pH range of 7.0–9.0, Cr(VI) and sulfide exist mainly in the forms of CrO$_4^{2-}$ and HS$^-$. The evident acceleration might be hypothesized by the following reaction equation:

$$\text{HS}^- + 2\text{Fe}^{3+} + \text{OH}^- = 2\text{Fe}^{2+} + \text{S} + \text{H}_2\text{O} \quad (11)$$
The reaction involved Cr(VI) reduction by Fe(II) to produce Fe(III), which was reduced to Fe(II) again by HS\(^{-}\); Equation (11); the change in reaction pathways of HS\(^{-}\) results in the increasing utilization of this sulfide species. This could provide some explanation as to why the acceleration in the mixtures of Fe(II) and S(II) occurred at pH 7.0–9.0; Fe\(^{3+}\) might act as the catalyst in this process (Lan et al. 2006). When the pH rises to 12.0, \( E = E_{Fe^{3+}/Fe^{2+}} - E_{S_2^{2-}/S^{2-}} = -0.08 \). It is recorded that it is difficult for the redox reaction to happen spontaneously at \( E < 0.2 \); so \( S^{2-} \) could not be oxidized by Fe\(^{3+}\) at pH 12.0, i.e. the catalytic effect could not happen in this pH condition. This conclusion could also be evidenced by the adding of extra Fe\(^{3+}\) to the system, but no Cr(VI) removal was observed (data not shown here).

**CONCLUSIONS**

Fe(II) can effectively reduce Cr(VI) in aqueous solutions, and the removal of Cr(VI) is irrespective of pH variation between pH 3.0 and 9.0, while Fe(II) is more likely to be oxidized by residual oxygen in solutions than by aqueous Cr(VI) at pH 12.0, thus leading to the decrease of Cr(VI) reduction.

The distribution coefficients of sulfide species (\( H_2S, HS^{-} \) and \( S^{2-} \)) in water are largely pH-dependent, and \( H_2S \) is the main sulfide species at \( pH < 7.0 \), which can reduce Cr(VI) effectively, while at \( pH \geq 7.0 \), sulfide species in solutions mainly exist in the forms of \( HS^{-} \) or \( S^{2-} \), and dynamic retardation might take place in the reduction of Cr(VI) and sulfide.

The removal of Cr(VI) by the mixtures of Fe(II) and S(II) decreases from 100% to 80% as pH increases from 3.0 to 9.0; this is probably attributed to the changing of sulfide species which possess varied reduction ability with increasing pH, while the apparent decrease of Cr(VI) removal at 12.0 could be explained by the oxidation of Fe(II) by \( O_2 \) and electronegativity of \( HS^{-} \) or \( S^{2-} \).

The reduction of Cr(VI) by the mixtures of Fe(II) and S(II) and the sum of Cr(VI) reduction by Fe(II) and S(II) is in close agreement at \( pH < 7.0 \) or \( pH = 12.0 \). In contrast, obvious increasing of Cr(VI) removal by the mixtures of Fe(II) and S(II) can be observed compared to the summing of removal by separate species at pH 7.0–9.0; it is predicted that the reaction pathways might be changed in this process. that is to say HS\(^{-}\) more easily react with the positively charged Fe\(^{3+}\) than with the electronnegative CrO\(_2\)^{2+}, and the generated Fe(II) could react with Cr(VI) again, thus increasing the utilization of this sulfide species and the removal of Cr(VI).

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