Adsorption of chromium(VI) from aqueous solution by a mesoporous aluminosilicate synthesized from microcline

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A B S T R A C T

A mesoporous aluminosilicate was hydrothermally prepared from microcline in an alkaline condition with cetyltrimethylammonium bromide as synthesis directing agent. The properties of the sample were determined by X-ray powder diffraction, nitrogen adsorption, and transmission electron microscope. The sample was employed for removal of Cr(VI) ions from aqueous solution. The effect of adsorption time, pH value of the medium and initial concentration of Cr(VI) on adsorption was studied. The adsorption was modeled by Dubinin–Radushkevich adsorption theory.

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1. Introduction

Since the discovery of mesoporous silica M41S (Beck et al., 1992), mesoporous materials have attracted much attention because of their potential applications in catalysis (Parida and Naik, 2009; Fuchs et al., 2009), membrane filtration and separation technology (Liu et al., 2009), and adsorption of ions or organic compounds of large sizes (Akasaka et al., 2009; Zanjanchi et al., 2008; Jang et al., 2009; Wu et al., 2007). Mesoporous materials usually have large pores and high specific surface areas compared with zeolites. Zeolites have shown good catalytic properties and adsorption of small metal ions. Adsorption of heavy metal ions on mesoporous materials is very attractive due to the large pores. Among heavy metal ions, chromium requires considerable attention. Industrial wastewater from textile industry, leather tanning, electroplating, pigmentation and dyes contain high concentrations of chromium salts. Cr(VI) is toxic and a suspected carcinogenic material. Chromates (Cr(VI)) are soluble in water almost over the entire pH range and mobile in the natural environment. Cr(VI) forms several species, the relative proportions of which depend on both pH and total Cr(VI) concentration. Conventional methods for the removal of chromium and chromate ions from waste streams include adsorption (Ahn et al., 2009), ion exchange (Cheng et al., 2009), electrocoagulation (Olmez, 2009), and photoelectrocatalysis (Cappelletti et al., 2008). Most of these methods require either high energy or large quantities of chemicals. The adsorption method is very popular due to its simplicity and low cost. Although activated carbon or cellulose is frequently used as general adsorbents of inorganic and organic compounds (Ahn et al., 2009; Gurgel et al., 2009), alternative adsorbents have been developed to improve the effectiveness (Aguado et al., 2009).

The mesoporous aluminosilicate was prepared using microcline as a starting material, cetyltrimethylammonium bromide (C16TMABr) as synthesis directing agent. The optimum conditions of adsorbing Cr(VI) on the mesoporous aluminosilicate were evaluated in a batch experiment.

2. Material and method

2.1. Materials

The microcline SOX-1 was from the Song County, Henan province in China, with an average molar mass of 68. The main components of SOX-1 are silica (65.0 mass%) and alumina (16.4 mass%), with a small amount of other metal oxide, such as Fe2O3, FeO, CaO, Na2O, and K2O. Other compounds used in the synthesis process (Na2CO3, C16TMABr, hydrochloric acid, silica, K2CrO4 and deionized water) were supplied by Beijing Chemical Reagents Company (China).

2.2. Preparation of the mesoporous aluminosilicate

The synthesis process was almost the same as previously reported (Wu et al., 2007), but was somewhat simplified: 50 mL of an aqueous solution of 7.3 g C16TMABr was mixed with the calcined microcline (milled, mixed with Na2CO3 (molar ratio 1:1.05) and calcined at 1103 K for 2.5 h), and silica (6.68 g, for adjusting the Si and Al molar ratio). The pH value of the mixture (measured by an acidometer PHS-3C) was adjusted to 11 with hydrochloric acid (5 mol/L). A gel was formed after...
2 h during stirring. The gel was transferred into a 70-mL Teflon-lined stainless autoclave and crystallized at 378 K for 72 h. After crystallization, the autoclave was cooled to 293 K automatically, and the solid product was filtered and dried at 378 K for >10 h. Finally, the powder was calcined in air at 823 K for 5 h to remove the surfactant, using a ramping rate of 2 K/min. The experiment was repeated three times for its exactness.

2.3. Characterization of the mesoporous aluminosilicate

The X-ray powder diffraction analysis (XRD, Siemens D5005, CuKα) was performed to identify the product phase and to derive the basal spacing. The surface area and pore size of the sample were measured by nitrogen isotherms at 77.4 K using AUTOSORB-B1 system. The sample was degassed for 10 h at 573 K before the measurement. The pore distribution of the sample was calculated using the Barrett–Joyner–Halenda model (BJH). The pore structure was visualized by a high-resolution transmission electron microscope (HRTEM) (JEOL, JEM-2011, acceleration voltage: 200 kV).

The compositions of SiO₂ and T(Fe₂O₃ + FeO) were determined by spectrometry of the silicone molybdenum and sulfosalicylic acid complexes. The contents of Al₂O₃ and CaO were determined by complexometry with EDTA in the presence of KF-Zn(Ac)₂ tests. The contents of Na₂O and K₂O were measured by the flame atomic absorption spectrometry.

2.4. Adsorption studies

A solution of 500 mg/L Cr(VI) was prepared by dissolving the required amount of K₂CrO₄. Solutions of lower concentrations were prepared by dilution. Deionized water was used in all the experimental runs. The concentration of Cr(VI) was determined by an X-ray atomic fluorescence spectrophotometer (AF-610A). In a typical adsorption process, 0.05 g adsorbent was dispersed in 40 mL aqueous solution with Cr(VI) at pH values adjusted between pH 2 and 7. The dispersion was shaken in a water oscillator (200 rpm) at 293 K for 10 to 60 min. The pH values of aqueous medium were adjusted with HCl or NaOH at the beginning of experiments and not controlled afterwards. The adsorption of Cr(VI) was calculated from the concentration differences.

3. Results and discussion

3.1. Calcination of microcline

To break down the aluminosilicate framework, SOX-1 was calcined at 1103 K in the presence of Na₂CO₃ (Wu et al., 2007; Ma et al., 2005). The composition of the calcined SOX-1, named SOX-2, is shown in Table 1. The main reaction occurred during the calcination process is shown in Eq. (1) (Wu et al., 2007). Na₂SiO₃ and KAlO₂ formed are used as Si and Al sources for synthesizing the mesoporous aluminosilicate.

\[
\text{KAlSi₃O₈ (microcline) + 3Na₂CO₃ \rightarrow 3Na₂SiO₃ + KAlO₂ + 3CO₂} \quad (1)
\]

3.2. Textural properties of the mesoporous aluminosilicate

The XRD pattern (not shown) of the sample AH-2 showed the (100) and (110) reflection at 2.2° (2θ₁) and 4.0° (2θ₂). The ratio of \( \sin^22\theta_1 : \sin^22\theta_2 \) was equal to 1:3, suggesting a hexagonal ordered pore arrangement (Dang et al., 2004) with a good long-range order. The

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOX-2</td>
<td>38.72</td>
<td>9.76</td>
<td>0.39</td>
<td>0.29</td>
<td>0.51</td>
<td>41.88</td>
<td>8.24</td>
<td>99.79</td>
</tr>
</tbody>
</table>

Fig. 1. N₂ adsorption–desorption isotherms of AH-2, and Fig. 1a BJH pore size distribution of AH-2.

Fig. 2. TEM images of AH-2.
basal spacing $d_{100}$ and the unit cell $a_0 = (2/3)^{1/2} d_{100}$ were 4.01 nm and 4.63 nm respectively.

Capillary condensation appeared at the relative pressure of 0.45–0.9 in the N$_2$ adsorption–desorption isotherms of AH-2 (Fig. 1), suggesting a large amount of mesopores. The BET specific surface area was 847 m$^2$/g, and the total pore volume was 1.01 cm$^3$/g. The mesoporous wall thickness $T$ was 2.13 nm, calculated from

$$T = a_0 - d_{\text{mes}}$$

(2)

where $a_0$ is the unit cell parameter, mesopore diameter roughly estimated by the pore size distribution curve.

The pore size distribution curves were derived from the adsorption branches (Fig. 1). The mesopore diameter was centered at around 2.5 nm. Between 7 and 149 nm, no obvious pores appeared (not shown).

The TEM image in Fig. 2(a) revealed the hexagonal ordered pore arrangement in the (001) direction, and the TEM image in Fig. 2(b) displayed the pores parallel to each other in the (100) or (010) directions.

3.3. Chemical composition of AH-2

The main components of AH-2 were SiO$_2$ (76.6 mass%) and Al$_2$O$_3$ (6.7 mass%), the molar ratio of Si and Al of about 10.1 was lower than of the starting composition (Si:Al = 15:1) (Table 2).

3.4. Adsorption study

3.4.1. Effect of contact time

The adsorption of Cr(VI) reached equilibrium after about 30 min (Fig. 3) and was slightly faster than the adsorption of Cr(VI) on mesoporous SBA-15 (40 min) (Li et al., 2008a), or on amino-functionalized mesoporous silica (60 min) (Li et al., 2008b).

3.4.2. Effect of pH

The adsorption showed a maximum between pH = 5–6 (Fig. 4). Adsorption maxima of Cr(VI), at different pH, were also observed in other cases. For Leersia hexandra Swartz biomass, the adsorption remained constant between pH 2 and 4, and then decreased (Li et al., 2009); for acetylacetone-loaded Amberlite it decreased rapidly between pH 2 and 7 (Memon et al., 2009). Lewatit-anion exchange resins showed an adsorption maximum at pH = 5 (Pehlivan and Cetin, 2009).

3.4.3. Effect of the initial concentration of Cr(VI)

The adsorption of Cr(VI) reached a plateau at 160 mg/L (Fig. 5). The maximum adsorbed amount of Cr(VI) was 112 mg/g at the initial concentration of 160 mg/L.

3.4.4. The Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich isotherm is given by the following equation:

$$Q = Q_m \exp(-k_\varepsilon^2)$$

(3)

and linearized

$$\ln Q = \ln Q_m - k_\varepsilon^2$$

(4)

where the Polanyi potential $\varepsilon$ is $[RT \ln(1 + 1/C)]$ ($R$: gas constant, J mol$^{-1}$ K$^{-1}$; $T$: absolute temperature, K; and $C$: equilibrium

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>T(Fe$_2$O$_3$ + FeO)</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Mass loss</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH-2</td>
<td>76.64</td>
<td>6.69</td>
<td>0.45</td>
<td>0.13</td>
<td>2.41</td>
<td>1.27</td>
<td>10.92</td>
<td>98.51</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of contact time on the adsorption of chromate ($C_0$: 50 mg L$^{-1}$; pH: 5; $m$: 0.05 g; temperature: 293 K).

Fig. 4. Effect of pH on the adsorption of chromate ($C_0$: 50 mg L$^{-1}$; $t$: 30 min; $m$: 0.05 g; temperature: 293 K).

Fig. 5. Effect of initial concentration of chromate (pH: 5.5; $t$: 30 min; $m$: 0.05 g; temperature: 293 K.)
concentration, mmolL$^{-1}$), $Q$ is the amount adsorbed per unit mass of adsorbent (mol g$^{-1}$). $k$ is a constant related to the adsorption energy (mol$^2$ kJ$^{-2}$) and $Q_0$ is the adsorption capacity (mol g$^{-1}$).

The values of $Q_0$ and $k$ were calculated from the intercept and slope of ln $Q$ versus $c^2$ plot and $k$ had two values (−0.0120 and −0.0031). The mean free energy of adsorption ($E$) was calculated from the $k$ values using the equation:

$$E = (-2k)^{-0.5}. \tag{5}$$

The magnitude of $E$ is useful for estimating the type of adsorption process. If $E$ is between 8 and 16 kJ/mol, the adsorption process proceeds followed by ion exchange, and if $E < 8$ kJ/mol, the adsorption is physical in nature. From Eq. (5) the numerical values of $E$ were calculated as 6.45 and 12.70 kJ/mol for the adsorption time of 0–20 min, and 20–30 min, respectively, indicating the first adsorption period is related to the particle diffusion, and the second one is a chemical interaction.

4. Conclusion

A mesoporous adsorbent was hydrothermally synthesized at alkaline condition using microcline and cetyltrimethylammonium bromide. The specific surface area was 847 m$^2$/g, the average pore diameter 2.5 nm, and roughly straight pore structures were observed with HRTEM. The maximum Cr(VI) adsorption was 112 mg/g at the optimal condition of pH 5.5, and initial Cr(VI) concentration of 160 mg/L. The application of the Dubinin–Radushkevich model indicated that the first 20 min were related to particle diffusion, and the following period of 20–30 min was related to the chemical interaction.

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References


