

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

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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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{Cr}_2\text{O}_7^{2-}$ 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).

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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 from 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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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 $5 \mu\text{m}$ 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.

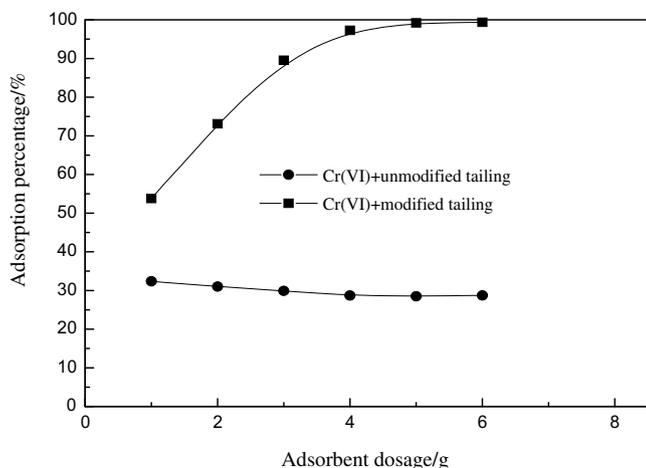


Fig. 1. Effect of tailings dosage on the adsorption percentage of Cr(VI) (solution volume 100 ml, shaking time 2 h, temperature 25 °C).

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.

From 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

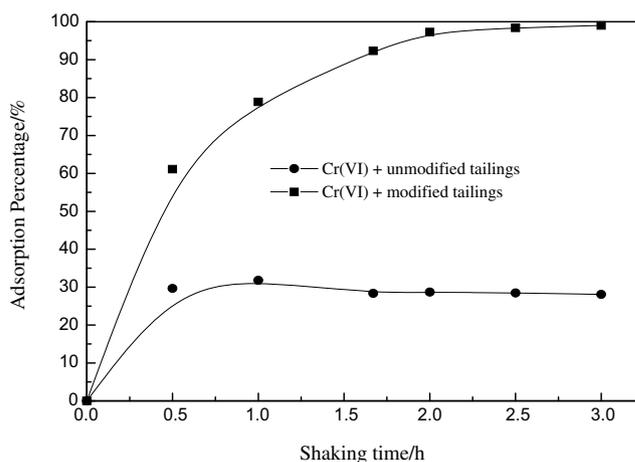


Fig. 2. Adsorption percentage of Cr(VI) as a function of the shaking time (solution volume 100 ml, 30 mg/L Cr(VI), 4 g adsorbent, pH 5–6, temperature 25 °C).

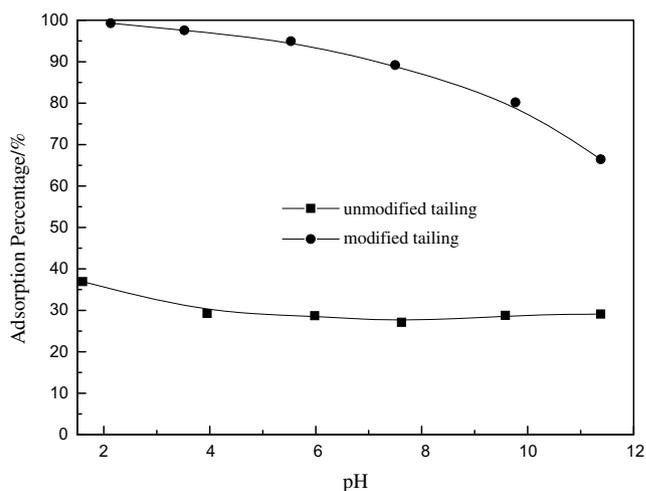
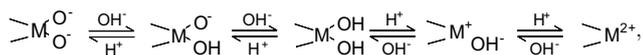


Fig. 3. The effects of pH on the adsorption percentage of Cr(VI) under the conditions that without the adding of tailings and with the adding of unmodified and modified tailings (volume of solution: 100 ml, 30 mg/L Cr(VI), 4 g adsorbent, shaking time 2 h, temperature 25 °C).

charge on the surface in aqueous solution through amphoteric dissociation (Abmed, 1966), as shown below:



where M stands for Al, Fe and Si, etc. These surfaces are positively charged at lower pH and consequently are favorable for the adsorption of Cr(VI) in the anionic form of $HCrO_4^-$.

4. Discussion

The objective of this study is to investigate the adsorption mechanisms of Cr(VI) by the bauxite flotation tailings. The zeta-potential, FTIR spectroscopy, adsorption isotherm and kinetic studies are carried out.

4.1. Zeta-potential measurement

The pH–zeta potential curves of unmodified and modified bauxite tailings in the presence of distilled water and 30 mg/L Cr(VI) are presented in Fig. 4. It can be seen that the values of zeta-potential in all suspensions increase as pH is decreased. This may be interpreted in terms of the mechanisms of the variable charge generation. As the solution pH is decreased, the surface positive charges of unmodified and modified bauxite tailings increase while the surface negative charges decrease due to the protonation of surface hydroxyl groups on unmodified and modified bauxite tailings. The changes of the surface charge result in the changes of zeta-potential in suspensions. Under the acidic conditions, unmodified bauxite tailings carry the net negative surface charges, but modified bauxite tailings possess net positive surface charges when pH is less than 5.0. Bauxite tailings are the mixture of aluminosilicates. The broken bonds on the surface of unmodified bauxite tailings are covalent Al–O bonds and Si–O bonds which are $\equiv Si-O^-$, $\equiv Si-OH$ and $\equiv Al-O^{-1.25}$, $\equiv Si-O^-$, $\equiv Si-OH$ and $\equiv Al-O^{-1.25}$ function keys (Jia, 2001), which can cause the absorption and electrostatic action with cationic reagents like ferric ion.

The value of negative charges on the surface of both modified and unmodified tailings decreases in the presence of Cr(VI) in the pH range of 2–12. The removal percentage of Cr(VI) is high in acidic condition which is in agreement with the previous results in Fig. 3.

4.2. FTIR spectroscopy

As shown in Fig. 5, the broad band observed at 3620 cm^{-1} belongs to the O–H stretching vibration of the Si–OH groups and

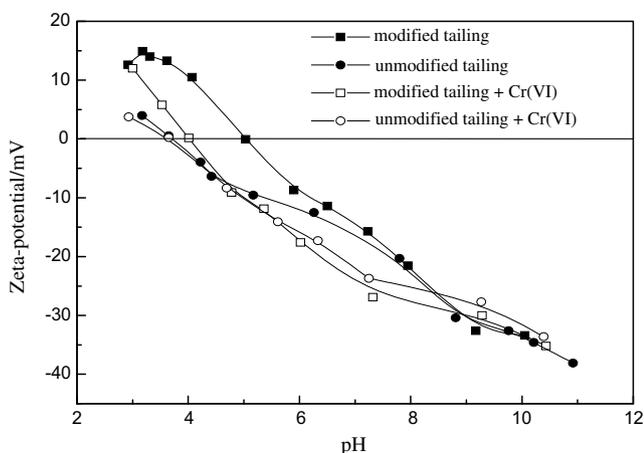


Fig. 4. Zeta-potentials vs pH in the solution of 30 mg/L Cr(VI) (containing solids 0.05% (mass fraction), temperature 25 °C).

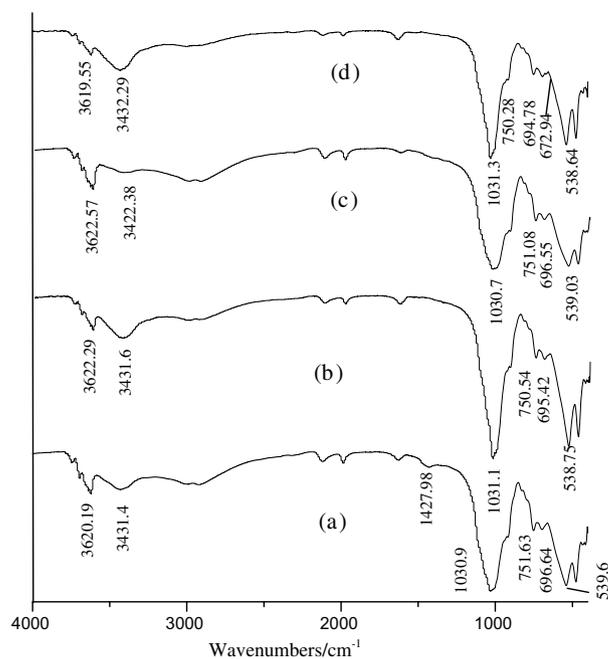
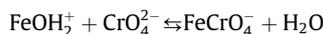


Fig. 5. IR spectrums (KBr) of unmodified tailing (a), modified tailing (b), Cr(VI) onto unmodified (c) and modified (d) tailings.

HO–H vibration of the water molecules adsorbed on the sample surface. The bands observed at 1030 cm^{-1} , 751 cm^{-1} and 696 cm^{-1} are caused by the tetrahedral sheet of Si–O–Si group and the deforming and bending modes of the Si–O bond. However, modified tailing samples show a strong band of O–H–O at 3431 cm^{-1} , which indicates that there are the adsorption of –OH on the surface of the tailings. The band of –C–CH₃ (1427 cm^{-1}) disappeared in Fig. 5b–d for the modified bauxite tailings, it is possible that the residual flotation reagents have been consumed by the modification reagents. The modification of the bauxite tailing samples with $FeCl_3 \cdot 6H_2O$ tends to weak the adsorption bands of Si–O and Al–O, respectively. This indicates that the modification of tailings may produce hydrated iron oxide (Hesham and Philip, 1997).

According to the results in Fig. 5c and d, the bands are generally similar to the results in Fig. 5a. Intense band at 3432 cm^{-1} and weaken bands of Si–O and Al–O can also be found in Fig. 5c in the presence of Cr(VI), and there is a new band at 672 cm^{-1} of $Cr_2O_7^{2-}$. It suggests that Cr(VI) adsorbs on the modified tailing surface in the form of chemical adsorption. In some reports, chromate can adsorb on the surface of hydrated iron oxide as below (Sun et al., 2003; Weerasooriya and Tobschall, 2000):



4.3. Adsorption isotherms

Langmuir and Freundlich isotherm models are applied to establish the relationship between the adsorption density of Cr(VI) on tailings and its equilibrium concentration in aqueous solution. The experimental data conform to the linear form of Langmuir model expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{2}$$

where C_e is equilibrium concentration of the Cr(VI) (mg L^{-1}), q_e is the adsorption density of Cr(VI) (mg/g). q_m and K_L are the Langmuir constants which relate to the adsorption density (mg g^{-1}) and the energy of adsorption (L g^{-1}), respectively. q_m and K_L constants

are obtained from the slope and intercept of the linear plot of C_e/q_e vs C_e , respectively (see Fig. 6).

The adsorption equilibrium data are also applied to the Freundlich model in logarithmic form given as follows (Ahmet et al, 2007):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (3)$$

where K_F (mg g^{-1}) and n are the constants of Freundlich which are related to adsorption density and adsorption intensity, respectively. K_F and $1/n$ are determined from the intercept and slope of linear plot of $\log q_e$ vs $\log C_e$, respectively.

The isotherm constants and correlation coefficients are calculated from the linear Langmuir and Freundlich plots by the plotting C_e/q_e vs C_e and $\log q_e$ vs $\log C_e$ (Fig. 6) and are represented in Table 1.

The adsorption pattern of Cr(VI) on tailings is well fitted by both Langmuir and Freundlich models with R^2 of 0.97–0.99. Both models are equally applicable. Similar results are also reported in other studies (Chen and Wang, 2007; Saad Ali Khan et al., 1995).

The K_F value of the Freundlich equation (Table 1) indicates that the modified bauxite tailings have a very high adsorption density for Cr(VI) ions in aqueous solutions. With high n values (between 1 and 10), the modification is beneficial to the adsorptions of metal ions (Tahir and Naseem, 2007).

4.4. Study of adsorption kinetics

Adsorption kinetics, the solute uptake rate, is one of the most important characteristics that represent the adsorption efficiency of the modified tailings. As shown in Fig. 2, the adsorption rates of Cr(VI) on the modified and unmodified tailings increase rapidly in the first 2 h and 0.5 h, respectively, and then reach equilibrium gradually at about 3 h and 1 h, respectively. In order to analyze the adsorption rate of Cr(VI) on modified tailings, the pseudo-first-order equation of Lagergren (3) and the pseudo-second-order rate equation (4) are evaluated based on the experimental data (Huang et al., 2007):

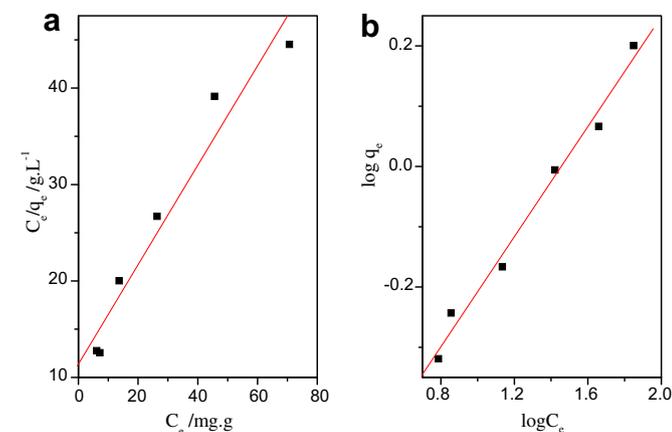


Fig. 6. (a) Langmuir and (b) Freundlich plots for the adsorption of Cr(VI) onto modified tailings.

Table 1
Langmuir and Freundlich constants and correlation coefficients of the adsorption of Cr(VI) on modified tailings

Langmuir equation			Freundlich equation		
q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	n	R^2
1.3998	0.04529	0.9755	0.2166	2.19044	0.9929

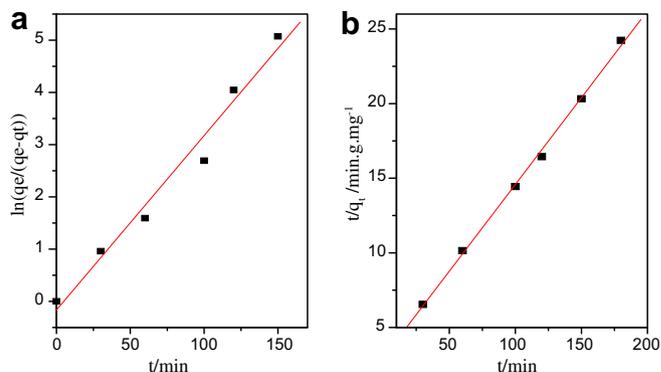


Fig. 7. (a) The pseudo-first-order and (b) the pseudo-second-order kinetic equation for adsorption of different concentrations of Cr(VI) by modified tailing at 300 ± 1 K.

Table 2
Kinetic parameters of Cr(VI) adsorbed on modified tailings

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
7.4257	0.0334	0.98829	8.599931	0.002288	0.99901

$$\ln \frac{q_e}{q_e - q_t} = k_1 t, \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{t}{q_e}, \quad (5)$$

where k_1 is the Lagergren adsorption rate constant (h^{-1}) and k_2 is the pseudo-second-order adsorption rate constant ($\text{g mg}^{-1} \text{h}^{-1}$). q_e and q_t are the amounts of metal ions absorbed (mg g^{-1}) at equilibrium and at time t , respectively. Plots of $\log(q_e)/(q_e - q_t)$ vs t and $t/(q_t)$ vs t are shown in Fig. 7. Clearly, it can be seen from Fig. 7 that the pseudo-second-order kinetic model provides a good correlation for the adsorption of Cr(VI) on modified tailings in contrast to the pseudo-first-order model. This is similar to other studies (Brigatti et al., 2000). In addition, the correlation coefficient of the pseudo-second-order kinetic model is bigger than that of the pseudo-first-order kinetic model (see Table 2).

5. Conclusions

Based on the present study, the following conclusions can be drawn.

- (1) The modified bauxite tailings by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ has shown good adsorptivity for Cr(VI) ions, and a maximum removal rate of Cr(VI) of 99.3% is obtained.
- (2) The pretreatment of bauxite tailings with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (modified tailings) raises its iso-electric point (IEP) from 3.6 to 5.0, and then the IEP is reduced from 5.0 to 4.2 in the presence of Cr(VI).
- (3) The IR spectra results reveal that the hydrated iron oxide is basically held on the unmodified tailings by the appearance of a strong band of O–H–O at 3431 cm^{-1} and the disappearance of a band of $-\text{C}-\text{CH}_3$ at 1427 cm^{-1} . The presence of hydrated iron oxide is perhaps responsible for the adsorption of Cr(VI) on the modified tailings and produces a new band of $\text{Cr}_2\text{O}_7^{2-}$ at 672 cm^{-1} .
- (4) Both Langmuir and Freundlich models fit well the experimental data of the adsorption of Cr(VI) on the modified tailings and the adsorption kinetics is well represented by the pseudo-second-order kinetic model.

Acknowledgements

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