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Influence of complex reagents on removal of chromium(VI) by zero-valent iron

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ABSTRACT

The removal of Cr(VI) by zero-valent iron (Fe(0)) and the effect of three complex reagents, ethylenediaminetetraacetic acid (EDTA), NaF and 1,10-phenanthroline, on this reaction were investigated using batch reactors at pH values of 4, 5 and 6. The results indicate that the removal of Cr(VI) by Fe(0) is slow at pH $\geqslant$ 5.0 and that three complex reagents play different roles in the reaction. EDTA and NaF significantly enhance the reaction rate. The zero-order rate constants at pH 5.0 were 5.44 μM min^{-1} in the presence of 4 mM EDTA and 0.99 μM min^{-1} in the presence of 8 mM NaF, respectively, whereas that of control was only 0.33 μM min^{-1}, even at pH = 4.0. This enhancement is attributed to the formation of complex compounds between EDTA/NaF and reaction products, such as Cr(III) and Fe(III), which eliminate the precipitates of Cr(III), Fe(III) hydroxides and $Cr_xFe_{1-x}(OH)_3$ and thus reduce surface passivation of Fe(0). In contrast, 1,10-phenanthroline, a complex reagent for Fe(II), dramatically decreases Cr(VI) reduction by Fe(0). At pH = 4.0, the zero-order rate constant in the presence of 1 mM of 1,10-phenanthroline was 0.02 μM min^{-1}, decreasing by 99.7% and 93.9%, respectively, compared with the results in the presence and absence of EDTA. The results suggest that a pathway of the reduction of Cr(VI) to Cr(III) by Fe(0) may involve dissolution of Fe(0) to produce Fe(II), followed by reduction of Cr(VI) by Fe(II), rather than the direct reaction between Cr(VI) and Fe(0), in which Fe(0) transfers electrons to Cr(VI).

1. Introduction

Chromium is considered as a priority pollutant by the US Environmental Protection Agency (Wielinga et al., 2001). The wide distribution of chromium contaminants in soil and groundwater is due to the widespread applications of chromium in many industries, such as the production of stainless steel, refractory industry, tanning of leather, pigment and chemical industry, and wood treatment (Xu et al., 2004).

As a transition metal, chromium exists in many oxidation states, but mainly in the oxidation states of Cr(VI) and Cr(III) in the natural environment. These two oxidation states are quite different in physical and chemical properties. Cr(VI) is highly soluble, mobile and toxic to humans, animals and plants. In contrast, Cr(III) is usually found in the form of $Cr(OH)_3$ with low solubility, which can be easily absorbed to the surfaces of clay minerals. Thus, one of the important approaches to control chromium contamination of soil and groundwater is to reduce Cr(VI) to Cr(III).

In recent years, the use of biomass for the reduction of Cr(VI) has been widely investigated because of its efficiency in removal of Cr(VI) (Park et al., 2004a,b, 2007; Sawalha et al., 2007). The removal mechanism of Cr(VI) by natural biomaterials is adsorption-coupled reduction (Park et al., 2007). The efficient removal of Cr(VI) by ascorbic acid is observed in a wide range of pH values from acidic conditions to weakly alkaline solutions, with or without sunlight (Xu et al., 2004). Li et al. (2007) recently reported that the reaction between Cr(VI) and citric acid was very slow at pH range 4.0–5.0. The reduction of Cr(VI) by organic compounds with oxygen-containing functional groups was also examined by Deng and Stone (1996a,b), who revealed that the half-lives of reactions ranged from months to many years at approximately neutral pH. Cr(VI) reduction by excess soil humic substances was slow under weakly acidic and neutral conditions (Wittbrodt and Palmer, 1995,1996). But, the removal of Cr(VI) by organic acids containing α-OH was dramatically catalyzed in the presence of transition metal ions, such as Mn(II) and Fe(III) (Wittbrodt and Palmer, 1996; Hug and Laubscher, 1997; Kabir-ud-Din et al., 2000; Li et al., 2007).

Thornton and Amonette (1999) showed that dilute hydrogen sulfide immobilized 90% to approximately 100% of Cr(VI) in soil columns. The reaction kinetics is a first-order with respect to both Cr(VI) and sulfide (Pettine et al., 1998; Kim et al., 2001). Elemental sulfur is a major product of sulfide oxidation by Cr(VI) under anaerobic conditions (Kim et al., 2001). Lan et al. (2005) further revealed that produced elemental sulfur greatly enhanced Cr(VI)

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reduction in the late stage of the reaction. Ferrous ions absorbed on the surfaces of soils and clay minerals also significantly accelerate the reaction between Cr(VI) and sulfide through a circle reaction pathway, involving Cr(VI) reduction by Fe(II), then produced Fe(III) reduction to Fe(II) by sulfide, and Cr(VI) reduction to Cr(III) by Fe(II) again (Lan et al., 2006, 2007).

A number of studies have demonstrated that Fe(II) and Fe(0) are efficient reductants for Cr(VI) (Powell et al., 1995; Buerge and Hug, 1997,1998,1999; Puls et al., 1999; Melitas et al., 2001). For example, Powell et al. (1995) reported that scrap iron filings and cast iron effectively reduced Cr(VI), and the removal efficiency varied with surface areas and compositions of iron. Spectroscopic analyses of Fe(0) surfaces after reaction with Cr(VI) reveal that the pathway of Cr(VI) removal involves the initial reduction of Cr(VI) to Cr(III), followed by adsorption of Cr(III) onto Fe(0) surfaces, or by precipitation of Cr(III) and Fe(III) hydroxides (Blowes et al., 1997; Wilkin et al., 2005). The buildup of such precipitates is considered to affect the performance of Fe(0) negatively since precipitation phases on the surfaces of Fe(0) can lead to surface passivation by acting as a physical barrier that prevents the access of pollutants to the surface of Fe(0) (Oh et al., 2007). For example, the investigations performed under the conditions close to field systems have demonstrated that the precipitation of reaction products diminishes the long-term performance of Fe(0) (Klausen et al., 2003; Vikesland et al., 2003; Kohn et al., 2005). Powell et al. (1995) observed that the presence of aluminosilicate aquifer materials markedly increased the reduction of Cr(VI) by Fe(0) because these aquifer materials generated protons, which maintained solution pH and thus reduced surface passivation of iron. Similarly, Oh et al. (2007) showed that the amendment of two surfaces, amorphous silica and silica sand, significantly enhanced the reduction of Cr(VI) by Fe(0). However, the rate enhancement by amended surfaces is presumed to arise from scavenging of Fe(0)–Cr(VI) reaction products by the provided surfaces (Oh et al., 2007). Therefore, it can be assumed that a method to reduce precipitation of Cr(III) and Fe(III) on Fe(0) surface can increase the removal of Cr(VI). Complex reagents are expected to enhance the activity of Fe(0) by eliminating precipitates on Fe(0) surface. However, little is known about the effect of complex reagents on removal of Cr(VI) by Fe(0).

Thus, the aim of this study is to investigate the suppression of precipitation of reaction products and to improve removal of Cr(VI) by Fe(0) using complex reagents. Kinetics experiments were conducted over a range of pH values and concentrations of EDTA and NaF. Also, a complex reagent for Fe(II), 1,10-phenanthroline, was employed to probe whether the primary pathway of electron transfer for Cr(VI) reduction by Fe(0) is directly from Fe(0) to Cr(VI) or from Fe(II) to Cr(VI) after the dissolution of Fe(0).

2. Materials and methods

Fe(0) was purchased from Development Center of Kemiou Chemical Reagent, Tianjin, China. Fe(0) powder was sieved and the fraction <0.11 mm was collected. The collected fraction was washed using 0.1 M NaOH, 0.1 M HCl and deionized water, sequentially, to remove oil film and oxides on the surface of Fe(0). After washing, Fe(0) was dried at 110 °C for 1 h and stored in a dessicator under the protection of N_2 prior to use. Specific surface area of Fe(0) was 0.22 $m^2\ g^{-1}$ and measured using Brunauer–Emmet–Teller (BET) gas adsorption isotherm with N_2 gas on a JW-004 surface area analyzer (Beijing Jing Wei Gao Bo). Diphenylcarbazide (DPC) was obtained from Sigma Aldrich Company. DPC stock solution used for photometric analysis of Cr(VI) was prepared by dissolving 0.2 g DPC in 100 ml acetone, and then stored in a brown bottle in a refrigerator prior to use. The stock solutions of EDTA, NaF and 1,10-phenanthroline were prepared by dissolving reagent-grade EDTA, NaF, and 1,10-phenanthroline into deionized water, respectively. All the chemicals used in the experiment were at least reagent-grade.

All the glassware used in the experiment was cleaned by soaking in 1 M HCl for 12 h and rinsed with tap water and then deionized water. Deionized water and buffer solution were thoroughly purged using high-purity nitrogen gas to remove dissolved oxygen prior to use. The dissolved oxygen in deionized water was reduced to below 12.5 μM, as measured by a JPB-607 model hand-held dissolved oxygen analytic instrument (Shanghai Precision and Scientific Co., Ltd).

The kinetics experiments were performed in a brown bottle in weak acidic solutions (pH 4.0–6.0). The constant acidity of the reaction systems was maintained by 0.1 M acetate buffer solution, prepared using acetic acid and NaOH. All reactions were started by introducing 0.0448 g Fe(0) into 200 ml acetate buffer solution containing an initial 100 μM Cr(VI). In addition, three concentration levels of EDTA (1, 2 and 4 mM), three concentration levels of NaF (8, 16 and 32 mM) and 1 mM 1,10-phenanthroline were added to three reaction systems, respectively, before introducing Fe(0) in order to investigate the effect of complex reagents on the Cr(VI) reduction by Fe(0). Suspension was mixed on a shaking water bath (SIM BS-31) at 25 ± 0.1 °C and 180 rpm. About 5 ml sample was drawn out from the suspension at certain intervals with a plastic syringe and filtered through a 0.45 μm membrane filter into a clean and dry glass tube, and then a 1 ml aliquot of filtrate was drawn out using a pipette for the analysis of Cr(VI) and Fe(II).

Cr(VI) concentration was measured by the DPC colorimetric method, using a phosphoric acid buffer to control pH for color development (Deng and Stone, 1996a,b; Lan et al., 2005). The absorbance was determined in a 1-cm cell at 540 nm on a UV-9100 spectrophotometer (Beijing Ruili Corp). When 1,10-phenathroline was introduced into the reaction system, the filtrate was divided into two parts in order to reduce the influence of complex compound of Fe(II) and 1,10-phenanthroline (with red color) on the measurements of Cr(VI) concentration. One portion was used for the analysis of Cr(VI) and the other used as the control. An Orion 868 pH meter, after two point calibration, was used to determine all solution pH values.

3. Results and discussion

3.1. Cr(VI) reduction by Fe(0) at different pH values

The Cr(VI) concentration in aqueous solution as a function of reaction time at 25 °C and pH 4, 5, and 6, which demonstrates the effect of pH on Cr(VI) removal by Fe(0), is illustrated in Fig. 1. The result indicates that the reduction of Cr(VI) by Fe(0) was weak at pH 5.0 and 6.0; initial Cr(VI) decreased by approximately 10% in the beginning of the reaction, but remained constant in the remaining period of the reaction. The rapid decrease of Cr(VI) concentration in the beginning of reaction is assumed to result from some Fe(II) ions present on the surface of Fe(0) and from active surfaces of Fe(0) before the formation of a passivated film on the surface of Fe(0). Compared with the results of pH 5.0 and 6.0, Cr(VI) reduction at pH 4.0 was fast, and Fe(0) was of excellent reductive capacity for Cr(VI) throughout the whole reaction. The Cr(VI) concentration decreased from initial 100 μM to 30 μM within 180 min, with an average reaction rate of 0.39 $\mu M\ min^{-1}$. The Cr(VI) removal kinetics at pH = 4.0 could be described by a zero-order kinetic model, as illustrated in Fig. 1. The reaction rate constant (k) and correlation coefficient (R^2), obtained from Fig. 1, are listed in Table 1. The observed Cr(VI) reduction rates by Fe(0) at pH $\geqslant$ 5.0 and 25 °C are not completely consistent with others' (Alowitz and