

Reduction kinetics of Cr (VI) using limonite in aqueous solution

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ABSTRACT

Cr (VI) is a known human carcinogen. The Reduction of Cr(VI) to Cr(III) is environmentally favorable as the latter species is not toxic to most living organisms and also has a low mobility and bioavailability. Limonite (FeO(OH).nH₂O) may contribute to redox transformations of a range of pollutants including Cr(VI). Main mechanism of Cr(VI) removal is its reduction into Cr(III) by the Fe(II) under acidic condition. The aim of the present work was to use limonite particles for reduction remediation of Cr (VI) in the water. The results of groping experiments revealed that the removal efficiency increased with increasing ironstone addition, but decreased with increasing initial Cr (VI) concentration. Moreover, low pH value could accelerate the rate of Cr (VI) removal. The smaller are the ironstone particles, the higher is the surface area, and the faster the reaction rate will be. The study showed clearly that the use of limonite (FeO(OH).nH₂O) for the removal of Cr(VI) through reduction reaction can be applicable to Cr(VI) contaminated solutions.

Key words: Cr (VI), Limonite, Reduction, Ferrous iron.

INTRODUCTION

Chromium has been recognized as one of the most serious pollutants among heavy metals in environment, thus remediation of chromium pollution receives much more concern (Xu *et al.*, 2005). It is well known that chromium exists mainly as two stable oxidation states, Cr(VI) and Cr(III), which have widely contrasting toxicity and transport characteristics (Xu *et al.*, 2005). 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). While Cr(VI) contamination is generally associated with industrial activity, it can occur naturally.

Effective means in terms of cost and maintenance to clean up chromium contaminated groundwater are desirable (Olazabal *et al.*, 1997).

In general, the treatment technologies for removing chromium from industrial waste include ion exchange, electrodepositing and chemical reduction with iron- and sulfur-containing solutions followed by a precipitation. Cr(VI) can also be reduced by biological means.

There have been several reported studies on the methods and possible mechanisms of reduction of Cr(VI) e.i. (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., Tor *et al.*, 2004., Xu *et al.*, 2005., Lee *et al.*, 2006., Lo *et al.*, 2006).

In Cr(VI)-polluted water and soil, reduction of Cr(VI) to Cr(III) is therefore desirable (Skovbjerg *et al.*, 2006). Over a wide range of conditions and especially in natural and engineered environments, effective reductants are zero-valent iron (Fe(0)), aqueous Fe²⁺ and structurally bound Fe(II) in minerals (Skovbjerg *et al.*, 2006).

Fe(II) is a commonly used reductant for Cr(VI) in waste water treatment. Cr(VI) reduction by Fe(II) is also of interest because Fe(II) is found in various types of soils and is a primary electron donor in subsurface environments (Hwang *et al.*, 2002).

Numerous observations indicate that ferrous iron [Fe(II)] could be an important reducing agent 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).

Hematite is a natural iron ore, with a stable colour up to 1000 °C (Ozel and Turan, 2003). Fewer studies have been carried out on aqueous Cr(VI) reduction by Fe(II) in hematite (Eary and Rai, 1989., Kendelewicz *et al.*, 1999).

Limonite ores are generally formed from the complex hematite (α -Fe₂O₃)-goethite (α -FeOOH) mixtures, and are somewhat soft with a proportion of goethite present (Kaneko *et al.*, 2002). Other elements found in limonites include aluminium, chromium, manganese and silicon (Rubisov *et al.*, 2000). The colour of limonite is in the shades of yellow and brown (Ozel and Turan, 2003). When iron trioxide (Fe₂O₃) is especially present, a red colour is exposed, while in cases where hydrous ferric oxide (Fe₂O₃.H₂O or FeOOH) dominates, the yellow colour is revealed (Bikiaris *et al.*, 1999).

Goethite, a stable iron ox hydroxide, is considered an important mineral, which can also control the sorption capacity of soils for toxic metals (Lehmann *et al.*, 2001). It was also often used as a model colloid in relevant studies (Zouboulis *et al.*, 2003). Goethite has been extensively used in Cr (VI) removal (Lazaridis *et al.*, 2005). Scott and Fendorf (1995) demonstrated the Cr (VI) reduction by Fe (II) in goethite.

The aim of this research was to use limonite (FeO(OH).nH₂O) particles for reduction remediation of Cr (VI) in the water. The main objective was to investigate the reaction mechanisms by emphasizing the role of ferrous Fe (II).

MATERIALS AND METHODS

Experimental method

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

A limonite particle was added to 1000-mL flask filled with 500mL of $K_2Cr_2O_7$ solution. The solution was continuously stirred at constant temperature (25 ± 0.5 °C). Oxygen was removed from the solution by continuous sparging with water-saturated nitrogen before and during the reaction. The samples were filtered through a 0.45 μ m filter.

Aqueous concentrations of Cr (VI) were determined by a diphenylcarbazide procedure at 540 nm using UV-VIS spectrophotometer (TU-1800PC, Beijing, China).

The morphology of the metal particles was observed under an XL30-ESEM.

Experiment conditions

The limonite used in this experiment was obtained from Hang Zhou weimin geologic sample factor. Limonite particle size range was separated and used in the experiments, having a mean particle size of around ($D < 100$ mesh). The pH value was initially 5.5 (the pH value of deionized water) and not controlled during the experiment.

A series of batch experiments was used to study the reduction kinetics of Cr (VI) with limonite under the following conditions:

1. Different limonite concentrations
2. different initial Cr (VI) concentrations
3. different pH values
4. different size limonite particles

Reaction kinetics model

The kinetic of Cr (VI) reduction by limonite can be represented by the following equation (Williams and Scherer, 2001., Alowitz and Scherer, 2002):

$$d [C] / dt = -K_{obs} [C] \quad (1)$$

Where the rate is proportional to dissolved Cr (VI) concentration ($[C]$) and K_{obs} (s⁻¹) is the observed first-order rate coefficient. Integration of equation 1 results in

$$[C] = [C_0] e^{-K_{obs} t} \quad (2)$$

Where $[C_0]$ is the initial concentration of dissolved Cr (VI).

Observed first-order rate coefficients were calculated from liner plots of $\ln ([C])$ versus time with $[C_0]$ set equal to the measured concentration at $t=30$ min.

Effect of limonite concentration on first-order rate coefficients

The correlation between K_{obs} and limonite concentration is shown in Figure. 1. The first-order rate coefficient increases progressively with increasing limonite concentration. This is due to the fact that at higher limonite there is more Fe (II) produced species, probably helping the Cr (VI) reduction. The results further evidence that limonite concentration is a critical factor for Cr (VI) reduction.

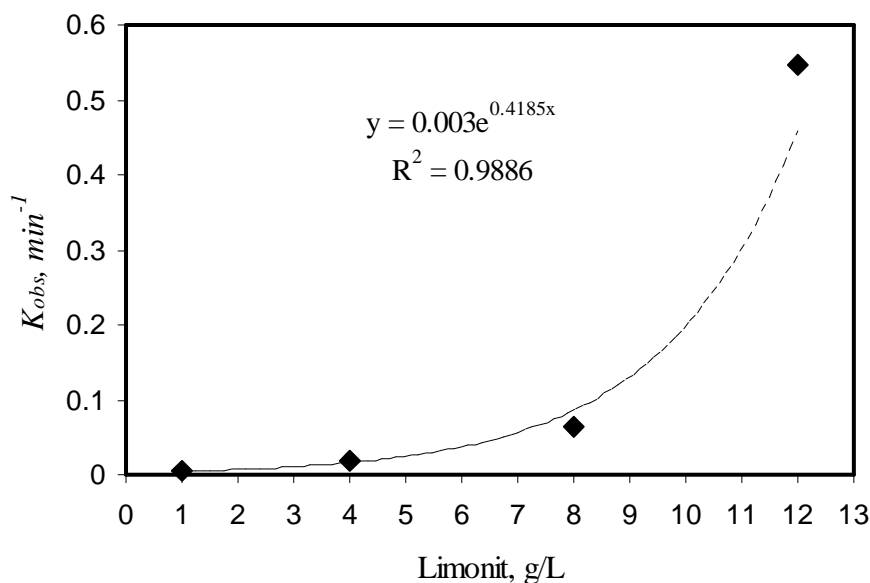


Fig . 1: Values of K_{obs} as a function of limonite concentration.

$$C_{Cr(VI)} = 10 \text{ mg/L}, \text{ pH}=5.5, t=25 \text{ }^\circ\text{C}, \omega=500 \text{ r/min}$$

Effect of Initial Cr (VI) concentration on first-order rate coefficients

The effect of Initial Cr (VI) concentrations on K_{obs} , the first-order rate coefficient is presented in Fig. 2. As the initial Cr (VI) concentrations increased, the first-order rate coefficient decreased, therefore; it can be concluded that the values of initial Cr(VI) concentrations is a significant factor for Cr(VI) reduction.

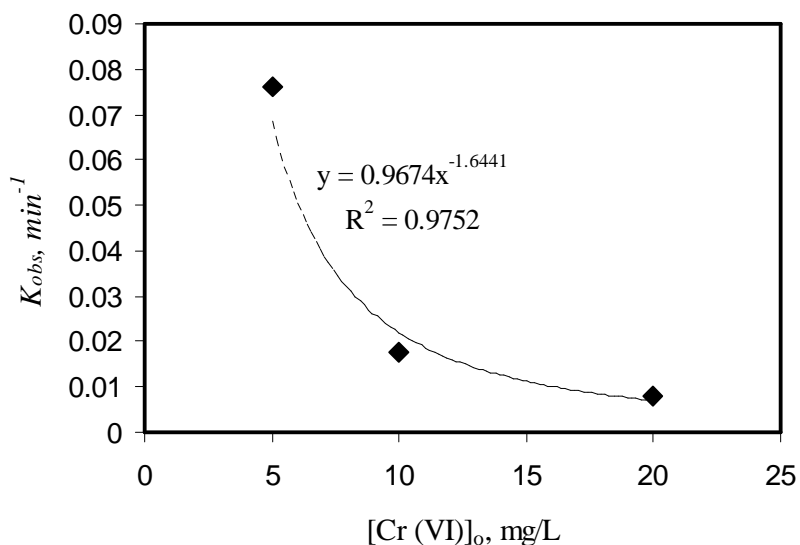


Fig. 2: Values of K_{obs} as a function of Initial Cr(VI) concentration.

$$C_{Fe} = 4 \text{ g/L}, \text{ pH}=5.5, t=25 \text{ }^\circ\text{C}, \omega=500 \text{ r/min}$$

Effect of pH on first-order rate coefficients

The pH value of the aqueous system is one of the most important parameters affecting the reduction of Cr (VI). The effect of pH between 3 and 9 on the first-order rate coefficient is presented in Fig. 3. The first-order rate coefficient in general, decreases as pH increases. The effect of pH on the observed first-order rate coefficients can be explained by considering how the

amount of Fe (II) changes as a function of pH. The correlation between K_{obs} and pH obtained indicate that the pH is a very important factor that affects the Cr (VI) reduction.

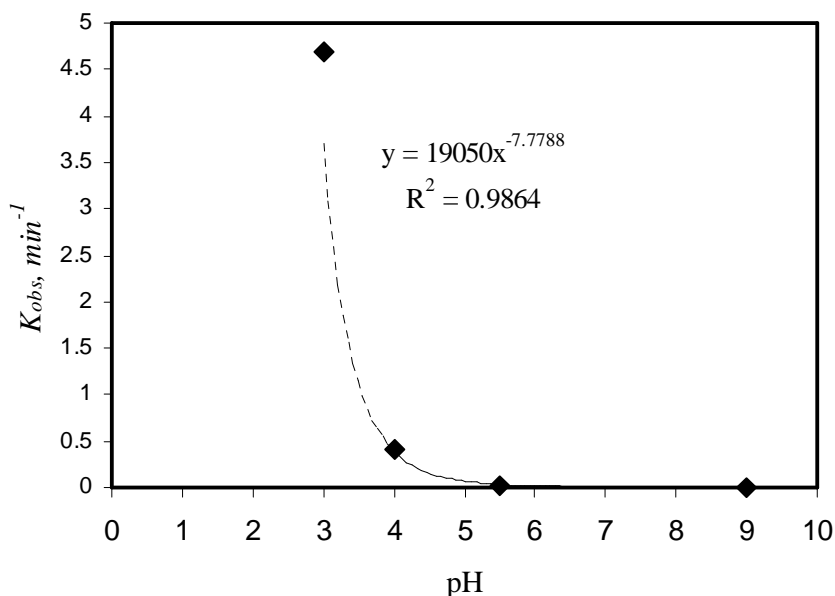


Fig. 3: Values of K_{obs} as a function of pH.

$C_{Fe}=4 \text{ g/L}$, $C_{Cr(VI)}=10 \text{ mg/L}$, $t=25^\circ\text{C}$, $\omega=500 \text{ r/min}$

Effect of different limonite particle type on first-order rate coefficients

Fig. 4 shows the correlation between the first-order rate coefficient and different limonite type. Limonite particle size has a significant effect on the Cr (VI) reduction rate due to the change of easily available reduction sites. The relatively higher reduction rates by smaller limonite particle yield a larger external surface area. There was a tendency that smaller particles needed shorter time to equilibrate.

The K_{obs} -limonite particle type relationship indicated that the limonite particle type was a significant factor throughout the reaction.

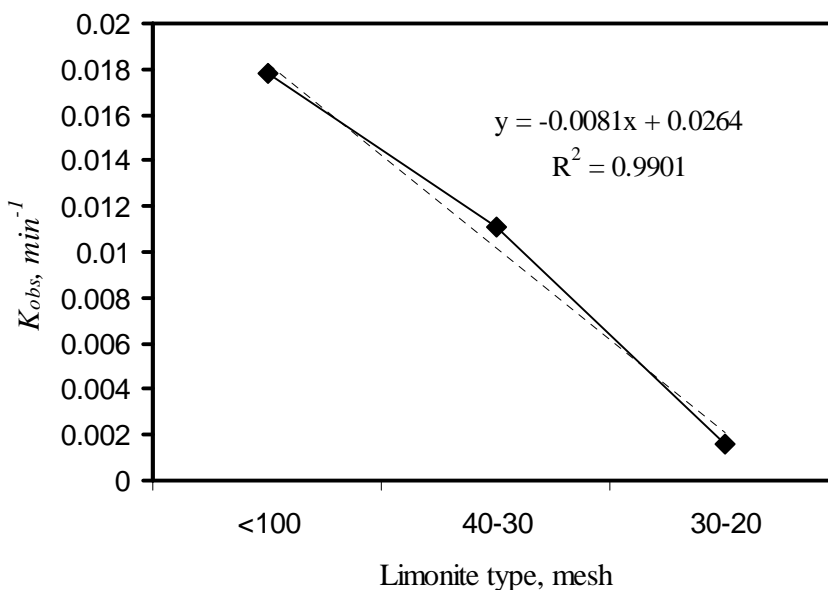


Fig. 4: Values of K_{obs} as a function of different limonite particle type

$C_{Fe}=4 \text{ g/L}$, $C_{Cr(VI)}=10 \text{ mg/L}$, $t=25^\circ\text{C}$, $\text{pH}=5.5$, $\omega=500 \text{ r/min}$

CONCLUSION

In this work, it was noted that the observed first-order rate coefficient increased with increasing limonite concentration but decreased with increasing pH and initial Cr (VI) concentrations. Moreover, it was shown clearly that the first-order rate coefficient was affected by Limonite particle size.

The obtained results revealed that the removal of Cr(VI) using limonite for the treatment of wastewater is an effective and economical alternative.

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