Study on Adsorption and Photocatalytic Properties of Rectorite-titanium Dioxide-Ag Composites

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Abstract. Using butyl titanate, silver nitrate, tired rectorite (REC) as raw materials, titanium dioxide (TiO2) and silver (Ag) were loaded onto the octahedron structure of the tired rectorite by Sol-Gel method, and REC-TiO2 and REC-TiO2-Ag Composites were successfully prepared. The Photocatalytic properties and adsorption properties were also studied. The results showed that the adsorption rate of REC-TiO2-Ag to methylene blue was higher than that of REC-TiO2. In the same proportion of REC-TiO2-Ag and REC-TiO2 Composites, REC-TiO2-Ag composites have better adsorption effect on methylene blue, and the balanced adsorption of REC-TiO2-Ag composites at 25℃ is 54.054 mg/g. The equilibrium adsorption amount of REC-TiO2 composites is 36.49 mg/g. At the same time, the photocatalytic degradation rate of REC-TiO2-Ag to methylene blue was 96%, which was significantly higher than that of REC-TiO2.

1. Introduction
Composite materials can be combined by certain methods, such as the sol-gel method, which have different physical and chemical properties and have some new properties such as excellent photocatalytic properties [1-3].

With the continuous improvement of science and technology, people's damage to the environment is getting worse. In recent years, the use of adsorbent materials as carriers to support photocatalysts on the surface or inside has greatly reduced the environmental conditions.

Photocatalysis technology is an efficient and safe environment-friendly environmental purification technology. At present, photocatalytic oxidation technology has been widely used in the treatment of pollutants and has good development prospects in environmental pollution control [4-7].

Rectorite (REC) is a rare layered silicate clay mineral with a special structure. Its main structure is the sequential aggregation of sodium mica and montmorillonite unit layers. The layered special structure makes the rectorite have good adsorption properties [8]. In addition, Rectorite has its unique structural characteristics.

Titanium dioxide (TiO2) has the characteristics of non-toxicity, good transparency, good brightness and strong adhesion. It is widely used as an inorganic pigment in industry. As an n-type semiconductor due to the different atomic arrangement, there are mainly three crystal forms of anatase, rutile and...
slate. The photocatalytic activity of anatase TiO$_2$ will be better than the other two crystalline materials and it has broad application prospects in the fields of photocatalytic degradation and hydrogen production[9]. However, simply using TiO$_2$ as the photocatalytic system and rectorite as the photocatalytic system will cause disadvantages such as uneven distribution of photogenerated electrons and weaken photocatalytic effect.

If noble metals are introduced into the TiO$_2$ photocatalytic system as photo-generated electrons (e$^-$), it can promote the carrier transport on the interface surface of the composite system. Preventing the recombination of catalyst electrons and holes can improve the photocatalytic activity of the catalyst [10]. Therefore, the main research object of this paper is REC-TiO$_2$-Ag composite material.

2. Reagents and instruments

2.1. Reagent
Butyl titanate (liquid, C.P) is provided by Sinopharm Group Chemical Reagent Co., Ltd. Anhydrous ethanol (liquid, A.R) is provided by Laiyang Kangde Chemical Co., Ltd. Methylene blue (solid, A.R) and silver nitrate (solid, A.R) are provided by Tianjin Damao Chemical Reagent Factory. Letostone is provided by Hubei Zhongxiang Co., Ltd.

2.2. Instruments
Water bath constant temperature oscillator (SHZ-82) is provided by Changzhou Nuojii Co., Ltd. Three-purpose UV Analyzer (ZF-7) is provided by Shanghai Yuezhong Instrument Equipment Co., Ltd. Powerful electric mixer (JB90-D) is provided by Shanghai Suoying Instrument Equipment Co., Ltd.

3. Experimental method

3.1. Preparation of REC-TiO$_2$ composite material
Take 40.0 mL of absolute ethanol and place in a 200 mL dry beaker. Take 15.0 mL of butyl titanate. After stirring at room temperature for 15 minutes, 6.0 mL of glacial acetic acid was added to the beaker as an inhibitor to slow the severe hydrolysis of butyl titanate. Solution A was obtained, and solution A was stirred for 15 min and stirred to be transparent. Add 6g of rectorite to solution A, put it in a constant temperature water bath at 30℃ and stir for 1 h to obtain B. To another dry beaker, add 3.4 g of NH$_4$NO$_3$, 12 mL of double distilled water and 10 mL of absolute ethanol into solution C. add C to B and adjust pH = 4 while adding.

It reacted at 40℃ for half an hour to form a gel state. The semi-finished product was allowed to stand at room temperature for 12 hours then centrifuged with a centrifuge, washed with deionized water several times until neutral and calcined at 300℃ for 3 hours.

3.2. Preparation of REC-TiO$_2$-Ag composite material
30 mL of absolute ethanol, 10 mL of distilled water and 4 mL of glacial acetic acid were added to a 150 mL beaker in sequence, and the pH of the solution was controlled by adding an appropriate amount of concentrated nitric acid to the beaker. Weigh 8.5g of silver nitrate into this beaker and stir mechanically at room temperature for 25 min to obtain a uniform mixed solution D. Take a beaker with a volume of 100 mL, add 30 mL of absolute ethanol, 15mL of butyl titanate, mechanically stir for 20 min, and mix it to obtain a mixed solution E. Put the mixed solution D on the mechanical stirrer and stir at the same time, drop the mixed solution E dropwise into the mixed solution D, and continue the mechanical stirring for 1 h to obtain a light yellow sol. The sol was aged at room temperature for 24 h to obtain a translucent gel, which was transferred to a petri dish and dried in a blast drying cabinet for 12 h to obtain pale yellow particles, which were ground into powder and calcined at 300℃ for 2 h to obtain the REC-TiO$_2$-Ag composite material.
3.3. Structural Characterization and Performance Test of REC-TiO$_2$ and REC-TiO$_2$-Ag Composite

3.3.1. Infrared spectroscopy
Put the REC-TiO$_2$ and REC-TiO$_2$-Ag composite materials into a vacuum drying oven to dry, and perform infrared scanning. The instrument has a resolution of 4 cm$^{-1}$, an analysis range of 300-4000 cm$^{-1}$, and a wavenumber accuracy of 0.01 cm$^{-1}$. Analyze the wavelength range of each absorption band, infer the functional groups that should be in the molecule, and then identify the sample.

3.3.2. Methylene blue adsorption experiment
Prepare 8 groups of methylene blue solutions with concentrations of 0.01 mg / L, 0.02 mg / L, 0.05 mg / L, 0.06 mg / L, 0.08 mg / L, 0.1 mg / L, 0.2 mg / L, 0.3 mg / L, and determine each The absorbance of the group solution makes the relationship curve between the concentration of the solution and the absorbance.

In the adsorption isotherm test, 8 parts of 0.010 g of REC-TiO$_2$-Ag composite material were weighed and added to 10 mL with different concentrations of methylene blue solution and shake in a constant temperature shaker at 25°C for 2 days at 110 rpm adsorption saturation. The absorbance of the methylene blue solution in each glass bottle was measured with UV-visible spectrophotometer.

Change the material to REC-TiO$_2$ and repeat the above experiment.

3.3.3. Photocatalytic degradation experiment
Weigh 10 mg REC-TiO$_2$ and 10 mg REC-TiO$_2$-Ag in a 50 mL beaker, add 10 mL of 0.1 mmol / L MB to the two beakers, and place the two beakers in a UV lamp with a wavelength of 365 nm and the data is obtained and the curve is drawn.

Put the sample in the dark and repeat the above operation.

4. Results and discussion

4.1. Infrared spectroscopy

4.1.1. Fourier infrared spectroscopy of REC-TiO$_2$ and REC-TiO$_2$-Ag composite materials

![Fig.1. Fourier infrared spectrum of composite material](image)

Figure 1 is the infrared spectrum of REC-TiO$_2$ and REC-TiO$_2$-Ag. In the infrared spectrum of REC, the absorption peaks at 3644 cm$^{-1}$ and 3440 cm$^{-1}$ are the bending vibration absorption peak of the hydrogen bond formed by water between REC layers and the stretching of the hydroxyl group of Si-OH [11] in REC, respectively. When TiO$_2$ particles were deposited on the REC sheet, the absorption peak changed significantly and the absorption peak at 3440 cm$^{-1}$ shifted blue, indicating that there is an interaction between the metal oxide particles and REC. The absorption peak at 550 cm$^{-1}$ is the bending vibration absorption peak of Si-O [12]. In addition, we can find that there is obvious infrared absorption in the wavelength range of 3000 cm$^{-1}$ to 3750 cm$^{-1}$ and there is a peak red shift at 1616.537 cm$^{-1}$, which is due to the deposition of nano-Ag particles on REC-TiO$_2$ caused by.
4.2. Methylene blue adsorption experiment

4.2.1. Adsorption kinetics

In order to clarify the kinetic mechanism of the adsorption process, the pseudo-second-order kinetic equation is used:

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

Where $k$ (mg/g·h) is the secondary adsorption rate constant, and $q_t$ (mg/g) and $q_e$ (mg/g) represent the amount of methylene blue adsorbed by the adsorbent at time $t$ (h) and equilibrium [13]. By plotting $t/q_t$ against $t$, a straight line can be obtained, as shown in Figure 4. Based on the slope and intercept of the line, $q_e$ and $k$ can be calculated. The relevant kinetic parameters obtained from the experimental data are shown in Table 1.
| Temperature | REC-TiO$_2$  | REC-TiO$_2$-Ag |  |
|-------------|-------------|----------------|---|
| 25°C        | 3.597       | 71.18          | 0.998 |
| 25°C        | 4.369       | 73.28          | 0.999 |
| 35°C        | 5.048       | 85.24          | 0.989 |
| 45°C        | 5.090       | 103.9          | 0.967 |

It can be seen from Table 1 that plotting $t/q$ against $t$ yields a straight line with a linear correlation coefficient $R^2 > 0.99$. The results show that the adsorption process of REC-TiO$_2$ and REC-TiO$_2$-Ag conforms to the quasi-second order kinetic equation. According to the second-order rate constant $k$ and the equilibrium adsorption amount $q_e$ of the adsorption process, the adsorption of methylene blue by REC-TiO$_2$-Ag is an endothermic process. The higher the temperature, the greater the equilibrium adsorption amount and the adsorption rate is significantly higher than that of REC-TiO$_2$. When equilibrium is reached at 45°C, the equilibrium adsorption capacity of REC-TiO$_2$-Ag for methylene blue is 103.9 mg/g, and the adsorption rate is 5.090 mg/g·h which is significantly higher than that of REC-TiO$_2$.

4.2.2. Adsorption isotherm

![Fig. 5. Adsorption model of methylene blue adsorbed by REC-TiO$_2$ and REC-TiO$_2$-Ag](image)

At 25°C, the adsorption isotherms of REC-TiO$_2$ composite material and REC-TiO$_2$-Ag composite material for methylene blue adsorption are shown in Figure 5 and Figure 6. At low concentration, the equilibrium adsorption amount $q_e$ increases rapidly with the increase of $C_e$. At a high concentration, when the equilibrium concentration of the REC-TiO$_2$ composite material reaches 0.0070 mg/L and the equilibrium concentration of the REC-TiO$_2$-Ag composite material reaches 0.0090 mg/L, the growth rate of the adsorption amount $q_e$ becomes slow.

The adsorption isotherm is fitted by the Langmuir model in the following mathematical form:
In the formula, \( q_e \) (mg / g) is the equilibrium adsorption capacity, \( q_{\text{max}} \) is the maximum adsorption capacity, and \( b \) (L / mg) is the Langmuir constant. The results obtained by fitting the data with the Langmuir model are shown in Table 2. The results show that the correlation coefficient \( R^2 = 0.966 \), Langmuir model is consistent with the process of REC-TiO2-Ag and REC-TiO2 adsorption of methylene blue. The maximum adsorption capacity of REC-TiO2-Ag and REC-TiO2 for the monolayer of methylene blue was 54.054 mg/g and 36.49 mg/g respectively. The results show that the adsorption performance of REC-TiO2-Ag composite is better than that of REC-TiO2 composite.

4.3. Photocatalytic degradation experiment

![Fig.7. Photocatalytic degradation curves of REC-TiO2 and REC-TiO2-Ag](image)

It can be drawn from Figure 7 that the degradation rate of the two composite materials under light conditions increases rapidly. After 2 hours, the degradation tends to be balanced. After the adsorption reaches equilibrium, the degradation rate of REC-TiO2-Ag is much higher than that of REC-TiO2. When the degradation reaches equilibrium, the degradation rate of REC-TiO2-Ag is 96% and that of REC-TiO2 is 94%.

![Fig.8. Adsorption curves of REC-TiO2 and REC-TiO2-Ag in the dark](image)

It can be concluded from Fig. 8 that the adsorption rate of the two composite materials under dark conditions increases rapidly and the adsorption rate of REC-TiO2-Ag under dark conditions is also higher than that of REC-TiO2. When the degradation reached equilibrium, the adsorption rate of REC-TiO2-Ag was 92% and the adsorption rate of REC-TiO2 was 83.4%.

5. Conclusion

REC-TiO2 composite material and REC-TiO2-Ag composite material were prepared by sol-gel method. According to the infrared spectrum, Ag has been successfully loaded on the REC. In order to explore the adsorption capacity of two composite materials with the same proportion, the adsorption experiment of methylene blue was analyzed through the composite material. The results proved that between the REC-TiO2 composite material and the REC-TiO2-Ag composite material with the same ratio, the adsorption capacity of REC-TiO2-Ag composite is better and the maximum adsorption
capacity is 54.054 mg/g. The photocatalytic experiments of the two composite materials were carried out and the photocatalytic performance of REC-TiO₂-Ag was more excellent than that of REC-TiO₂. Under the condition of UV lamp irradiation, the degradation rate of MB by REC-TiO₂-Ag is 96% and that by REC-TiO₂ is 83.4%.

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