



Removal of hexavalent chromium by limonite in aqueous solutions



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ARTICLE INFO

Article history:

Received 7 February 2013
Received in revised form 23 May 2013
Accepted 28 May 2013
Available online 28 June 2013

Keywords:

Cr(VI) removal
Limonite
Reduction–sorption
Acidic environment

ABSTRACT

Cr(VI) is a toxic pollutant and its reduction to relatively less toxic Cr(III) can solve this problem to a greater extent. In the present study, coupled reduction–sorption of Cr(VI) in aqueous solutions using limonite was investigated as a function of pH, limonite dose and particle size. Results demonstrated that the smaller limonite particle size and low pH aqueous medium favored high Cr(VI) removal. Significant Cr(VI) removal ($>55 \pm 1\%$) was achieved with 100–200 mesh, whereas only $25 \pm 0.7\%$ and $10 \pm 0.5\%$ removals were attained using 30–40 mesh and 20–30 mesh, respectively, after 2 h reaction. Acid pH proved beneficial and the complete Cr(VI) removal was observed at $\text{pH} < 4.0$ compared to that of $10 \pm 0.5\%$ at $\text{pH} 9.0$. Moreover, above $53 \pm 2.5\%$ of Cr(VI) removal rates were maintained in the first three batch experiment runs and then drastically decreased to below $5 \pm 0.3\%$ in experiment Run-7. The Brunauer–Emmett–Teller (BET) surface area and sorption capacity of limonite were $35.22 \text{ m}^2 \text{ g}^{-1}$ and 10.03 mg g^{-1} , respectively. The reaction mechanism demonstrated that under acidic aqueous medium, the dissolved Fe(II) and S(II) on limonite surface reacted with Cr(VI) and formed Cr_3S_4 and Cr_5Si_3 precipitates. But the resultant precipitates on limonite surface hindered further Cr(VI) removal and passivated, affirmed in XRD and ESEM analyses. This study suggested that limonite can be used for the effective removal of Cr(VI) from contaminated water environments.

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1. Introduction

Water pollution from heavy metals is turned to become a severe environmental problem worldwide. With growing impact of chromium (Cr) on public health in recent years, it is considered one of the priority pollutants and received researchers' attentions (Erdem et al., 2004). In the aqueous environment, chromium exists in two stable oxidation states: (Cr(VI) and Cr(III)) which possess contrasting characteristics in toxicity and mobility. Cr(VI) is characterized with high solubility, mobility as well as toxicity and considered one of the potential mutagen and carcinogen. Recently, IARC (International Agency for Research on Cancer) has confirmed the carcinogenic effect of Cr(VI) in humans (Costa and Klein, 2006). World Health Organization (WHO) set 0.05 mg L^{-1} Cr(VI) permissible limits in wastewaters and many countries have also regulated this standard for drinking water supplies. In contrast, Cr(III) has low toxicity and limited solubility, and always considered less toxic (Boddu et al., 2003; Costa and Klein, 2006; Kimbrough et al., 1999). Subsequently, the reduction of Cr(VI) in to Cr(III) is environmentally favorable and usually practiced for Cr(VI) removal from contaminated water sources.

Many treatment technologies have been reported for the removal of Cr(VI) from waters and wastewaters including chemical reduction, ion-exchange, photochemical and electrochemical reduction, adsorption, membrane processes and biological reduction (Dzyazko et al.,

2007; Fan et al., 2013; Inoue et al., 2010; Kannan and Thambidurai, 2008; Kim et al., 2002; Liu et al., 2005, 2007; Malaviya and Singh, 2011; Rayman and White, 2009; Sahu et al., 2009; Sharma et al., 2009; Wang et al., 2009; Zaitseva et al., 2013). In these methods, Cr(III) was precipitated after Cr(VI) reduction. Consequently, most of the removal processes are practically not applicable due to complex technical procedures and high operation costs. Thus, some new low-cost sorbents with good sorption potential: like Fe^0 or some natural mineral mixtures containing majorly of iron-oxide minerals have received researchers' attentions (Ahmad and Qureshi, 1991; Allowitz and Scherer, 2002; Blowes et al., 1997; Jiang et al., 2013; Ponder et al., 2000; Tong et al., 2011). Allowitz and Scherer (2002) evaluated various factors including the types of iron metal, initial concentration and pH value on the removal of Cr(VI) by Fe^0 .

Naturally, iron minerals are ubiquitous and play a pivotal role in the geochemical cycling of trace elements. Particularly, coupled Fe(III)–Fe(II) redox acts as an electron-transfer mediator for many biological and chemical species. The reductions of Cr(VI) by various iron minerals are more effective and that includes; biotite, vermiculite, mackinawite, illite, smectites, chlorite, maghemite, magnetite, ilmenite, Fe(II)–hematite, Fe(II)–goethite, and sulfides (He and Traina, 2005; Ilton and Veblen, 1994; Jiang et al., 2013; Kendelewicz et al., 1999, 2000; Mullet et al., 2004; Patterson et al., 1997; White and Peterson, 1996). Pyrite has been proved experimentally as an efficient Cr(VI) reducing agent and the resultant hydroxo-Cr(III) species were precipitated on pyrite particles (Zouboulis et al., 1995). At neutral aqueous medium (pH 7), magnetite surface was found to become passivated

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and hindered to act as an electron donor for Cr(VI) reduction (Peterson et al., 1997). Additionally, goethite might be formed on magnetite surface due to the dissolution of magnetite and/or dissolution of newly formed magnetite intermediate followed by precipitation (He and Traina, 2005). However, adsorption of Cr(VI) using hematite and goethite is considered of highly pH-dependent (Ajouyed et al., 2010).

Limonite ores are the complex mixtures of hematite (α -Fe₂O₃)–goethite (α -FeOOH), and considered to be soft in the presence of high amount of goethite content (Kaneko et al., 2002). Generally, goethite has been recognized to control the adsorption capacity of soils for toxic metals (Lehmann et al., 2001). Interestingly, it has been extensively used for the removal of Cr(VI) (Lazaridis and Charalambous, 2005) and the reduction of Cr(VI) was mainly relied on the amount of Fe(II) (Fendorf and Li, 1996). Hematite is a natural iron ore that contains Fe(II) and the removal of Cr(VI) in aqueous solutions using hematite has also been documented (Eary and Rai, 1989; Kendelewicz et al., 1999). Though, realizing the mineralogical and morphological importance of soil constituents; Cr(VI) removal using limonite was not being widely studied so far. In the present study, an attempt has been made to use limonite for the coupled reduction–sorption of Cr(VI) from synthetic water samples.

This study investigates, to our knowledge for the first time, granulated limonite surface capacity for the removal of Cr(VI) from synthetic water samples and discusses the possible reaction mechanisms. Various operating conditions including limonite particle size, Cr(VI) removal in different batch experiment-runs and the effects of solution pH on Cr(VI) removal were investigated. Additionally, mineralogical and morphological changes appeared on limonite surface before and after the reaction were also examined using ESEM, XRD and BET techniques.

2. Materials and methods

2.1. Materials and reagents preparation

Limonite was obtained from Hangzhou Weimin Geologic Sample Factory in Yuhang, Zhejiang Province, China. The materials were located on the ground surface in a vibrating mill and the respective parts were granulated and sieved (US standard mesh). The sieved materials were used in batch experiments without any further treatment.

Analytical reagent (K₂Cr₂O₇) was desiccated at 120 °C for 2 h to prepare Cr(VI) aqueous solution. Cr(VI) stock solution (1000 mg L⁻¹) was prepared by dissolving 2.829 g of potassium dichromate (K₂Cr₂O₇) in 1 L de-ionized (DI) water. Working concentrations (10 mg L⁻¹) of Cr(VI) solutions were prepared by suitable dilution of the stock solution for subsequent experiments. HCl (0.1 M) and NaOH (0.1 M) aqueous solutions were used to adjust solutions pH.

All the chemicals used in this study were of analytical grade and used as received without any pretreatment. DI water was used to prepare all the solutions.

2.2. Experiment and analytical methods

All the glass wares were soaked in nitric acid solution for 24 h and then washed with DI water before the experiments. Batch experiments were carried out in 1.5 L capacity flasks. Limonite particles were added in to 1.5 L flasks filled with 1 L K₂Cr₂O₇ solutions (initial Cr(VI) concentration = 10 mg L⁻¹). Initial solution pHs were adjusted to 3.0, 4.0, 5.5 and 9.0, respectively, using HCl and NaOH. Initial limonite doses (4 g L⁻¹) with the particle sizes of 20–30, 30–40 and 100–200 mesh were used in the reactions. The solutions in the flasks were continuously stirred in rotary shaker (500 r min⁻¹) at constant temperature (25 ± 0.5 °C).

In order to investigate the capacity of limonite for Cr(VI) removal, 2.0 g limonite was added in to a three-neck flask containing 500 mL of 10 mg L⁻¹ Cr(VI) solution and stirred in rotary shaker at 500 r min⁻¹.

After 2 h of the reaction, the supernatant was poured out after being precipitated, and a new 500 mL solution of the same concentration was added into the flask. Moreover, all these steps were repeated until the Cr(VI) concentration reduced to below 10% in 2 h. However, in the whole reaction process, the limonite was not replaced.

All the samples were filtered through Φ 25 mm aperture 0.45 μ m filter membranes before being analyzed. Cr(VI) concentration was measured at 540 nm using UV–VIS spectrophotometer (Puxitongyong TU-1800PC, Beijing) by 2-diphenylcarbazide spectrophotometric method. Total chromium and iron in liquid phase were determined by flame atomic absorption spectrophotometer (Shimadzu AAG300, Japan). pH values of the aqueous solution were measured from a digital pH meter (Mettler Toledo SG2, Shanghai, China).

Surface compositions of limonite were detected by X-ray diffraction analyzer (DMax-RA, 12 kW, target-turning, Rigaku, Japan). In this method, XRD analyzer was used to detect the surface of solids and acquired some spectrum characteristics. The spectra were then analyzed by the respective analysis' software. The characteristic spectrum of the detected solid was compared to the substance standard cards in the software and then the substance could be identified by the characteristic spectrum in the figure. The numbers before ">" in the figures represent the cards' numbers, such as "05-0490". Environmental scanning electron microscopy (ESEM) (Philips-XL30ESEM with 200 \times and 4000 \times magnifications) was performed to identify the changes appeared on limonite surface after different reaction times. BET analysis was also performed and the particle size was approximately <100 mesh. The isothermal adsorption and desorption curves of limonite and the pore size distribution curve of micro-porous structures on limonite were detected by Quantachrome Autosorb automated gas sorption system (Autosorb-1-C).

2.3. Statistical analysis

Statistical analysis was performed by considering errors of the means for each test. As a result, these standard errors were applied to calculate \pm 95% confident interval of the means and plotted in figures. Means of any three tests would be considered significantly variant to each other when their mean values (\pm Cr(VI)) would not overlap, as described earlier (Baig et al., 2011). However, common data analysis errors in batch adsorption studies have also been reported (Khairiy and Malash, 2011).

3. Results and discussions

3.1. Limonite characterizations

Fig. 1a and b presents the surface mineralogical compositions of limonite before and after the reaction. In comparing to substance standard cards stored in the analysis' software, we have noticed more SiO₂ and Fe₂O₃ amounts in limonite with a smaller number of FeS₂ prior to the reaction. Iron phase goethite and the significant amounts of quartz are the main components, as reported earlier (Georgiou and Papangelakis, 2004). After 2 h of the reaction with K₂Cr₂O₇ solution, Cr₃S₄ and Cr₅Si₃ were formed on the surface of limonite, while SiO₂, Fe₂O₃ and FeS₂ compositions were still remained the same (Fig. 1b). Moreover, large peak of Fe₂O₃ appeared at $2\theta^\circ = 33$ before and after the reaction (Fig. 1a and b) was consistent with the earlier study (Zhao et al., 2012). The dissolution of FeS₂ in acidic medium might generate Fe(II) which could enhance the reduction of Cr(VI) into Cr(III) and subsequent sorption. However, the concentration of total Cr was higher in the solution than that of Cr(VI) which reiterated that Cr(III) could also present in the solution. It can be concluded that Cr(VI) was deoxidized by limonite and some Cr remained on limonite surface in the form of Cr₃S₄ and Cr₅Si₃, while some Cr were remained in the solution as Cr(III).

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