

Absorption of copper ions from wastewater by organically modified bentonite

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Received 1 September 2018; Accepted 8 January 2019

ABSTRACT

Ca-bentonite was modified firstly by Na_2CO_3 and then by octadecyl trimethyl ammonium chloride to prepare organically modified bentonite, and Ca-bentonite and organically modified bentonite were characterized by infrared spectroscopy and X-ray diffraction, respectively. The factors affecting the absorption of copper ions on organically modified bentonite were investigated by absorption experiments, and the absorption mechanism was discussed. The results showed that the absorption performance of organically modified bentonite for copper ions was improved. The 100 mL copper ion solution at a concentration of 10 mg L^{-1} was absorbed by organically modified bentonite, under the condition of initial solution pH of 4.00, absorbent dosage of 3.0 g L^{-1} and absorption time of 30 min, a removal rate of 98.40% was achieved at an absorption capacity of 3.28 mg g^{-1} . Quasi-second-order kinetic equation can well describe the reaction process of organically modified bentonite absorbing copper ions.

Keywords: Organically modified bentonite; Copper ions; Absorption

1. Introduction

Copper is one of the essential trace elements in human body, and it plays an important role in human metabolism [1]. However, excessive intake of copper can lead to poisoning and even threatening life [2]. Copper ions entered into the human body through the food chain, but due to the discharge of industrial wastewater, such as electroplating wastewater, mine wastewater, etc., a large number of copper is discharged into the nature. The transmission of copper ions through the food chain poses a great threat to human health [3]. The treatment of copper ions in wastewater is of great significance [4,5].

In recent years, many processes have been used to treat wastewater containing copper, such as precipitation method [6], electrochemical method [7], ion exchange method [8], and absorption method [9]. Among them, absorption method is widely used in wastewater treatment technology because of its strong selectivity and low cost [10]. Bentonite has good

absorption properties because of its special crystal structure, while Ca-bentonite has its own properties, which make its application effect worse [11,12]. Therefore, in this paper, Ca-bentonite was modified and copper ion solution was used as simulated wastewater to study the influencing factors and absorption mechanism of organically modified bentonite for copper ion absorption, so as to provide some experience for the treatment of actual wastewater containing copper ions.

2. Materials and methods

2.1. Reagents and instruments

Ca-bentonite was obtained from Jianping, Liaoning Province; with cation exchange capacity (CEC) of 82.95 mmol/100 g. Distilled water was used in the experiment. Major reagents included sodium carbonate (chemical formula Na_2CO_3 , Shanghai Hongguang Chemical Plant, China), Octadecyl trimethyl ammonium chloride (chemical formula

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C₂₁H₄₆ClN, China Pharmaceutical Group Chemical Reagents Co. Ltd.), HCl (Liaoning Minsheng Chemical Co. Ltd.), NaOH (Tianjin Damao Chemical Reagent Factory), CuSO₄·5H₂O (China Pharmaceutical Group Chemical Reagents Co. Ltd.) and Ethylene glycol (chemical formula C₂H₆O₂, Tianjin Hengxing Chemical Reagent Manufacturing Co. Ltd.). All the above reagents are of analytical purity.

Main analytical instruments include TXB622L electronic balance, PHS-25 pH meter, JJ-1 agitator, DZKW-C thermostat water bath, QJ5-2 five-axis high speed mixer, ZNN-D6 six-speed rotary viscometer, RK/ZL-260/200 multifunctional vacuum filter, 202 A constant temperature drying box, HY-2 variable speed multipurpose oscillator and GGX-600 atomic absorption spectrophotometer.

2.2. Preparation of organically modified bentonite

2.2.1. Sodification of calcium bentonite

Calcium bentonite was ground, weighed 22.5 g below 200 mesh, and added into the stirring cup. 6% Na₂CO₃ was added to the cup with 350 mL distilled water. After 30 min of stirring, the slurry was aged for 24 h, filtered, dried and ground passing 200 meshes to produce sodium bentonite.

2.2.2. Organic modification

10 g sodium bentonite in 500 mL distilled water was agitated in a thermostat water bath. 3.48 g octadecyl trimethyl ammonium chloride was weighed and dissolved with a certain amount of ethylene glycol, then added into the sodium bentonite slurry. The temperature was set at 60°C, the mixture was stirred for 2 h, and left idle for 24 h after stopping stirring. Then, the slurry was filtered and washed with 1% AgNO₃ solution, dried and ground passing 200 meshes.

2.3. Characterization of bentonite

2.3.1. Infrared spectrum analysis

Fig. 1 shows the infrared spectra of Ca-bentonite (a) and organically modified bentonite (b). As indicated in Fig. 1a,

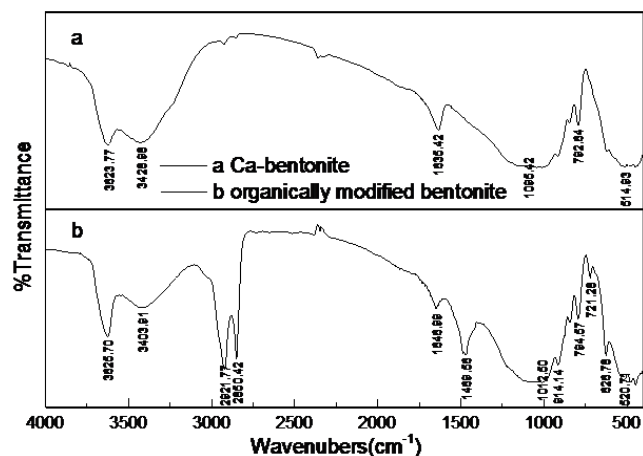


Fig. 1. (a) Infrared spectra of Ca-bentonite and (b) organically modified bentonite.

the Ca-bentonite exhibits the absorption peak at 514.93 cm⁻¹ is bending vibration of Si–O. The absorption peak at 792.64 cm⁻¹ is stretching vibration of Si–O and weaker vibration of Si–O–Si. The absorption peak at 1,095.42 cm⁻¹ is stretching vibration of Si–O and peak at 1,635.42 cm⁻¹ is bending vibration of OH and interlayer water. At 3,427.05 and 3,623.77 cm⁻¹, the stretching vibration peaks of OH and interlayer water are observed. Compared with Figs. 1a and b, organically modified bentonite has more obvious characteristic peaks than Ca-bentonite. The absorption peak at 721.28 cm⁻¹ is medium intensity vibration of –(CH₂)_n– and Peak at 1,469.56 cm⁻¹ is vibration of CH₂ that in side chain, namely CH₃CH₂–. At 2,850.42 and 2,921.77 cm⁻¹, the stretching vibration peaks of –CH₂– are observed [13,14]. The above analysis shows that octadecyl trimethyl ammonium chloride has successfully entered the interlayer of Ca-bentonite to render Ca-bentonite organic.

2.3.2. X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction patterns of Ca-bentonite (a) and organically modified bentonite (b). From Fig. 2 it can be seen that the interlayer spacing and 2θ of organically modified bentonite change with 2θ decreasing, Ca-bentonite $d_{001} = 12.52$ nm and organically modified bentonite $d_{001} = 24.12$ nm. This indicates that ion exchange occurs between long chain alkyl in octadecyl trimethyl ammonium chloride and Na⁺ in sodium-treated bentonite layer, increasing the interlayer spacing of bentonite [15].

3. Experimental results and discussion

Parameters of solution pH, absorbent dosage and absorption time were investigated. 100 mL CuSO₄ solution (the concentration of copper ion is 10 mg L⁻¹) prepared with distilled water was added to a conical bottle of 250 mL. HCl or NaOH were used to adjust the pH value of solution. A certain amount of organically modified bentonite was added into the conical bottle and oscillated on an oscillator for a certain time. The concentration of copper ion in the filtrate was determined after conical funnel filtration with a filter paper. The removal rate and absorption capacity of organically modified bentonite for copper ions in simulated wastewater were calculated.

3.1. pH value experiment

The effect of pH value on the removal rate and absorption capacity of copper ion by organically modified bentonite was investigated at an organically modified bentonite dosage of 2.0 g L⁻¹ and absorption time of 30 min. The results are shown in Fig. 3.

Fig. 3 shows that at pH = 1.65, the removal rate of copper ion by organically modified bentonite is low. This is due to the existence of H⁺ in the solution at low pH, which causes a large number of positive charges on the surface of bentonite and produces electrostatic repulsion force with copper ion. With the increase of pH, the concentration of H⁺ in the solution decreases, the electrostatic repulsion force weakens gradually, and the removal rate of copper ion by organically modified bentonite increases gradually. When the pH

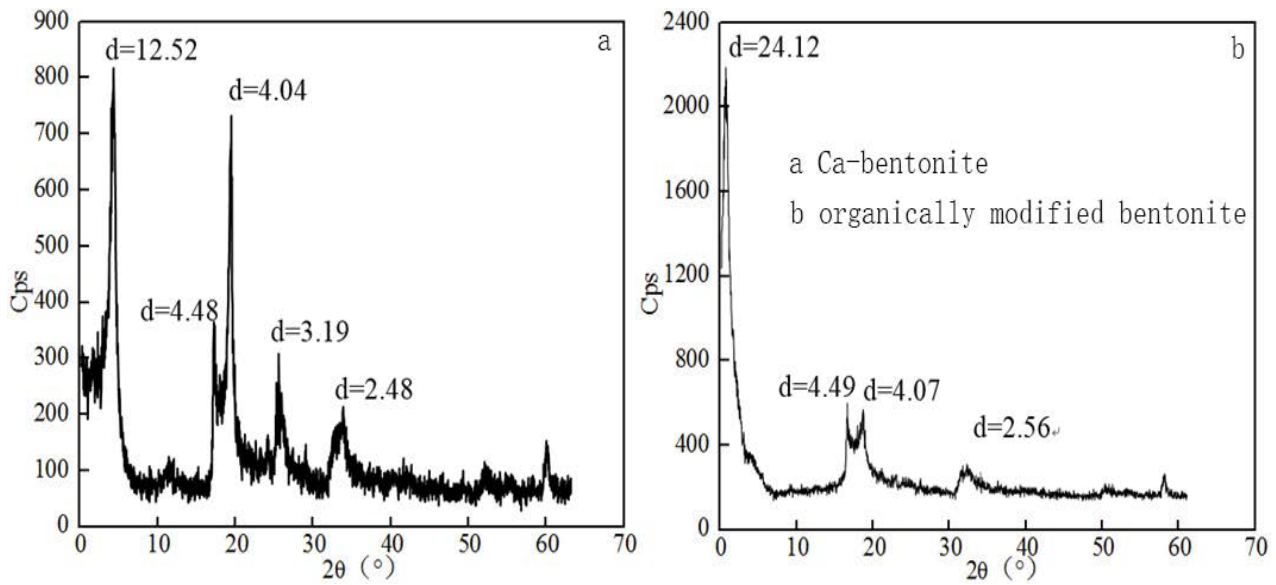


Fig. 2. (a) X-ray diffraction patterns of Ca-bentonite and (b) organically modified bentonite.

is about 4.00, the removal rate reaches 98.75%. The removal rate decreases at pH 5.08, and copper ions will precipitate with hydroxide radicals with a further increase of pH. The trend of absorption is consistent with the removal rate. Therefore, the optimum pH of organically modified bentonite for copper ion absorption is 4.00.

3.2. Absorbent dosage experiment

The effect of absorbent dosage on the removal rate and absorption capacity of copper ion by organically modified bentonite was investigated at an initial solution pH of 4.0 and absorption time of 30 min. The results are shown in Fig. 4.

From Fig. 4, it can be seen that the removal rate of copper ion by organically modified bentonite increases gradually with the increasing dosage of organically modified bentonite, but the absorption capacity decreases gradually.

This is because with the increase of the dosage of bentonite, the absorption sites of copper ion on bentonite increase, and the removal rate of copper ion on organically modified bentonite increases gradually. Because the initial concentration of the solution is the same, with the increase of the dosage of bentonite, the concentration of copper ion in the solution decreases gradually, and the amount of copper ion on the unit absorbent decreases gradually, so the absorption amount per unit of bentonite decreases with the increase of the dosage of bentonite. The optimum dosage of organically modified bentonite is 3.0 g L^{-1} , and the removal rate is 98.70%.

3.3. Absorption time experiment

The effect of absorption time on the removal rate and absorption capacity of copper ion by organically modified bentonite was investigated at an initial solution pH of 4.0

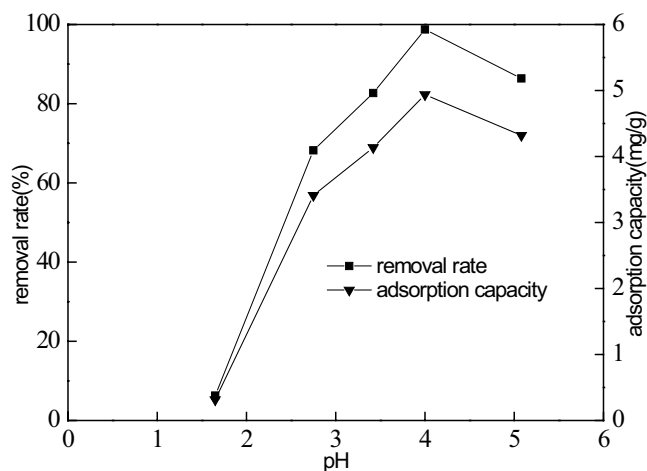


Fig. 3. Effect of pH on absorption of copper ions on organically modified bentonite.

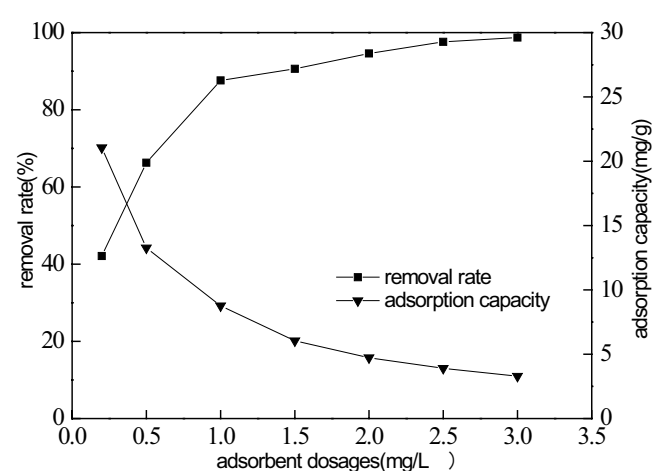


Fig. 4. Effect of absorbent dosage on absorption of copper ions on organically modified bentonite.

and an organically modified bentonite dosage of 3.0 g L⁻¹. The results are shown in Fig. 5.

Fig. 5 shows that, with the increase of absorption time, the removal rate and absorption capacity of organically modified bentonite to copper ion gradually increase. At 30 min, the absorption capacity of organically modified bentonite to copper ion basically reaches saturation, the absorption rate is 98.40%, and the absorption capacity is 3.28 mg g⁻¹. Therefore, the optimum absorption time of organically modified bentonite for copper ion is 30 min.

3.4. Study on absorption kinetics

Quasi-first-order kinetic model [16] and quasi-second-order kinetic model [17] were used to fit the absorption process of organically modified bentonite for copper ions.

The expression of the quasi-first-order dynamic equation is as follows:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \quad (1)$$

where q_t is amount of solute sorbed on the surface of the sorbent at any time t (mg g⁻¹) and q_e is the amount of solute sorbed at equilibrium (mg g⁻¹), k_1 is the rate constant of first order sorption (1 min⁻¹).

The expression of the quasi-second-order dynamic equation is as follows:

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

where q_t is amount of solute sorbed on the surface of the sorbent at any time t (mg g⁻¹) and q_e is the amount of solute sorbed at equilibrium (mg g⁻¹), k_2 is the rate constant of second order sorption (1 min⁻¹).

By fitting the quasi-first-order kinetic equation, it is found that the value of q_e is quite different from the actual value, which indicates that, the quasi-first-order kinetic

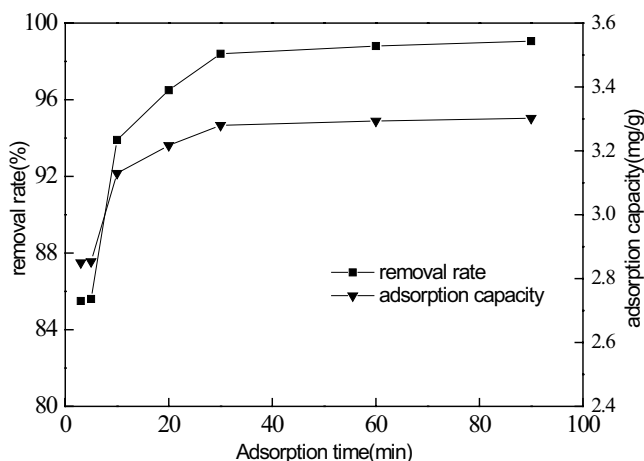


Fig. 5. Effect of absorption time on absorption of copper ions on organically modified bentonite.

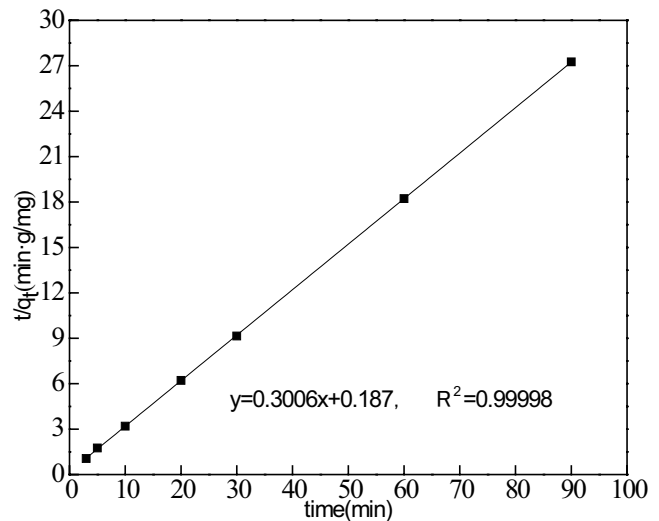


Fig. 6. Quasi-second-order kinetic fitting curve for the absorption of copper ions onto organically modified bentonite.

model is not suitable for describing the absorption kinetics of this experiment [18–20]. Quasi-second-order kinetic equation was used to fit the absorption of copper ions on organically modified bentonite as shown in Fig. 6.

Fig. 6 shows that the quasi-second-order kinetic equation fits well the absorption effect of organically modified bentonite on copper ions, and the correlation coefficient R^2 is 0.99998. The equilibrium absorption amount calculated by quasi-second-order kinetic equation is 3.33 mg g⁻¹, which is close to the actual value of 3.28 mg g⁻¹ [21–24]. It shows that the quasi-second-order kinetic equation can well simulate the kinetic mechanism of organically modified bentonite absorbing copper ions. The second-order kinetic equation is divided into external liquid membrane diffusion, surface absorption, and ion internal diffusion. It shows that the absorption of copper ion by organically modified bentonite is mainly chemical absorption. Copper ions pass through the liquid membrane on the surface of organically modified bentonite and enter the interlayer of bentonite [25,26]. Under the action of static electricity, ion exchange occurs, which makes copper ions absorb on organically modified bentonite, and achieves the effect of removing copper ions [27,28].

4. Conclusion

Na₂CO₃ was used as a sodium modifier and octadecyl trimethyl ammonium chloride as an organic modifier, organically modified bentonite was prepared by organic modification of Ca-bentonite, which increased the interlayer spacing of bentonite.

Adsorption experiments were conducted in 100 mL copper ion solution at a concentration of 10 mg L⁻¹ with organically modified bentonite. At an initial solution pH of 4.00, an adsorbent dosage of 3.0 g L⁻¹, and an absorption time of 30 min, a removal rate was obtained at 98.40% with an absorption capacity of 3.28 mg g⁻¹.

The absorption process of organically modified bentonite for copper ion was studied by kinetic equation, indicating

that the absorption process is mainly chemical absorption which is easy to occur under experimental conditions.

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