Research article

An investigation of Cr(VI) removal with metallic iron in the co-presence of sand and/or MnO$_2$

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ABSTRACT

This study focused on the influence of sand and/or MnO$_2$ co-presence on the mechanism and kinetics of Cr(VI) removal with Fe^0. The process was investigated under acidic and well-mixed conditions, over the temperature range of 6–32 °C. It was shown that both mechanism and kinetics of the removal process were highly dependent on composition and dose of reactive mixture added to Cr(VI) solution. At 22 °C, indirect chemical reduction with Fe(II) was the main removal path in H$_2$O–Fe^0–Cr(VI) and H$_2$O–Fe^0–Sand–Cr(VI) system, while in H$_2$O–Fe^0–MnO$_2$–Cr(VI) and H$_2$O–Fe^0–MnO$_2$–Sand–Cr(VI) system removal of Cr(VI) occurred mainly via adsorption on MnO$_2$. The pseudo zero-order kinetic model provided the best match for H$_2$O–Fe^0–Cr(VI) and H$_2$O–Fe^0–Sand–Cr(VI) system, while in H$_2$O–Fe^0–MnO$_2$–Cr(VI) and H$_2$O–Fe^0–MnO$_2$–Sand–Cr(VI) system the process fitted well to the pseudo second-order model. Temperature influenced the efficiency and kinetics of the process in all investigated systems, and the removal mechanism only in H$_2$O–Fe^0–MnO$_2$–Cr(VI) and H$_2$O–Fe^0–MnO$_2$–Sand–Cr(VI) system.
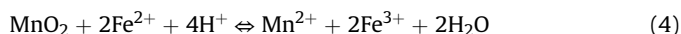
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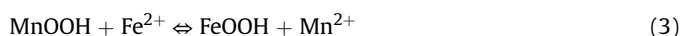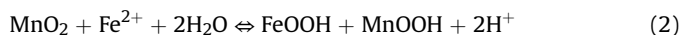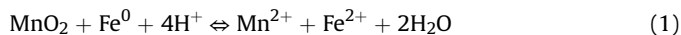
1. Introduction

Because it is industrially important, chromium is one of the most significant environmental heavy metal contaminants. The major way chromium enters the aquatic ecosystem is through the discharge of contaminated effluents from a large number of industrial activities. In aquatic systems, chromium exists primarily in two of its most stable valence states: hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)), with differing solubility, mobility and toxicity. Under relevant environmental pH values Cr(VI) is present as highly soluble and mobile chromate and hydrogen chromate anions, known to be toxic to all living organisms. On the other hand, Cr(III) is present mainly as relatively insoluble and immobile hydroxides, being up to 1000 times less toxic than Cr(VI) and an essential micronutrient for living organisms (Fendorf, 1995; Gheju, 2011). Because Cr(VI) is more mobile and toxic than Cr(III), it is essential to remove Cr(VI) compounds from contaminated effluents before they are discharged into natural water bodies. Over the last decades, metallic iron (Fe^0) has been demonstrated to represent a highly efficient reagent for in situ remediation of

groundwater, wastewater treatment, and safe drinking water production, due to its low cost, widely availability, simple operation and low maintenance of Fe^0-based technologies (Chakrabarti et al., 2014; Ghauch, 2015; Gheju, 2011; Noubactep et al., 2012a; Noubactep, 2013a). The fundamental mechanism responsible for Cr(VI) removal in Fe^0–H$_2$O system is the oxidative dissolution of Fe^0 coupled with physicochemical processes involving Cr(VI), including adsorption, direct reduction, indirect reduction, co-precipitation/ enmeshment in the mass of precipitates (Ghauch et al., 2011; Gheju, 2011; Noubactep, 2013a). Even though important efforts have been made in order to study the influence of various inorganic species on the removal of Cr(VI) with Fe^0 (Gheju, 2011), only few works have investigated the influence of sand and MnO$_2$. Experiments carried out by Song et al. (2005) and Oh et al. (2007) showed that Cr(VI) removal efficiency was significantly increased in the presence of sand, the presumed role of this material being to provide surfaces to preferentially adsorb reaction products, reducing thus surface passivation of Fe^0. Sand has been proved to be especially important in reactive Fe^0 filter packs, where it can be used as a non-reactive material with the role of increasing filter porosity and preventing premature clogging due to pore filling with in situ generated corrosion products (Btatkeu et al., 2015; Kaplan and Gilmore, 2004; Noubactep et al., 2012b; Noubactep, 2013b). The
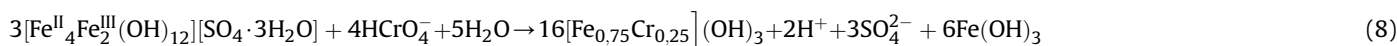
co-presence of MnO_2 may sustain Fe^0 oxidative dissolution, and therefore the process of contaminant removal in $H_2O–Fe^0$ system, by: (1) accelerating Fe^0 oxidative dissolution, and (2) avoiding or delaying the formation of oxide film on the surface of Fe^0 by consuming Fe(II) (preventing Fe^0 surface passivation), according to Bafghi et al. (2008); Noubactep et al. (2011, 2012b); Postma and Appelo (2000):

$$MnO_2 + Fe^0 + 4H^+ \Leftrightarrow Mn^{2+} + Fe^{2+} + 2H_2O \tag{1}$$

$$MnO_2 + Fe^{2+} + 2H_2O \Leftrightarrow FeOOH + MnOOH + 2H^+ \tag{2}$$

$$MnOOH + Fe^{2+} \Leftrightarrow FeOOH + Mn^{2+} \tag{3}$$

$$MnO_2 + 2Fe^{2+} + 4H^+ \Leftrightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O \tag{4}$$

$$MnO_2 + 2Fe^{2+} + 2H_2O \Leftrightarrow 2FeOOH + Mn^{2+} + 2H^+ \tag{5}$$

A multi-elemental aqueous system containing Cr(VI), Cu(II), Mo(VI), Sb(V), U(VI), and Zn(II) conducted under non-disturbed conditions confirmed the suitability of MnO_2 to sustain the long-term Fe^0 reactivity (Noubactep et al., 2011). The goal of the present paper was to investigate the mechanism and kinetics of Cr(VI) removal in $H_2O–Fe^0–Cr(VI)$ system amended with sand and/or MnO_2. The effect of sand and/or MnO_2 on the mechanism and kinetics of Cr(VI) removal with metallic iron was studied in well-mixed batch system, for values ranging from 6 to 32 °C.

2. Materials and methods

Commercially available MnO_2 (pyrolusite $\geq$ 90%, ~10 μm) and Fe^0 ($\geq$99%, ~10 μm), both from Merck, were used in this assay. Sand with grain size ranging from about 0.1 to 0.5 mm was obtained from a local aquifer and used as received. Cr(VI) stock solutions (10 g/L) were prepared by dissolving 28.29 g $K_2Cr_2O_7$ in 1000 mL of distilled deionized water. Working solutions of the desired initial Cr(VI) concentration (2 mg/L) were prepared by diluting the stock solution. Experiments were conducted in a 1.5 L Berzelius flask open to the atmosphere, containing 1000 mL of Cr(VI) working solution. The reactive solids we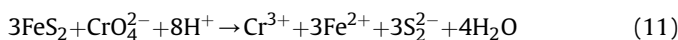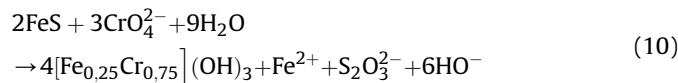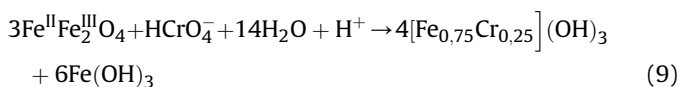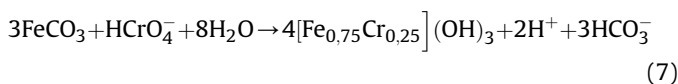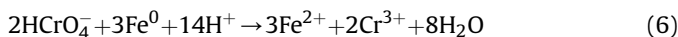re added to the Cr(VI) solution and the flask content was mixed continuously by a Heidolph vertical agitator equipped with a polymethacrylate stirring shaft. Initial Cr(VI) concentration (2 mg/L), working volume (1000 mL), solution pH (2.5), mixing rate (200 rpm) and temperature (22 °C) were held constant throughout the study. pH 2.5 was selected because it was previously reported as optimum value for Cr(VI) removal with Fe^0 (Gheju et al., 2008). Additional experiments were conducted at 6, 27 and 32 °C in order to study the influence of temperature, keeping all other conditions equal. Samples were collected at predetermined time intervals, filtered and analyzed. Chromium and iron dissolved species were determined by colorimetric methods, using a Jasco V 530 spectrophotometer (Gheju et al., 2008). The pH was adjusted to 2.5 by small addition of concentrated H_2SO_4 and measured in samples collected before and after the reaction using an Inolab pH-meter.

3. Results and discussion

3.1. Removal of Cr(VI) in $H_2O–Fe^0–Cr(VI)$ system

Even though numerous studies have investigated the Cr(VI) removal in $H_2O–Fe^0–Cr(VI)$ system, there is still some controversy in what concerns the mechanism and kinetics of the process. Therefore, in this study we have also examined the removal of Cr(VI) with bare Fe^0 (no sand or MnO_2), at two doses, 0.5 and 1.0 g/L; the results are presented in Figs. 1 and 2. In order to investigate the mechanism of Cr(VI) removal in $H_2O–Fe^0–Cr(VI)$ system, the pH, Cr(VI), Cr(total), Fe(II) and Fe(total) concentrations were analyzed at the end of batch experiments with a 0.5 g/L Fe^0 dose, in the presence and absence of Cr(VI). It was observed that final Cr(total) concentration (1.9 mg/L) was lower than initial Cr(VI) concentration (2 mg/L) and greater than final Cr(VI) concentration (1.4 mg/L) (Fig. S1B, supplementary material). This means that, from the 0.6 mg of Cr(VI) that disappeared from solution at the end of experiment, 0.5 mg (83.3%) were removed by reduction to Cr(III) and 0.1 mg (16.7%) by adsorption of $HCrO_4^-$ and/or adsorption/precipitation of Cr^{3+} on Fe^0 surface. However, since the final pH was 2.6, neither precipitation nor adsorption of Cr^{3+} can be considered plausible. Therefore, under the specific conditions involved in this study (initial pH 2.5, vigorous mixing, short-term duration), chemical reduction of Cr(VI) to Cr(III) was the main cause of Cr(VI) removal with metallic iron. This process may occur along two parallel pathways: one is the heterogeneous reduction, involving electron transfer from Fe^0 surface (Eq. (6)) or from solid minerals containing Fe(II) formed onto the Fe^0 surface (Eqs. (7)–(11)). The other is the homogeneous reduction, occurring in the solution, in the presence of dissolved Fe^{2+} or H_2 (Eqs. (12) and (13)) generated during the heterogeneous reduction of Cr(VI) and Fe^0 corrosion (Eq. (14)) (Gheju, 2011):

$$2HCrO_4^- + 3Fe^0 + 14H^+ \rightarrow 3Fe^{2+} + 2Cr^{3+} + 8H_2O \tag{6}$$

$$3FeCO_3 + HCrO_4^- + 8H_2O \rightarrow 4\left[Fe_{0.75}Cr_{0.25}\right](OH)_3 + 2H^+ + 3HCO_3^- \tag{7}$$

$$3[Fe^{II}_4Fe^{III}_2(OH)_{12}][SO_4 \cdot 3H_2O] + 4HCrO_4^- + 5H_2O \rightarrow 16\left[Fe_{0.75}Cr_{0.25}\right](OH)_3 + 2H^+ + 3SO_4^{2-} + 6Fe(OH)_3 \tag{8}$$

$$3Fe^{II}Fe^{III}_2O_4 + HCrO_4^- + 14H_2O + H^+ \rightarrow 4\left[Fe_{0.75}Cr_{0.25}\right](OH)_3 + 6Fe(OH)_3 \tag{9}$$

$$2FeS + 3CrO_4^{2-} + 9H_2O \rightarrow 4\left[Fe_{0.25}Cr_{0.75}\right](OH)_3 + Fe^{2+} + S_2O_3^{2-} + 6HO^- \tag{10}$$

$$3FeS_2 + CrO_4^{2-} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{2+} + 3S_2^{2-} + 4H_2O \tag{11}$$