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Bentonite-Loaded Chitosan Adsorption Treatment of Cu^{2+} in Aqueous Solution

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Abstract: A modified chitosan-bentonite composite adsorbent has been prepared by loading chitosan using bentonite as a carrier, and the modified bentonite has been characterized by scanning electron microscope (SEM) analysis and thermogravimetric (TG) analysis. The prepared chitosan-bentonite is used to remove copper ions in aqueous solution. The effects of reaction time, pH value, initial concentration of copper ions and addition amount of bentonite-loaded chitosan adsorbent on the adsorption effect were investigated. In this experiment, the single-factor investigation of the adsorption of copper ions by this material showed that: when the mass ratio of chitosan and bentonite is 0.08: 1, the adsorption effect of copper ions is better when the time is 50min, pH=11 and the adsorption temperature is 20℃ the removal rate is higher, which can reach 95%. The material is green and environmentally friendly, which realizes the efficient use of chitosan and bentonite, and has certain utilization value for the removal of copper ions.

1. Introduction

With the further development of China's industrialization and the deepening of urbanization, heavy metal pollution is becoming more and more obvious. As a kind of extremely harmful pollutant, heavy metals can cause harm to the water environment through the accumulation of water and direct or indirect transmission of the food chain. Among them, copper pollution comes from mining, electroplating and electrolysis processes [1-5]. Excessive use of copper will not only hinder the absorption of nutrients by plants, but also damage the function of human secretory glands, stimulate the digestive system, and cause a series of diseases such as abdominal pain, vomiting, and conjunctivitis. Therefore, the treatment of copper ions is urgent. At present, the methods commonly used in the treatment of waste water containing copper ions are chemical method, ion exchange method, biological method and adsorption method [6]. Among these methods, the adsorption method has the characteristics of safety, low energy consumption, and simple operation, so it has been payed more and more attention at present [7].

Bentonite is a clay mineral dominated by montmorillonite, and has a wide range of adsorption, but the adsorption capacity of a single bentonite is limited, and it cannot meet the demand for wastewater treatment in practical production applications, so in many cases, it is improved by the ways to improve its adsorption [8-9]. Chitosan comes from chitin, which is abundant in nature and cheap and easily available. It is widely found in the cell walls of crustaceans such as shrimp shells, crab shells and fungi, and algae plants [10]. Chitosan is the second largest polysaccharide after cellulose. It is a natural polysaccharide that is easily degraded. Because it contains a large number of hydroxyl and amino groups with excellent adsorption properties, it is easy to form a chelate with heavy metals through coordination, so as to achieve the effect of adsorbing heavy metals. In order to improve the limitation of the single adsorption of bentonite and chitosan, this experiment modified the bentonite by using the chitosan, taking advantage of their respective advantages, and exerting a compound synergistic effect, in order to expect a stronger and cheaper adsorption capacity. Biodegradable, environmentally friendly bentonite-based chitosan adsorbent composite material provides a certain technical basis for copper ion pollution and treatment.

2. Experimentals

2.1 Main instruments and reagents

Apparatus: constant temperature oven, constant temperature water bath, ion agitator, precision PH meter, ultraviolet-visible spectrophotometer (Shimadzu uv-1800), reagents: chitosan $(C_6H_{11}NO_4)$ n copper sulfate $(CuSO_4.5H_2O)$ 4 % Acetic acid (CH_3COOH) Copper reagent (DDTC-Na) Ammonia $(NH_3.H2O)$ are of analytical grade. The experimental water is deionized water.

Table 1 The main components of bentonite used in the experiment

Chemistry Composition	Na_2O	SiO_2	Fe_2O_3	K_2O	MgO	CaO	Al_2O_3
mass fraction (%)	0.86	67.26	3.16	2.16	1.57	1.54	16.3

2.2 Preparation method of composite adsorbent

Chitosan solution was prepared by adding Chitosan into 100 ML 4% acetic acid. After all of them are dissolved, add different quality bentonite and place it under an ion mixer at 200r/min for 4 hours. The supernatant was washed repeatedly with distilled water until the pH value of the solution was neutral, and then the precipitate was dried in a constant temperature drying box at 100°C, taken out and sealed for use.

2.3 Characterization of composite adsorbent

The scanning electron microscope (Quanta 2000 type) of FEI Company was used to observe the surface morphology of the sample. The STA449F3 integrated thermal analyzer of the German Netz company was used to analyze and test the thermogravimetric analysis of the thermal decomposition behavior of the composite adsorbent. The test temperature was 25~1000℃, the test atmosphere was oxygen, and the heating rate was 10℃·min^{-1}

2.4 Adsorption experiment and data processing

Add the prepared adsorbent material to 50ml of Cu^{2+} solution with a concentration of 50mg/L, with a stirring speed of 200r min, and perform adsorption under this condition. Absorb for a period of time, take the supernatant for filtration, use ultraviolet-visible spectrophotometer at 451nm to measure its absorbance, and use the linear equation of copper ion concentration and absorbance to find the concentration of copper ion in the supernatant. The amount of Cu^{2+} adsorbed is calculated according to the following formula:

$$q_e = (C_0\text{-}C_1)\ V / m, \qquad \eta = (C_0\text{-}C_e) / C_0 \times 100\%$$

Where: q_e is the adsorption capacity (mg/g), η is the removal efficiency of copper ions, C_0 is the initial concentration of copper ions (mg/L), C_1 is the concentration of copper ion after adsorption (mg/L), m is the input amount of the loaded material (g), V is the volume of the solution to be tested (mL),

3. Results and discussion

3.1 Drawing of standard curve

Accurately weigh 0.39 grams of copper sulfate pentahydrate, use deionized volume to 1L to configure 100mg / L copper stock solution, then take 10mL volume to 100mL to configure 10mg/L stock solution, and accurately transfer 10mg/L Cu^{2+} reserve A total of 6 groups of 0ml, 5ml, 10mL, 15mL, 20mL, and 25mL solutions were placed in 100mL volumetric flasks respectively, and a drop of DDTC-Na solution with a concentration of 50g/L was added as the developer. The concentration of 0mg/L, 0.5mg/L, 1.0mg/L, 1.5mg/L, 2.0mg/L, 2.5mg/L was measured at 451nm with distilled water as the blank.

Taking the copper ion concentration as the X axis and the measured absorbance value on the Y axis for regression analysis, the obtained regression equation is A = 0.13789C + 0.00125 (R^2 = 0.9995), indicating that Cu^{2+} is in the range of 0-2.5mg/L, the absorption value and concentration show a good linear relationship.

3.2 Structural characterization of composite adsorbent

3.2.1 SEM analysis

The morphology of the chitosan-bentonite composite adsorbents was observed using a scanning electron microscope. As shown in Figure 1, it can be seen from the figure that the chitosan modified bentonite particles are composed of granular or massive structures of different sizes, with a rough surface, with many tiny holes, and have good dispersion, but there are still some denser stacked structures. These small pieces are distributed on the surface with tiny particles of uniform size, which may be the crystallites of chitosan coated on the surface of bentonite.

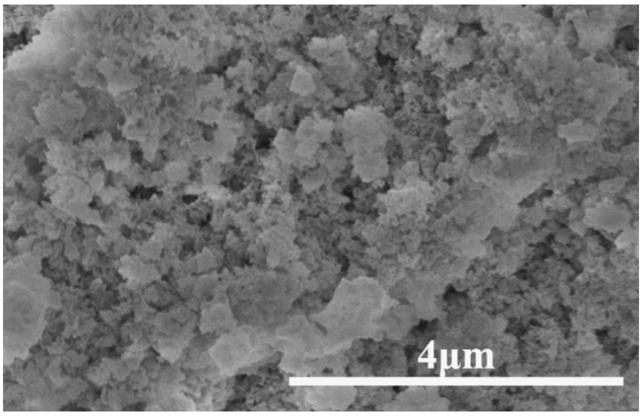

Figure. 1 Scanning electron micrograph of composite adsorbents

3.2.2 Thermogravimetric analysis

Figure 2 is the thermogravimetric curve of the chitosan modified bentonite sample. In the TG curve of the product sample, the weight loss of the sample before 50°C indicates the loss of water content in the sample. The rapid weight loss at 50-250°C is caused by the degradation of chitosan chain and oxidative degradation of chitosan. After the bentonite intercalated chitosan forms a composite material, the product will not change after 250°C. From the thermal analysis results of the TG diagram, it can be seen that the polymer and bentonite are effectively compounded, and the compound has high thermal stability, which is suitable for use as an adsorbent.

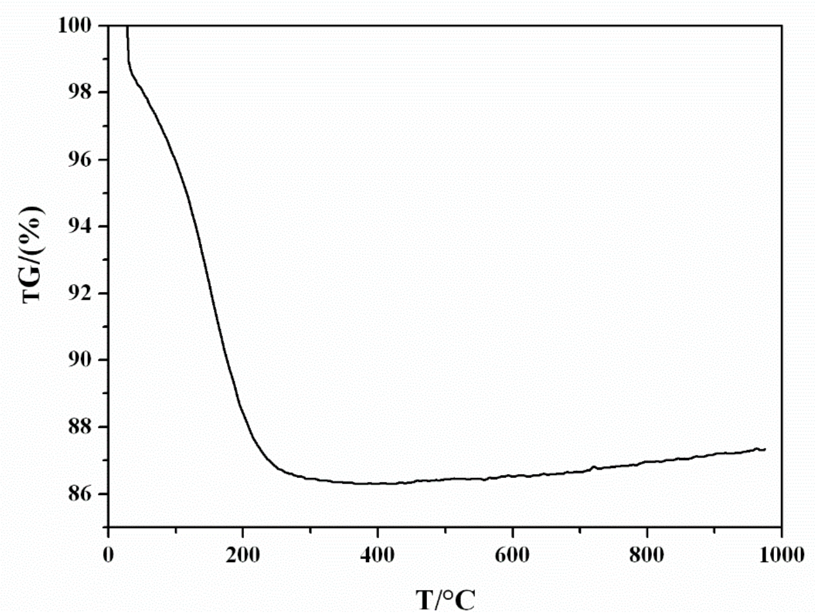

Figure. 2 Thermogravimetric curve of composite adsorbent

3.3 Effect on Cu^{2+} adsorption performance

3.3.1 The effect of chitosan loading amount on the adsorption capacity of copper ions

Separately, 0.5 g of the composite material with different mass ratios of 0.04, 0.06, 0.08, 0.1, 0.12 with varying chitosan-bentonite content was added to 50 mL of 50 mg / LCu^{2+} solution to adjust the pH of the solution to 11. Stir for 1 hour at 20°C with an ion stirrer. The adsorption capacity of the adsorbent for the adsorption of copper ions is shown in Figure 3:

From the results in Figure 3, it can be observed that when the mass ratio of bentonite to chitosan is less than 0.08, the adsorption capacity of the adsorbent for copper ions increases with the increase of the input mass ratio of chitosan, indicating that the appropriate amount of chitosan input comparison, the adsorption of Cu^{2+} plays a promoting role. However, as the mass ratio of chitosan continues to increase, the adsorption amount of Cu^{2+} decreases slightly after 0.08, indicating that a certain input of chitosan will saturate the adsorption capacity of Cu^{2+}. In order to obtain the conditions where the adsorbent is used less and the adsorption capacity is relatively high, the follow-up tests are all carried out using adsorbents with a mass ratio of 0.08 of chitosan and bentonite.

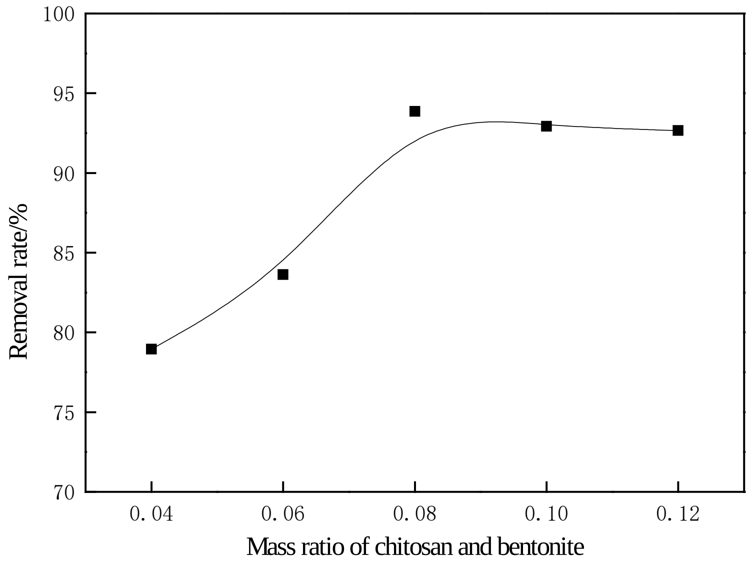

Figure. 3 The effect of *the different mass ratio of chitosan and bentonite on adsorption*

3.3.2 Effect of different adsorption time on adsorption capacity

Take 0.5g of chitosan-bentonite adsorbent into 50ml of Cu^{2+} solution with concentration of 50mg/L to adsorb at 20 ℃, the adsorption time is 10-80min, adjust the solution pH to 11. The result is shown in Figure 4:

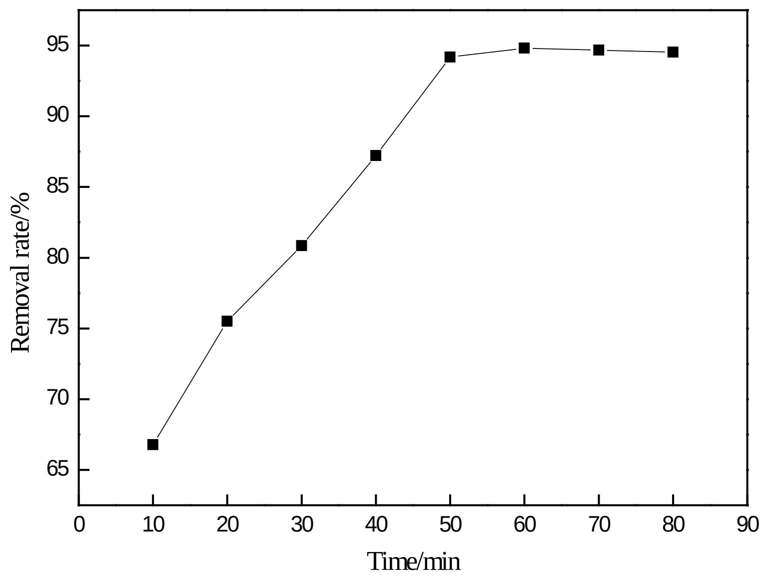

Figure. 4 The effect of different adsorption time on adsorption capacity

From the results in Figure 2, it can be observed that the adsorption capacity of the bentonite and chitosan composite adsorbent increases continuously with the adsorption time. The change of the adsorption amount increases rapidly within 0-20min. It rises slowly, and the adsorption capacity reaches the highest point and tends to saturation at 50min. Therefore, 50min was adopted as the adsorption time of the experiment.

3.3.3 The effect of pH on adsorption capacity

The research in this paper shows that the removal rate of copper ions decreases in the acidic range. The reason may be that in the acidic range, there is a competitive relationship between hydrogen ions and copper ions. In the materials, there is competitive adsorption, which leads to a reduction in the removal rate. Under alkaline conditions, it has a strong adsorption capacity for metal ions [11]. Therefore, in the alkaline range, different pH values were adjusted to 8-13 with ammonia water, and 0.5g of chitosan-bentonite adsorbent was added to 50ml of Cu^{2+} solution with a concentration of 50mg/L. Adsorption at 20℃, adsorption time of 50min, to study the effect of different pH values on adsorption under alkaline conditions, the results are shown in Figure 5.

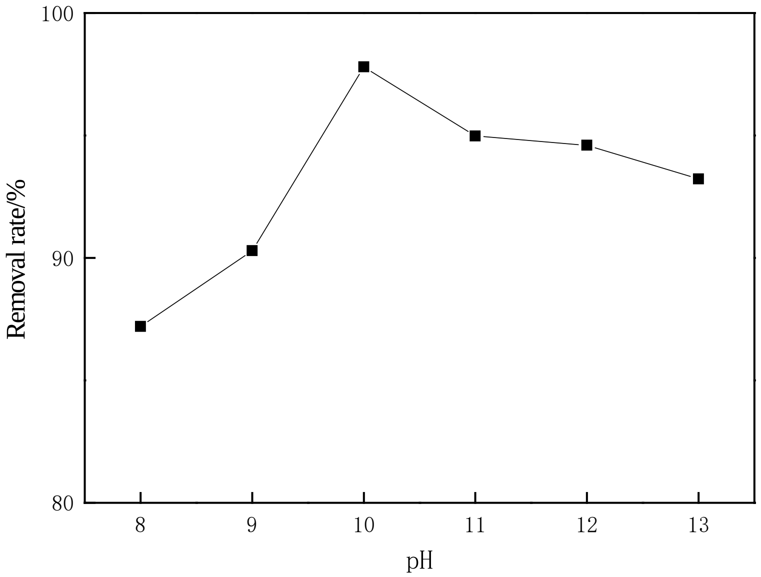

Figure. 5 The effect of pH on the adsorption capacity

From the results in Figure 5, it can be observed that the adsorption capacity of the adsorbent continuously increases with the increase of pH value, which affects the surface ionization degree and charge characteristics of the adsorbent adsorbent [12]. After the pH is greater than 7, the removal rate of copper ions rises because the formation of $Cu(OH)_2$ precipitates may be formed. The higher removal rate is the combined effect of the adsorption effect and the formation of precipitates, but it is saturated with copper ions at pH 11, the adsorption amount reaches the maximum value. After the pH value was higher than 11, the copper ion adsorption decreased slightly, consistent with the literature.

3.3.4 Effect of different initial concentrations of copper ions on adsorption

Take 0.5g of chitosan-bentonite adsorbent, add 50ml of Cu^{2+} with different concentrations of 20, 40, 60, 80, 100, 120,.140mg / L, and adsorb at 20℃, adsorption time is 50mins and pH is11. The results of the experiment are shown in Figure 6:

It can be seen from Fig. 6 that as the concentration of the copper ion solution continues to increase, the chitosan-bentonite adsorbent still has a good adsorption effect on the high-concentration adsorbent, and the adsorption amount is also rising. When the initial concentration increased from 20mg / L to 140mg / L, the corresponding adsorption capacity also increased from 39.8mg / g to 176.5mg / g. The increase of ion concentration promotes the increase of the adsorption reaction [13-15]. However, it can still be seen that the adsorption capacity of the adsorbent for copper ions still has not reached the saturation state, and there is room for further improving the adsorption capacity of the adsorbent in order to achieve effective and full utilization of the adsorbent.

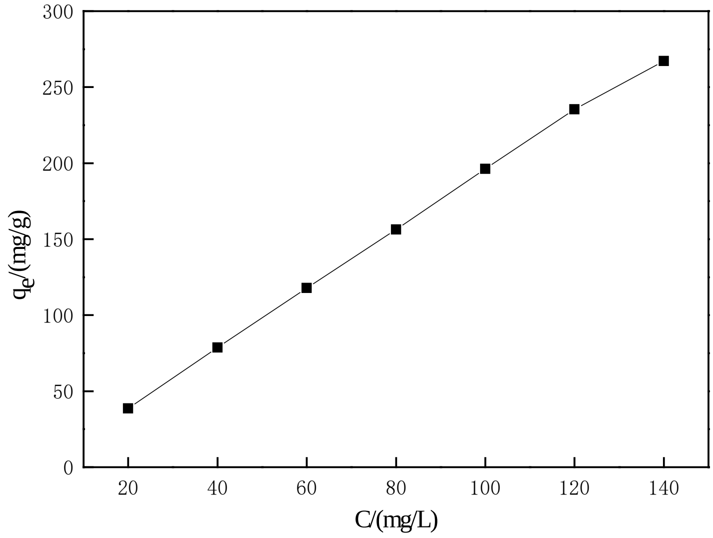

Figure. 6 The effect of different concentrations of Cu^{2+} adsorption

3.3.5 The effect of different temperatures on adsorption

Add 0.5g of chitosan-bentonite adsorbent to 50ml of Cu^{2+} solution with a concentration of 150mg/L, and perform the adsorption under the condition of adsorption time is 50mins and pH is 11. The different temperature when controlling adsorption is 20, 30, 40, 50, 60, 70℃. The effect of chitosan-bentonite adsorbent on the adsorption capacity of copper ions at different temperatures was observed. The results are shown in Figure 7:

It can be seen from the results in Fig. 7 that the removal rate of copper ions with temperature rise will be further improved. But the increase is not too much, because the movement between molecules is accelerating with the increase of temperature, which is conducive to further full contact between the adsorbent and copper ions, thereby further improving the adsorption capacity of the adsorben for copper. For cost considerations, the temperature of the materiasl can be selected at room temperature, and the copper ion adsorption rate is still 94.80%.

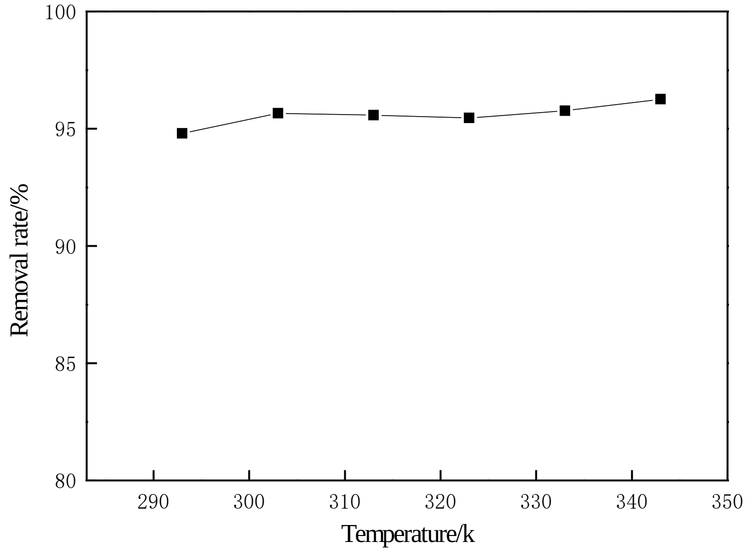

Figure. 7 The effect of different temperatures on adsorption

4. Conclusion

In this experiment, the bentonite was modified to prepare a green and efficient composite adsorbent. The application of copper ion adsorption treatment in aqueous solution was studied. The results showed that the mass ratio of chitosan and bentonite was 0.08:1, the time of adsorption 50mins, pH= 11, the adsorption temperature is 20℃, the adsorption effect of copper ions is better, and the removal rate is higher. The bentonite-loaded chitosan further enhances the adsorption of Cu^{2+}. The material is green and environmentally friendly, which realizes the efficient use of chitosan and bentonite, lays a certain practical foundation for the removal of copper ions, and provides a certain technical foundation for the treatment of actual heavy metal wastewater.

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