Study on the Adsorption of Methyl Red by Bentonite / Chitosan Composites

Pengzhi Xiang¹,², Chao Deng¹,², Longjiang Liu¹,² and Yao Huang¹,²,*

¹School of Chemical Engineering, Yunnan Open University, Kunming, P.R. China
²School of Chemical Engineering, Yunnan Vocational College of National Defense Industry Kunming, P.R. China

*Corresponding author e-mail: 1711307828@qq.com

Abstract. A composite material is formed by using chitosan and bentonite under the condition of dissolution with acetic acid. The material was characterized by scanning electron microscope thermogravimetric analysis and infrared spectroscopy. The effects of initial concentration of methyl red, adsorption time, pH, and amount of adsorbent on adsorption were investigated. Then, the adsorption process was analyzed from kinetics, and related parameters were calculated. The results showed that the composite material has a wider pH range than using chitosan as an adsorbent to adsorb methyl red; The mass ratio of chitosan to bentonite is 0.08:1, the removal rate of methyl red is the best; The amount of adsorbent used is 0.7mg to reach saturation for a volume of 25mL of methyl red solution with a concentration of 20ug/l; the adsorption of methyl red by the material conforms to the pseudo-second-order kinetic model.

1. Introduction

China is a large printing and dyeing country, and the dyes in wastewater are difficult to handle [1]. For example, the methyl red structure in the dye is difficult to destroy and the biodegradability is poor. The adsorption method is used to treat printing and dyeing wastewater with methyl red, which is economical and cheap [2]. Activated carbon and resin as an adsorbent, it has the disadvantage of being expensive, which affects its application in actual water treatment [3].

Bentonite is a non-metallic mineral with montmorillonite as the main mineral component. The montmorillonite structure is a 2:1 type crystal structure composed of two silicon-oxygen tetrahedrons and a layer of aluminum-oxygen octahedrons [4]. It has a variety of uses. Non-metallic ore, which has good adsorption, is widely used in metallurgy, petroleum, chemical industry and environmental protection [5]. Bentonite also shows good performance in the adsorption of organic dye wastewater. Chitosan is a natural polymer material with a wide range of sources. The molecular structure contains a large number of amino groups and hydroxyl groups. It has the characteristics of natural environment protection and good adsorption capacity [6]. Therefore, chitosan is an adsorbent material with excellent properties in the field of water environment treatment.

Shao Hong et al. used chitosan to modify bentonite [7]. The modified material adsorbed acidic red printing and dyeing wastewater with a removal rate of up to 97%. Li Yu jie et al. used bentonite-supported chitosan to adsorb copper ions in water [8]. The results showed that the composite material is better than single bentonite and chitosan. The literature indicates that the introduction of chitosan
changes the dispersion effect of bentonite in solution, thus showing better adsorption effect [9]. At present, there are reports in the literature that bentonite and chitosan constitute a composite material to treat methyl red in water. In this paper, a new type of composite material is prepared by mixing bentonite and chitosan according to a certain ratio. Temperature, concentration, and adsorption time were used to study the adsorption of methyl red in water.

2. Experimental

2.1. Materials and reagents
Bentonite, Chitosan, Methyl Red (abbreviation MR, analytical grade).

2.2. Instrument
UV1800 (Shimadzu, Japan), Spectrum Two type infrared spectrometer (PE company in the United States), SHA-C constant temperature vibration box (Changzhou Guohua Electric Co., Ltd.).

2.3. Preparation method of bentonite / chitosan composite material
In 50ml 4% acetic acid, add chitosan to make a chitosan solution. After it is completely dissolved, add 6g of bentonite. After stirring for 4 hours under an ion stirrer, take it out and rinse repeatedly with distilled water until the solution is neutral. The filter residue is dried in a constant temperature drying oven at 100 degrees Celsius and then used.

2.4. Methyl red concentration analysis
Take 0.01g of methyl red dissolved in 60% ethanol solution and make up to 100ml. The methyl red solution configured as 100mg/L was diluted to different concentrations (0.1.2.3.4.6.8mg/l) of methyl. The red solution was measured for its absorbance at 428nm. The equation of standard curve for absorbance and methyl red concentration is $A = 0.0673C + 0.0028$ ($R = 0.9998$).

2.5. Calculation method of adsorption rate and adsorption amount
Use the analysis method of 2.4 to obtain the concentration before and after the adsorption of methyl red, and then obtain the adsorption rate $\eta$ and the adsorption amount $q_t$ according to the formulas (1) and (2), respectively.
\[ \eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1) \]
\[ q_t = \frac{(C_0 - C_t)V}{m} \quad (2) \]

\( \eta \) is the adsorption rate, \( q_t \) is the adsorption capacity (mg·g\(^{-1}\)) when equilibrium is reached, \( C_0 \) is the initial concentration of methyl red (mg·L\(^{-1}\)) before adsorption, \( C_t \) is the concentration after adsorption (mg·L\(^{-1}\)), and \( V \) is the volume of the methyl red solution (the volume of the solution is adjusted so that the volume of the methyl red solution before and after adsorption remains unchanged), \( m \) is the mass (g) of the adsorbent material.

2.6. Adsorption test
Add 2.5mg/L methyl red solution to different quality modified materials, adjust the appropriate pH value with HCl, and add a buffer solution to form a 25ml adsorption solution. Shake for a period of time at a constant temperature (25°C). Go to the upper layer on a clear night and measure the methyl red concentration.

2.7. Adsorption kinetics
Take 25ml 2.5mg/L methyl red into a 250ml Erlenmeyer flask and add 7mg of modified material to each of them for different time 30min 60min 90min 120min 150mn 180min and then filter, analyze the absorbance value of the filtrate and calculate its content.

3. Results and discussion

3.1. Material characterization

![Figure 2](image-url)

Figure 2. Scanning electron microscope of bentonite / chitosan composite.

The morphological characterization of the composite material was performed using an electron microscope. As can be seen from Fig.2, the surface of the material is not smooth which are many grooves. Fig.3 shows the thermogravimetric curve of the material, which has dropped significantly from 200°C to 1200°C. The maximum thermal stability temperature is about 250°C. As can be seen from Figure 4, the infrared spectrum shows that the composite retains the infrared spectral characteristics of chitosan and contains a large number of hydroxyl and amino groups.
3.2. Material adsorption effect

3.2.1. Effect of pH on adsorption.

Take 25ml 2.5mg/L methyl red solution and add 3mg composite material to adjust the pH with HCl for adsorption experiments. After 1 hour of adsorption, measure the amount of adsorption. The pH has a large number of cations and anions in the solution. Influence, methyl red ionizes a large number of anions in the aqueous solution, and the chitosan in the modified composite contains a large number of
hydroxyl groups and amino groups. These two groups are positively charged after protonation, so that the methyl group is electrostatically charged. Red dye is adsorbed. Jia Hai hong et al. used chitosan to study the adsorption of methyl red, and found that the pH is less than 3.4, which is beneficial for adsorption [10]. Du Jingting used chitosan-biocarbon microspheres to adsorb methyl red and found that the adsorption effect was best at pH 3 [11]. This article mainly examines the effect of pH on adsorption in the acidic range. It can be seen from the figure that the adsorption effect is better when the pH range is 1~2, and the adsorption amount is slightly decreased when the pH range is 2~6 without much change. This result has a wider pH range than using chitosan as an adsorbent to adsorb methyl red.

3.2.2. Input ratio of chitosan and bentonite. As two different materials, the mass ratio of chitosan to bentonite will inevitably have a greater impact on adsorption. 3mg bentonite (0.04: 1), (0.06: 1) (0.08: 1) (0.1: 1) (0.12: 1) with different mass ratios were taken for one hour and then filtered to measure the absorbance to calculate the content. The results are shown in Fig. 6, which shows that when the mass ratio of chitosan to bentonite is 0.08: 1, the removal rate of methyl red is the best. The reason may be that too large a load of chitosan will lead to blockage of the bentonite pores, which is not beneficial for the adsorption of methyl red. Therefore, the mass ratio of chitosan to bentonite was selected as 0.08: 1 in the subsequent experiments.

![Figure 6. Input ratio of chitosan and bentonite.](image)

3.2.3. Influence of the amount of composite materials.

![Figure 7. Effect of composite amount on adsorption.](image)
Take 25ml of 2.5mg/l methyl red solution, choose chitosan and bentonite to input modified material with mass ratio (0.08: 1), and input materials with different quality 2 3 4 5 6, 7, 8, 9mg for 1 hour for adsorption Measure the adsorption rate. When the amount of adsorbent is in the range from 0.2mg to 0.7mg, as the amount of adsorbent increases, the removal rate of methyl red also increases. When it exceeds 0.7mg, the removal rate remains basically unchanged. This shows that for a volume of 25 ml of methyl red solution with a concentration of 20ug/l, the amount of adsorbent used is 0.7mg to reach saturation.

3.3. Adsorption kinetics

Studying the adsorption kinetics helps to understand the process of the material's adsorption of methyl red. This section explores the effect of time on the adsorption of different methyl red concentrations. The experimental data are fitted by quasi-first-order and quasi-second-order kinetic equations. The pseudo-first-order and quasi-second-order kinetic equations are expressed as follows [12]:

\[
\begin{align*}
\lg(q_e - q_t) &= \lg q_e - k_1 t / 2.303 \quad (3) \\
\frac{t}{q_t} &= 1/k_2 q_e + t/q_e \quad (4)
\end{align*}
\]

Where \( t \) is the adsorption time (min), \( q_t \) is the adsorption capacity (mg·g\(^{-1}\)) when the adsorption time is \( t \), \( q_e \) is the adsorption capacity (mg·g\(^{-1}\)) when equilibrium is reached, and \( K_1 \) is the first-order reaction Rate constant (min\(^{-1}\)), \( K_2 \) is the secondary reaction rate constant (g·mg\(^{-1}\)·min\(^{-1}\)). The results are shown in Tab. 1. The pseudo-first-order equations \( R^2 \) are all less than 0.9, and the pseudo-first-order equations \( R^2 \) are all greater than 0.98. This indicates that the adsorption of methyl red by the material conforms to the pseudo-second-order kinetic model, which indicates that the adsorption process is chemical adsorption process.

**Table 1.** Kinetic parameters of methyl red adsorption.

| Initial mass concentration of methyl red/(mg·L\(^{-1}\)) | Pseudo first order dynamics | Pseudo two order dynamics |
|-------------------------------------------------------|-----------------------------|--------------------------|
|                                                       | \( q_e \) (mg·g\(^{-1}\)) | \( K_1 \) (min\(^{-1}\)) | \( R^2 \) | \( q_e \) (mg·g\(^{-1}\)) | \( K_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) | \( R^2 \) |
| 1                                                     | 24.0807                     | 0.03901                  | 0.8604 | 27.049                     | 0.02642                      | 0.9857  |
| 2.5                                                   | 44.4406                     | 0.02473                  | 0.8904 | 58.377                     | 0.02139                      | 0.9956  |
| 5                                                     | 26.0076                     | 0.01596                  | 0.8651 | 66.45                      | 0.1021                       | 0.9970  |

3.4. Elovich and the internal diffusion model

The Elovich equation is used to characterize the adsorption and desorption in the adsorption process. Its equation is as follows:

\[
q_t = \ln(\alpha/\beta) + \ln(t/\beta) + \alpha \ln(\beta)
\]

The quantities in the above formula are: \( t \) is the adsorption time (min), \( q_t \) is the adsorption capacity (mg·g\(^{-1}\)) when the adsorption time is \( t \), and \( \alpha \) is the adsorption rate constant (g·mg\(^{-1}\)·min\(^{-1}\)), \( \beta \) is a desorption rate constant (g·mg\(^{-1}\)). It can be seen in Tab.2 that as the initial mass concentration of methyl red increases, \( \alpha \) also increases and \( \beta \) decreases; and \( \alpha \) is much larger than \( \beta \). This shows that the composite material has better adsorption performance for methyl red.

The intra-particle diffusion process can be described by the intra-particle diffusion equation, which can be expressed by the following equation:

\[
q_t = k_d t^{0.5}
\]

Where \( t \) is the adsorption time (min), and \( q_t \) is the adsorption capacity (mg·g\(^{-1}\)) when the adsorption time is \( t \). \( K_d \) is the internal diffusion rate constant (g·mg\(^{-1}\)·min\(^{0.5}\)). From the internal diffusion model parameters in Tab.2, it can be seen that as the initial methyl red mass concentration increases, \( K_d \) also increases. It shows that the adsorption process is not only on the surface of the composite material, but also involves the internal diffusion process.
Table 2. Elovich and internal diffusion model parameters.

| Initial mass concentration of methyl red/(mg·L⁻¹) | Elovich model parameters | Diffusion model parameters |
|-------------------------------------------------|--------------------------|---------------------------|
|                                                 | α/(g·mg⁻¹·min⁻¹) | B/(g·mg⁻¹) | R² | K_d/(g·mg⁻¹·min⁻⁰·⁵) | R² |
|-------------------------------------------------|-------------------|------------|----|---------------------|----|
| 1                                               | 1.595             | 0.07585    | 0.9631 | 1.75013 | 0.8966 |
| 2.5                                             | 2.707             | 0.1085     | 0.9897 | 2.1898  | 0.9487 |
| 5                                               | 61.676            | 0.1666     | 0.9748 | 2.6139  | 0.9043 |

4. Conclusion

(1) The surface of the material is not smooth which are many grooves using an electron microscope. The maximum thermal stability temperature is about 250°C. The infrared spectrum shows that the composite material contains a large number of hydroxyl and amino groups.

(2) This result that composite material has a wider pH range than using chitosan; The mass ratio of chitosan to bentonite is 0.08: 1, the removal rate of methyl red is the best; The amount of adsorbent used is 0.7mg to reach saturation for a volume of 25ml of methyl red solution with a concentration of 20μg/l.

(3) The result indicates that the adsorption of methyl red by the material conforms to the pseudo-second-order kinetic model which indicates that the adsorption process is chemical adsorption process.

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