Minerals Engineering 21 (2008) 913–917

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Adsorption mechanisms of Cr(VI) on the modified bauxite tailings

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ARTICLE INFO

Article history:
Received 23 December 2007
Accepted 11 April 2008
Available online 27 May 2008

Keywords:
Environmental
Waste processing
Surface modification
Tailings

ABSTRACT

The main waste product generated during the bauxite flotation in China is the aluminosilicate tailings. It is desirable to develop an application of these aluminosilicate tailings for the treatment of waste streams containing dissolved heavy metals. The Cr(VI) adsorption capacity and mechanisms of the bauxite tailings modified by $FeCl_3 \cdot 6H_2O$ are investigated in the present study. A maximum removal rate of Cr(VI) by the modified bauxite flotation tailings is obtained at 99.3% in batch experiments. The IEPs of the unmodified and modified bauxite tailings are 3.6 and 5.0, respectively. The IEP of the modified bauxite tailings shifts to lower pH value in the presence of Cr(VI), which indicates that an adsorption of anionic species happens on the modified bauxite tailings. A new band of $Cr_2O_7^{2-}$ appears in the FTIR determination of the modified bauxite tailings, which shows that Cr(VI) adsorbs on the modified bauxite tailings in the form of chemical adsorption. Furthermore, the adsorption data of Cr(VI) on the modified bauxite tailings are well described by both Langmuir and Freundlich models. The pseudo-second-order kinetic model also fits experimental data for the adsorption of Cr(VI).

1. Introduction

Hazardous species, such as Cr(VI), As(V), Pb(II) and Cd(II), exist in aqueous waste streams of metal plating facilities, mining operations and tanneries (Myroslav et al., 2006). Several treatment processes, including chemical precipitation, phytoextraction, reverse osmosis, electrodialysis, ion exchange and membrane filtration or adsorption, have been developed to remove heavy metals from industrial wastewater (Moore and Ramamorthy, 1994). However, most of these methods have some disadvantages such as complicated process, high cost and high energy consumption. The main disadvantage of adsorption treatment method is the high cost of the adsorbents. Therefore, it is necessary to find new adsorbents with low cost and high efficiency for the treatment of wastewater.

Silicate minerals have great potential applications as inexpensive and efficient adsorbents in the treatment of wastewater because of availability of large quantity, chemical and mechanical stability, high surface area and special structure property. In recent years, a number of researches have been carried out using silicate minerals for adsorption of hazardous substances (Osvaldo et al., 2007; Jyotsnamayee et al., 1999).

The main waste product, generated during the aluminum production from bauxite by a combined method of flotation followed by the Bayer process, is aluminosilicates tailings. It is reported that 0.2 t of aluminosilicates tailings is generated form every 1 t bauxite ores processed by flotation. In China, a large quantity of bauxite tailings is stored in the tailing dam after flotation (Liu and Yuan, 2004; Wang et al., 2004). The main minerals in bauxite flotation tailings are diaspore, kaolinite, illite and pyrophyllite. Some investigations and trials for the utilization of bauxite tailings in cement, absorbent materials, building materials and ceramics have been carried out in recent years. However, there are no reports on the utilization of bauxite flotation tailings for the treatment of industrial wastewater.

The adsorption of Cr(VI) from aqueous solution by unmodified and modified bauxite flotation tailings are investigated in the present study. The adsorption mechanisms of Cr(VI) onto the bauxite tailings are determined by the measurement of zeta-potential and FTIR spectroscopy.

2. Materials and methods

2.1. Materials

The bauxite flotation tailings sample is obtained from Zhongzhou bauxite flotation plant in China. These samples are dried at 85 °C and screened at a 45 mesh screen. The particle size of tailings sample is also determined by a laser granulometer (CILAS-1064) and the average particle size is 25.5 μm. The chemical compositions of sample are 39.5% Al_2O_3, 28.9% SiO_2, 3.1% TiO_2, 0.5% MgO, 0.6% CaO, 7.3% total Fe, 0.1% S, 4.7% K_2O and 0.8% Na_2O. Diaspore, kaolinite, illite, anatase, hematite and quartz are determined as the main minerals in bauxite flotation tailings by an X-ray powder diffractometry (XRD, Shimadzu D/MAX-rA model).

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doi:10.1016/j.mineng.2008.04.003

2.2. Adsorption tests

Solution of Cr(VI) (40 mg/L) is prepared from 1000 mg/L stock solution of Cr salts using distilled water. With 100 ml Cr(VI) solution, the adsorption percentage of Cr(VI) as a function of adsorbent dosage, solution pH and shaking time is investigated at a shaking speed of 170 ± 3 strokes min^{-1} at 30 + 91 °C. After the filtration, the concentration of Cr(VI) ions in filtrated water is determined by ultraviolet–visible spectrophotometry. The solution pH value is modified by HCl and NaOH.

The adsorption percentage is determined as below:

$$C = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\%, \quad (1)$$

where C is the adsorption percentage of Cr(VI) on tailings (%). C_0 and C_e are the initial and the equilibrium concentration of Cr(VI) (mol/L), respectively. The average of adsorption percentages with three repeats is reported in this study.

2.3. Zeta-potential measurements

A zeta meter (Brookhaven Zeta plus, USA) is used for the determination of zeta-potentials. The samples are ground to 5 μm in an agate mortar. Suspensions containing solids 0.05% (mass fraction) are conditioned in a beaker for 15 min before the measurement and pH value is measured at 25 °C.

2.4. Fourier transform infrared spectroscopy

The infrared spectra for powder samples of bauxite tailings with or without reagents pretreatment are measured using FTIR-750 Infrared Spectrophotometer from Nicolet Co., USA. The samples are air-dried at room temperature (25 °C).

3. Results

3.1. Effect of adsorbent dosages

The adsorbent dosage is an important parameter for the determining of the adsorbability of adsorbent at a given initial condition. The influences of modified and unmodified bauxite tailings on the adsorption of Cr(VI) are shown in Fig. 1. The adsorption percentage of Cr(VI) increases with the dosage of modified bauxite tailings, but it changes little with the dosage of unmodified bauxite tailings.

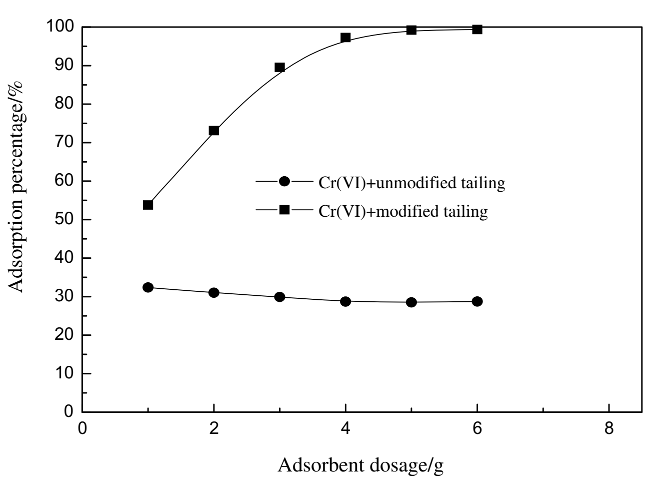

Fig. 1. Effect of tailings dosage on the adsorption percentage of Cr(VI) (solution volume 100 ml, shaking time 2 h, temperature 25 °C).

3.2. Effect of the shaking time

The effects of the shaking time on the adsorption of Cr(VI) are shown in Fig. 2. The results indicate that the removal of Cr(VI) by modified bauxite tailings is considerably improved by increasing the shaking time, while in the case of unmodified bauxite tailings, the adsorption percentage of Cr(VI) is not influenced by the shaking time.

3.3. Effect of pH

The solution pH is another important parameter and it has a strong effect on the adsorption of metal ions on the surface of the minerals. The effect of pH on the adsorption of Cr(VI) is investigated in the pH range of 2–12, and the results are shown in Fig. 3.

Form Fig. 3, it can be found that the adsorption percentage of Cr(VI) increases as pH is decreased. The reduced adsorption percentage of Cr(VI) at high pH is due to the competition adsorption of OH^- on the available exchange sites of minerals. The oxides of aluminum, iron and silicon are presented in varying amounts in bauxite tailings. The hydroxylated surfaces of oxides develop a

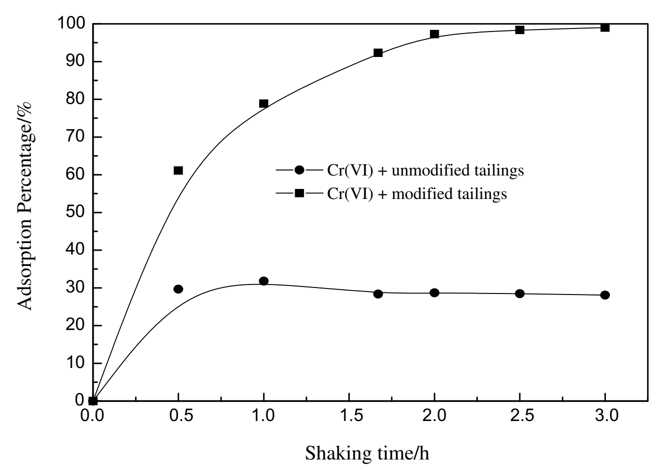

Fig. 2. Adsorption percentage of Cr(VI) as a function of the shaking time (solution volume 100 ml, 30 mg/L Cr(VI), 4 g adsorbent, pH 5–6, temperature 25 °C).

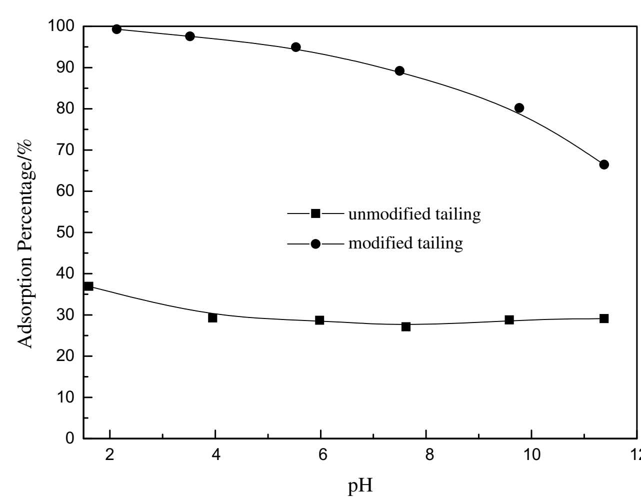

Fig. 3. The effects of pH on the adsorption percentage of Cr(VI) under the conditions that without the adding of tailings and with the adding of unmodified and modified tailings (volume of solution: 100 ml, 30 mg/L Cr(VI)), 4 g adsorbent, shaking time 2 h, temperature 25 °C).