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Reduction Remediation of Hexavalent Chromium by Pyrite in the Aqueous Phase

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Abstract: The objective of this study was to investigate the reduction remediation of hexavalent chromium by pyrite in the aqueous phase, batch experiment indicated that: (1) the rate of chromate removal was dependent on the initial pyrite concentration; (2) the Cr (VI) reduction rate increased with an decrease in initial Cr (VI) concentration; (3) the Cr (VI) reduction was found to be pH dependent, the high reduction of Cr (VI) under acidic conditions; (4) the rate of chromium removal increased with increased temperature; (5) the Cr (VI) reduction depends on the pyrite type. The effective removal of Cr (VI) by pyrite suggests that the use of pyrite for the treatment of wastewater containing Cr (VI) is an innovative method that constitutes a simple, effective and economical means for wastewater treatment.

Key words: Pyrite, hexavalent chromium, reduction, ferrous iron

INTRODUCTION

Chromium, with its great economic importance in industrial use, is a major metal pollutant of the environment (Konovalova *et al.*, 2003). Chromium pollution as a consequence of effluent discharge from tanneries and other industries, which include metal plating, manufacturing industries and ferrochrome production (Shrivastava *et al.*, 2003). Chromium is found in the environment predominantly as Cr (VI) and Cr (III) (Chirwa and Wang, 2000). Hexavalent chromium (Cr (VI)) is mobile in the environment, Subject to biological uptake and is highly toxic (Guha *et al.*, 2003). Furthermore, they are widely distributed as an anthropogenic pollutant (Vainshtein *et al.*, 2003). Trivalent chromium (Cr (III)) is less toxic than Cr (VI) and is less susceptible to biological uptake (Guha, 2004).

Chromium (VI) can be reduced by biological and chemical means. There have been several studies on the methods and possible mechanisms of reduction of hexavalent chromium (Stollenwerk and Grove, 1985; Siegel and Clifford, 1988; Palmer and Wittbrodt, 1991; Anderson *et al.*, 1994; Deng and Stone, 1996; Wittbrodt and Palmer, 1996; Vitale, 1997; Beukes *et al.*, 1999; Puls *et al.*, 1999; Ponder *et al.*, 2000; Wielinga *et al.*, 2001; Alowitz and Scherer, 2002; Daulton *et al.*, 2002; Hansel *et al.*, 2003; Lee *et al.*, 2003; Vainshtein *et al.*, 2003; Bojic *et al.*, 2004; Tora *et al.*, 2004; Xu *et al.*, 2005; Lee *et al.*, 2006; Lo *et al.*, 2006). Numerous observations indicate that ferrous iron [Fe (II)] could be

an important of Cr (VI) in natural waters (Sedlak and Chan, 1997; Pettine *et al.*, 1998; Schlautman and Han, 2001; Hwang *et al.*, 2002; Nunez *et al.*, 2003; Tzou *et al.*, 2003; Erdema and Tumen, 2004).

Iron minerals are ubiquitous in nature and play a critical role in the geochemical cycling of trace elements. In particular, the Fe (III)-Fe (II) redox couple is an important electron-transfer mediator for many biological and chemical species. Pyrite and other reactive iron-sulfide minerals are important to sedimentary trace element behaviour (Morse and Luther, 1999). Pyrite, an extremely cheap and readily available waste material, may be suitable for the removal of hexavalent chromium (Zouboulis *et al.*, 1995). Furthermore, Pyrite was found to act as an efficient Cr (VI) reducing agent (Doyle *et al.*, 2004).

Studies have demonstrated the heterogeneous reduction of Cr (VI) by Fe (II) in biotite, vermiculite, illite, smectites, chlorite, magnetite, ilmenite, Fe (II) hematite, Fe (II)-goethite and sulfides (Ilton and Veblen, 1994; White *et al.*, 1996; Patterson and Fendorf, 1997; Kendelewicz *et al.*, 1999; Kendelewicz *et al.*, 2000; Mullet *et al.*, 2004; He *et al.*, 2005). In comparison, fewer studies have been carried out on aqueous Cr (VI) reduction by pyrite (Zouboulis *et al.*, 1995; Benincasa *et al.*, 2002; Kim *et al.*, 2002; Doyle *et al.*, 2004; Chon *et al.*, 2006).

The primary objective of this study is to prepare pyrite particles for degradation of Cr (VI). The specific objectives are to (1) characterize the pyrite particles with environmental scanning electron microscope (ESEM); (2)

quantify the effect of pyrite particles dosage, Cr (VI) concentration, initial pH and temperature on the rate of Cr (VI) reduction; (3) compare the effectiveness of Cr (VI) reduction by different type of pyrite particles.

MATERIALS AND METHODS

Chemicals: The pyrite used in this experiment was obtained from Hangzhou weimin geologic sample factor. Pyrite particle size range was separated and used in the experiments, having a mean particle size of around (<100 mesh). Cr (VI) stock solutions were prepared by dissolving a weighed amount of dried $K_2Cr_2O_7$ in distilled deionized water. The pH of the samples was previously adjusted with small amount of dilute HCl or NaOH solutions in order to have the desired final pH after the addition of Cr (VI).

Batch experiments: Batch kinetic experiments were performed to evaluate the removal rate of Cr (VI) in the presence of pyrite particles.

A pyrite particle was added to 1000 mL flasks filled with 500 mL of $K_2Cr_2O_7$ solution. The solution was continuously stirred at constant temperature ($25 \pm 0.5^\circ C$). Oxygen was removed from the solution by continuous sparging with water-saturated nitrogen before and during the reactions. The samples were filtered through a $0.45 \mu m$ filter.

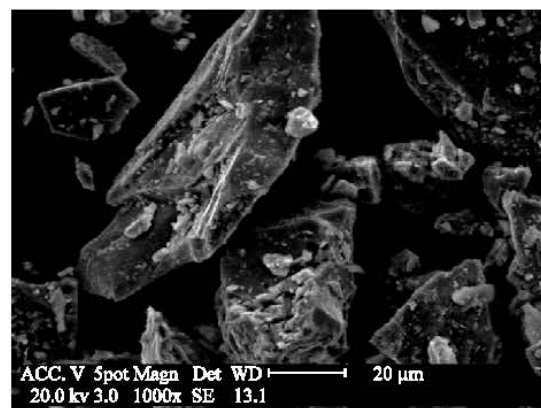
A series of batch experiments was used to study the reduction kinetics of Cr (VI) with pyrite under conditions of (1) different pyrite concentrations, (2) different initial Cr (VI) concentrations and (3) different pH values, (4) different temperatures and (5) different size pyrite particles.

The pH value was initially 5.5 (the pH value of deionized water) and not controlled during the experiment.

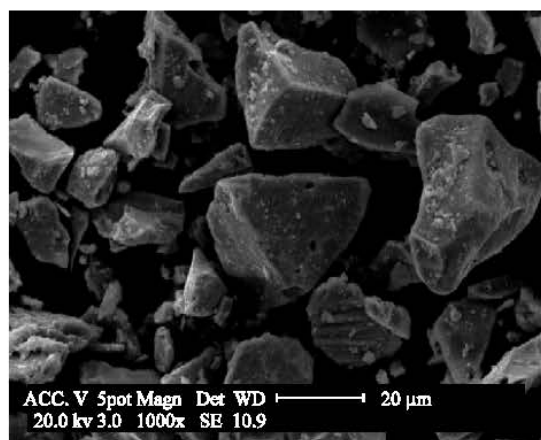
Characterization and analytical methods: The morphology of the metal particles was observed under an XL30-ESEM. Aqueous concentrations of Cr (VI) were determined by a diphenylcarbazide procedure at 540 nm using UV-VIS spectrophotometer (TU-1800PC, Beijing, China).

RESULTS AND DISCUSSION

Characterization of pyrite: Figure 1 compares the SEM image of the pyrite particles before or after reaction. Single crystals were observed in the both micrographs. The platy morphology of the crystals suggests that most of the FeS_2 may be present as marcasite (a dimorph of pyrite). While pyrite is typically present as cubes or octahedra, marcasite often assumes a tabular



(a)



(b)

Fig. 1: ESEM image of pyrite particles (a) before reaction and (b) after reaction

morphology (Rakovan *et al.*, 1995). Figure 1a is shown that the surface morphology of the crystals was characterized by some cracks. Figure 1b is shown that the surface of crystals deposit was smooth uniform coating, there was no evidence of any cracking or significant grain structure, this is due to the precipitation of the hydroxide solid $(Cr, Fe)(OH)_3$.

Effect of pyrite concentration: The effect of initial pyrite particles concentration on the reduction of the Cr (VI) was investigated. The reduction rates depending on the initial pyrite concentration are shown in Fig. 2. At the same initial Cr (VI) concentration, the reduction ratio increased with the increase of initial pyrite concentration. When the initial pyrite concentration was $28 g L^{-1}$, the Cr (VI) reduction rate reaches 98.18% at time of 30 min and when the initial pyrite concentration was $4 g L^{-1}$, the Cr (VI) reduction rate reaches only 12.73% at the time of 30 min as a consequence, it can be concluded that the higher initial

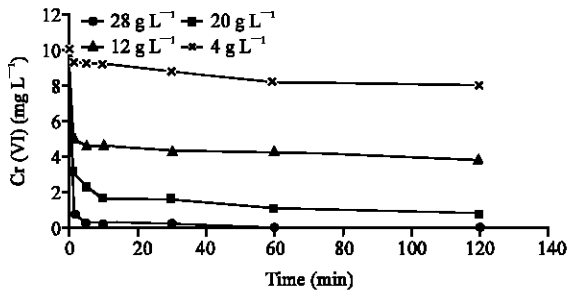


Fig. 2: Cr (VI) concentration vs. time at different pyrite concentration $C_{Cr(VI)} = 10 \text{ mg L}^{-1}$, $\text{pH} = 5.5$, $T = 25^\circ\text{C}$, $\omega = 500 \text{ r min}^{-1}$

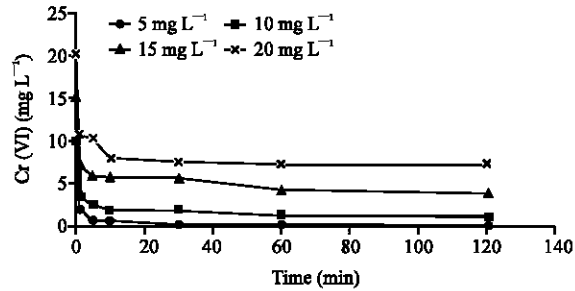
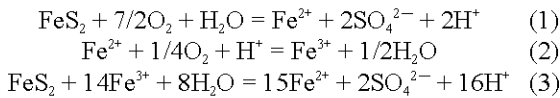


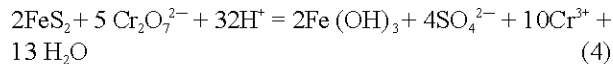
Fig. 3: Cr (VI) concentration vs. time at different initial Cr (VI) concentrations $C_{Fe} = 20 \text{ g L}^{-1}$, $\text{pH} = 5.5$, $T = 25^\circ\text{C}$, $\omega = 500 \text{ r min}^{-1}$

concentration ratio of pyrite resulted in higher reduction ratio. This is probably because that there were more amounts of Fe (II), thus helping the Cr (VI) reduction.

The oxidation of pyrite is generally described by (Chon *et al.*, 2006):



The reduction of Cr (VI) to Cr(III) involves the oxidation of Fe(II) and S_2^{2-} on the pyrite surfaces, following the reaction (5) (Benincasa *et al.*, 2002).



Initial Cr (VI) concentration effect: Figure 3 shows the removal of Cr (VI) when contacted with pyrite particles. When Cr (VI) concentrations were less than 5 mg L^{-1} all Cr (VI) were removed within 30 min however, the required reaction times for the complete removal of Cr (VI) increased substantially as initial Cr (VI) concentrations increased up to 10 mg L^{-1} . for example, approximately 2 h was needed to remove Cr (VI) when the initial Cr (VI) was 10 mg L^{-1} . the model fits in Fig. 3 which indicates that the Cr (VI) reduction in this research follow a first-order reaction.

Effect of pH: Chon *et al.* (2006) demonstrated the importance of solution pH on reaction rates: the reaction rate of chromate reduction by pyrite was faster at pH 3 than pH 4.

The removal rate of hexavalent chromium at a fixed Cr (VI) concentration (10 mg L^{-1}) as a function of pH is shown in Fig. 4. The reduction of the Cr (VI) was found to depend on the pH of the solution. Reduction capacity was found to decrease with an increase in the pH, it is evident that the reduction rate of Cr (VI) was higher at lower pH

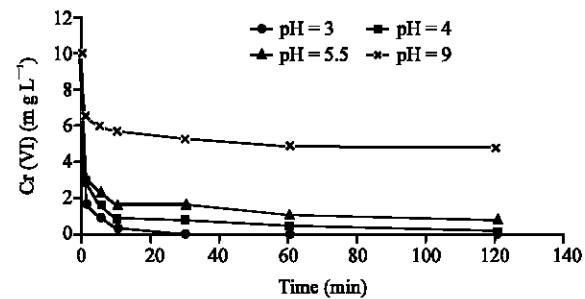


Fig. 4: Cr (VI) concentration vs. time at different initial pH values $C_{Fe} = 20 \text{ g L}^{-1}$, $C_{Cr(VI)} = 10 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$, $\omega = 500 \text{ r min}^{-1}$

(pH = 3) and the removal percentage made up to 100% in 30 min with the pH increased, the removal of Cr (VI) decreased.

Iron exists in the ferric (Fe^{3+}) or ferrous (Fe^{2+}) form, depending upon the pH and dissolved oxygen concentration (Mohan and Chander, 2006). At neutral pH and in presence of oxygen, soluble Fe^{2+} is oxidized to Fe^{3+} , which readily hydrolyzes to ferric hydroxide that is insoluble in water (Mohan and Chander, 2006). In most of the surface waters, Fe^{3+} predominates (Mohan and Chander, 2006). Ferrous (Fe^{2+}) on the other hand is soluble and dominates under anaerobic conditions (Mohan and Chander, 2006). The increase in the solubility and the surface changes of the minerals at lower pH accelerate the reduction of chromate by the Fe (II) ions and structural Fe (II) and therefore, results in rapid reduction in more acidic conditions (Chon *et al.*, 2006). Above pH 9 soluble $\text{Cr}(\text{OH})_4^-$ species are formed, having as a consequence the lowering of respective Cr (VI) removals (Zouboulis *et al.*, 1995).

Temperature effect: The effect of temperature on the Cr (VI) removal was investigated at 25 and 37°C . the reduction rats at different temperatures indicated that

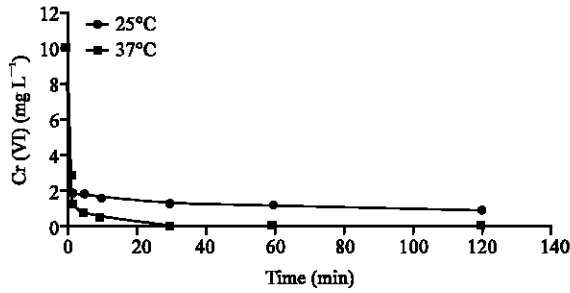


Fig. 5: Cr (VI) concentration vs. time at different temperatures $C_{Fe} = 20 \text{ g L}^{-1}$, $C_{Cr(VI)} = 10 \text{ mg L}^{-1}$, $\text{pH} = 5.5$, $\omega = 500 \text{ r min}^{-1}$

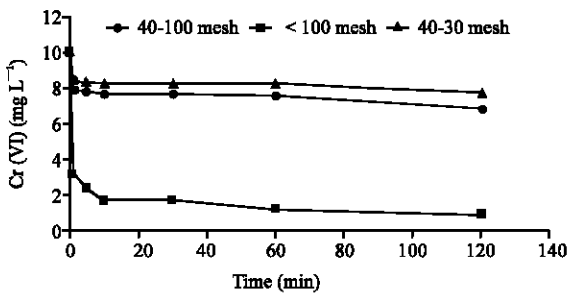


Fig. 6: Cr (VI) concentration vs. time at different pyrite type $C_{Fe} = 20 \text{ g L}^{-1}$, $C_{Cr(VI)} = 10 \text{ mg L}^{-1}$, $\text{pH} = 5.5$, $\omega = 500 \text{ r min}^{-1}$

there are significant changes in the Cr (VI) removal. The highest Cr (VI) reduction was observed at 37°C. The model fits in Fig. 5 which indicates that the Cr (VI) reduction in this research was dependent on temperature. The effect of temperature on the observed reaction rates can be explained by considering how the speciation of Fe (II) changes as a function of temperature (Sedlak and Chan, 1997).

Comparison of different pyrite type: The experiments about studying the effect of pyrite particles type on Cr (VI) reduction was carried out in the presence of three different pyrite particles 40-100, 40-30, <100 mesh. The Cr (VI) reduction and the change of pyrite particles type are presented in Fig. 6. As shown in Fig. 6, the particle size of around (<100 mesh) acquired the best results of Cr (VI) reduction, with the reduction ratio of 91.81% being obtained at time of 2 h. And the reduction of Cr (VI) in this pyrite particles type was faster than the other two. Compared with the particle size of around (40-30 mesh), whose reduction ratio was only 22.73% at time of 2 h. The pyrite particle size of around (<100 mesh) exhibited higher removal efficiency because particle as a good dispersant.

CONCLUSION

Commercial processes and unregulated disposal of the chromium containing effluent has led to the contamination of surface and ground waters. Chromium (VI) is highly toxic and carcinogenic even when present in very low concentration in water.

In this study, higher concentrations of pyrite increased the Cr (VI) reduction. Cr (VI) reduction rates increased with decreasing initial Cr (VI) concentration. A result shows that pH significantly affects the rate of Cr (VI) reduction, with more rapid reduction occurring at pH 3. Cr (VI) reduction rates were dependent on temperature and pyrite particles type. This study has shown that the use of pyrite for the removal of chromate through reduction reaction is applicable to Cr (VI) contaminated solutions; these data also facilitate the understanding of pyrite interaction in natural communities exposed to hexavalent Cr. The rapid reduction of chromate suggests that abiotic reduction of chromate may be an important transformation process in natural systems and engineered remediation technologies based on iron metal (Fe (II)). The chemical reduction of Cr (VI) to Cr (III) by pyrite may provide a less costly approach remediation.

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