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Study on Adsorption Mechanism of Acid-Modified Bentonite

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Abstract: The acid-modified bentonite was prepared by sulfuric acid acidification, we compared it in chemical composition, layer structure and adsorption performance before and after the adsorption of Cu2+ by joint analysis of FT-IR, XRD, and ICP. The results indicated that: XRD showed that Cu2+ went into the bentonite layer, the analysis of ICP showed: Cu2+ exchange reaction didn't take place, only coordination reaction occurred, i.e. acid-modified bentonite adsorbs cooper irons mainly in a way of cooperation reaction; the adsorption of acid-modified bentonite conforms to the Langmuir monolayer model and the pseudo-second-order kinetic model.

1. Introduction

It's been a very interesting issue to remove heavy metal irons from polluted waste water in environment field. A number of studies on the removal of Cu^{2+} from waste water or aqueous solutions using different kinds of adsorbents have been reported [1-3].

The removal of heavy metals from contaminated wastewater is a matter of great interest in the field of environmental restoration, especially in this era of environmentally sustainability. Yu Ruilian carried out a study with the acid-modified bentonite prepared by activation modification of natural bentonite with sulfuric acid, it was found that under the suitable condition of removing Cu^{2+}, the removal ratio of Cu^{2+} by acid-modified bentonite can reach greater than 99.9%[4].

However, it lacked the systematic research and effective method of characterization on the ion structure, electronic effects, as well as the framework in the adsorption. In this paper, we studied the adsorption behavior and mechanism, and characterized the relationship between the adsorption process and material structure effect with methods of FT-IR, XRD, and ICP, etc.

2. Experimental

1.1. Preparation of the acid-modified bentonite

A layer of purified bentonite was added at an ark with thickness less than 1 cm, and then was baked in a resistance furnace at 100℃ for 3.5h. After that, it was dispersed in a boiling flask-3-neck by adding sulfuric acid solution (ρ=15％) and keeping solid-to-liquid ratio of 1:3, and continued to stir at 95℃ for 8h, then centrifuged and rinsed several times with water until pH reached 4-5. Afterwards, the solution was kept at 120℃ for 2h for activation. Finally, it was dried at 105℃, ground and sieved to 120 meshes.

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1.2. Characterizations of adsorbents

The FT-IR spectra were obtained (KBr) using a Nicolet 5700 Fourier Transform Infrared pectrometer (Thermo Nicolet Ltd, USA) to observe the surface functional groups at ranging from 400 to 4000 cm^{-1}. The XRD patterns of the sample before adsorption and adsorption were obtained with an X-ray diffract meter (X'TRA, ARL Co. Ltd, Switzerland) in the scanning range of 2θ =0°-90°. The elements analysis of the solution was performed by using Inductively Coupled Plasma generating apparatus (ICP).

1.3. Adsorption studies

All batch Cu^{2+} adsorption experiments were carried out in conical flask. First, a series of different concentrations of copper ion solution were prepared. A certain amount of copper ion solution was placed in a 50mL cuvette respectively, diluted to 25mL to measure the absorbance, and the working curve of the solution was prepared. Afterwards, the acid-modified bentonite and copper ion solution were added to the conical flask, and mixed on a shaker at certain speed. At pre-determined time intervals, certain amount of the mixture was taken to the cuvette, diluted to 25mL to measure the absorbance. The adsorption data of copper ions in acid-modified bentonite were calculated using the working curve. Then copper ions were adsorbed on the bentonite adsorption material at room temperature (20℃) with copper ion concentration as a variable, and the adsorption data of copper ions were calculated.

3. Result and discussion

1.4. FT-IR analysis

Figure 1 shows that in the FT-IR spectra of the acid-modified bentonite sample, the position and shape of the band are slightly changed. Stretching vibration originated from AlAlOH, AlFeOH and AlMgOH form broad band at about 3620 cm−1[4]. The presence of three bending vibrations of hydroxyl groups (AlAlOH at 920 cm−1, AlFeOH at 885 cm−1 and AlMgOH at 845 cm−1) indicated that Al3+ was substituted by Fe2+ or Mg2+ in octahedral layer, respectively. The adsorption mechanism of the acid-modified bentonite on the metal ions is as follows: sulfate acid acts on positive ions between bentonite first, then acts on positive ions in octahedron. The dissolution of calcium, magnesium, aluminum, iron and other cations in the interlayers and octahedrons causes the bentonite to become a skeleton with a lot of voids and enhance the electronegativity of acid-modified bentonite.

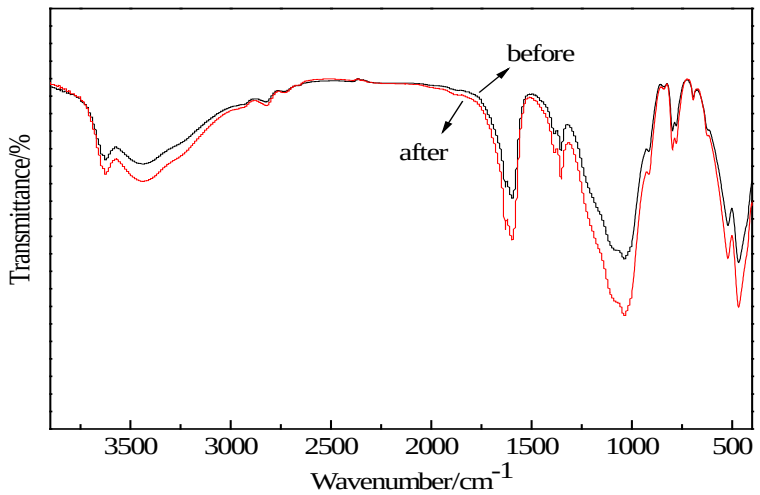


Figure 1. FT-IR spectrogram for acid-modified bentonite before and after adsorption

From Figure 1 we know that acid-modified bentonite adsorption before the wave number of 472cm^{-1}, the absorption wave number after adsorption of 468cm^{-1}. Radius of aluminum ions in alumina

octahedral sheet is 0.62 and radius of magnesium ions is 0.74. Nevertheless, radius of cooper ions is 0.96, which proves cooper ions enter alumina octahedral sheet aluminum (magnesium)-oxygen octahedron lattice, then forms coordination complex with magnesium hydroxyl or aluminum hydroxyl and occurs coordination reaction between tiers.

1.5. XRD analysis

Bentonite in the four sections with X-ray diffraction peaks, respectively for: d(001)=(1.2-1.5)nm, 2θ=(5.88-7.36)°; d(003)=(0.4-0.5)nm, 2θ=(17.71-22.20)°; d(005)=(0.24-0.3)nm, 2θ=(29.74-37.43)°; d(060)=(0.149-0.150)nm, 2θ=(61.77-62.24)°[5]. Among them, the intensity of d(001) was the largest. The peak at 26.5°is ascribed to SiO_2.

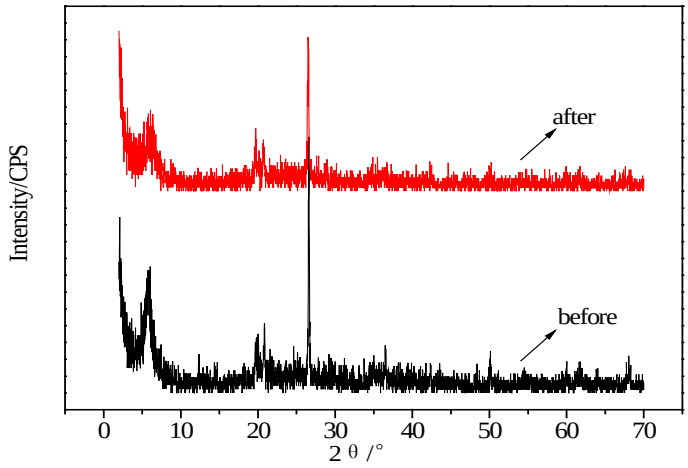


Figure 2. X-ray spectrogram for acid-modified bentonite before and after adsorption

From Figure 2 and Table 1 , after acid-modified bentonite adsorbing cooper ions, diffraction peak of (001) plane and (006) plane mainly have no excursion. But the diffraction peak of the (001) plane is much more sharp than that of the adsorbed surface, the interlayer spacing d(001) of (001) plane before and after adsorption are 1.462nm and 1.452nm separately, and the interlayer spacing d(060) of (060) plane before and after adsorption are 0.150nm. Diffraction peak of (003) plane shifted to the left after adsorption, and d(003) increased from 0.426 nm to 0.450 nm.

Table 1. the interlayer spacing of acid-modified bentonite before and after adsorption

status	interlayer spacing		
	d(001)/nm	d(003)/nm	d(060)/nm
Before adsorption	1.462	0.426	0.150
After adsorption	1.452	0.450	0.150

1.6. ICP analysis

Table 2. The contents of main ions in Cu^{2+} solution

	Cu^{2+}/(mg/L)	Ca^{2+}/(mg/L)	K^{+}/(mg/L)	Mg^{2+}/(mg/L)	Na^{+}/(mg/L)
Before adsorption	10	0	0	0	0
After adsorption	1.97346	2.21889	0.097168	0.079996	0.104356

In the case of constant volume, if copper ions are adsorbed in the form of ion exchange, when acid-modified bentonite adsorbs 1mg/L cooper ions, 1 mg/L of cation (Ca^{2+}, Mg^{2+} etc.) or 2 mg/L of cation (K^{+}, Na^{+} etc.) can be desorbed. If copper is adsorbed in the form of surface coordination or interlayer coordination, the bentonite adsorption material desorbs water while adsorbing copper ions and does not cause an increase in cation in the solution.

As can be seen from Table 2, after adsorption, the concentration of copper ions in the acid-modified bentonite was reduced by 8.027 mg/L, and the total amount of Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} desorbed was 2.500mg/L, which indicated that the adsorption of copper on bentonite mainly relied on complexation, and only a small amount of ion exchange existed. This is consistent with FT-IR and XRD analysis.

1.7. Adsorption mechanism

(1) Kinetic research

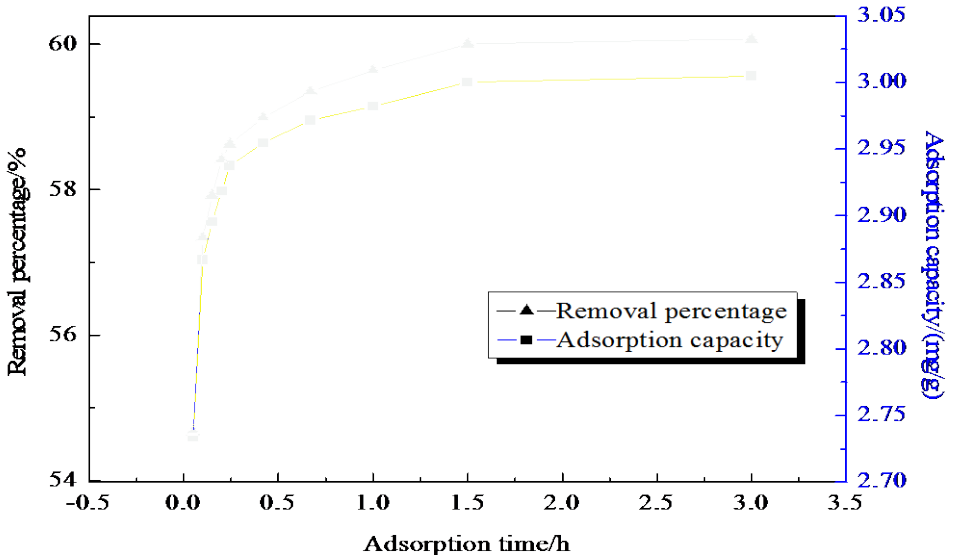


Figure 3. The influence of time on adsorption performance of acid-modified bentonite

The adsorption capacity of acid-modified bentonite versus the contact time is shown in Figure 3 The figure revealed that the adsorption capacity reached the maximum when the exposure time increased to 1.5 hours. Therefore, the optimum exposure time is selected to be 1.5 hours.

The pseudo-first-order and the pseudo-second-order kinetic model (Eq. (1) and (2)) were applied for the interpretation of experimental data, and the model equation is expressed as follows [6,7]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{2}$$

Table 3. The fitting result of order kinetic equation

pseudo-first-order kinetic equation	Y=-2.09941-1.23516 X	R^2 0.85923	k_1 1.23516	q_e 0.123
pseudo-second-order kinetic equation	Y=0.00219+0.33215 X	R^2 1	k_2 50.37608	q_e 3.011

Comparing table 3, the process of cooper ions adsorbed by acidic bentonite and pseudo-second-order kinetic reach high fitting, correlation index R^2 is greater than 0.9999 , and fitted saturated

adsorption capacity q_e is familiar to the capacity tested in experiment. Therefore, adsorption of acid-modified bentonite on cooper ions conforms to pseudo-second-order kinetic model.

(2) Adsorption isotherm

The Langmuir and Freundlich adsorption isotherm models were applied to describe the RB19-modified clay system. The linear forms of Langmuir (Eq. (3)) and Freundlich (Eq. (4)) adsorption isotherm models can be described with the following equations, respectively [8,9]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \tag{3}$$

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e \tag{4}$$

Table 4. The linear fitting result of adsorption isotherm

Langmuir	Y=0.59208+0.13475 X	R^2 0.99701	q_{max} 7.42	K_L 0.2276
Freundlich	Y=0.29817+0.34490 X	R^2 0.84036	K_F 1.3474	n 2.90

Comparing table 4, the correlation index R^2 in linear fitting of Langmuir isothermal adsorption equation is larger than which in Freundlich isothermal adsorption equation, which means that Equilibrium data were fitted well to the Langmuir isothermal model in the studied concentration range of copper ion.

Known from above, adsorption of acidulated bentonite conforms to Langmuir adsorption model means it is adsorption of monomolecular layer. Saturated adsorption capacity of single molecular tier of acid-modified bentonite is 7.42mg/g and limit of adsorption capacity of bentonite is saturated adsorption capacity of monomolecular layer. This illustrates saturated adsorption capacity doesn't increase as the time extend, which indicates that adsorption of acid-modified bentonite to cooper ions is mainly chemical adsorption [10].

4. Conclusions

This study carries out study on the adsorption of copper ions in wastewater by acid-modified bentonite, and the results are as follow:

1) Combining results of chemical composition, interlayer structure and link structure of acid-modified bentonite which be researched by FT-IR, XRD, with ICP indicate that the adsorption of cooper ions by acid-modified bentonite mainly depends on surface and interlayer coordination.
2) Saturated adsorption capacity of acid-modified bentonite is 7.42mg/g.
3) The adsorption of cooper ions by bentonite adsorbent fits the pseudo-second-order kinetics equation and Langmuir adsorbing model, which means the adsorption, is monomolecular layer adsorption and mainly be chemical adsorption.

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