Adsorption and Photocatalytic Properties of Modified Rectorite-Titanium Dioxide Composites

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Abstract. Using rectorite as raw material, REC is modified by nitric acid, TiO_2 is attached to the surface of the acidized modified REC tablet to form modified REC-TiO_2 composite materials by the sol-gel method, and its adsorption performance and photocatalytic properties were studied. The results show that the adsorption of REC, modified REC, modified REC-TiO_2 composite materialtoporads to methylene blue increased with the increase of equilibrium concentration. The process of adsorption MB of modified REC-TiO_2 composite materials is an endothermic process. The adsorption of REC, modified REC, modified REC-TiO_2 composite materials to MB increased with the increase of temperature. When the temperature is 25 degree, the maximum adsorption capacity of REC is 93.985 mg/g, the maximum adsorption capacity of modified REC is 107.006 mg/g, and the maximum adsorption capacity of modified REC-TiO_2 is 120.773 mg/g. The degradation rate of MB and p-nitrophenol by modified REC-TiO_2 composite under illumination are 99% and 98%, respectively. The decontamination rate of MB and 4-NP of modified REC-TiO_2 composites under darkness was 50% and 0.8%, respectively. Under light conditions, the degradation rate of MB and 4-NP in modified REC-TiO_2 composite materials is improved.

1 Introduction

At present, the wanton discharge of agricultural and industrial wastewater has caused serious environmental pollution, which has aroused widespread concern of the society.

The REC and montmorillonite are deposited alternately as one layer. It itself is a good adsorbent, but the adsorption capacity is limited. It can be greatly improved by some chemical modification. It has a very wide application and good development prospects in environmental protection.

As a promising semiconductor photocatalytic material, TiO_2 is widely used in various fields due to its good biochemical characteristics, high catalytic activity and good oxidation performance , which is bound to lead the new direction of environmental protection industry. Therefore, the modified rec composite can be prepared on the basis of acidification modified REC, so that the prepared composite has good adsorption performance and photocatalytic performance.

2 Experimental methods

2.1 Preparation of modified REC-TiO_2 composite

2.1.1 Preparation of modified REC

Weigh 10.00 g REC with an electronic balance, put it into a 250 mL beaker, add 100 mL 3 mol/L nitric acid for pickling, put it into a 100 ℃ constant temperature water bath, mechanically stir it for 3h with a powerful electric mixer, wash the sample with deionized water and centrifuge it with a low-speed centrifuge, repeat several times until pH≈7. The modified rec was dried at 105 ℃ for 12h. The modified rec was obtained by grinding the sample with mortar and passing through 200 mesh sieve.

2.1.2 Preparation of modified REC-TiO_2 composites by sol-gel method

Use a measuring cylinder to accurately measure 40.0 mL absolute ethanol and add it into a 200 ml dry beaker. Accurately measure 15.0 mL butyl titanate with a measuring cylinder, slowly add it along the beaker wall, and mechanically stir the solution at room temperature for 15 min . Accurately measure 6.0 mL glacial acetic acid, and slowly drop it into the beaker with a rubber tipped burette (delay the violent hydrolysis of butyl titanate). The obtained solution was stirred vigorously for 15 min with a strong electric mixer until the solution was transparent. Weigh 6.00 g of modified rec with an electronic balance, add it to the transparent solution, mechanically stir it in a constant temperature water bath

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at 30 ℃, and react for 1 h to obtain solution A.

Weigh 3.40 g ammonium nitrate with an electronic balance, add it into a 200 mL dry beaker, transfer 12 mL deionized water and 10 ml absolute ethanol respectively, and prepare solution B.

Slowly add solution B to solution a with a rubber tip dropper and mechanically stir until pH ≈ 4. Put the mixture into a constant temperature water bath at 40 ℃. After mechanical stirring 0.5 h, the gel was made. The semi-finished products were sealed with fresh-keeping film for 12 h, washed with deionized water and centrifuged at low speed for several times until the pH was 7. Put the sample into 105 ℃ electric blast drying oven, and dry for 12 h till drying. The modified REC-TiO_2 composite was obtained by grinding in a mortar, passing through a 200 mesh sieve, calcining in an intelligent box type high temperature furnace at 300℃ for 3 h [1].

2.2 Adsorption experiment of methylene blue

2.2.1 Drawing of standard curve

Accurately weigh 0.0005 g, 0.0010 g, 0.0015 g, 0.0020 g and 0.0025 g MB solids with an electronic analytical balance, put them into different beakers, dissolve them, transfer them into a 250 mL volumetric flask with labels, add deionized water to make a constant volume to the scale line, shake them well, and prepare them into 2 mg/L, 4 mg/L, 6 mg/L, 8 m L and 10 mg/L The absorbance of MB solution was measured with UV-vis spectrophotometer and recorded. The standard curve of concentration (c) and absorbance (A) of MB solution was drawn.

2.2.2 Adsorption kinetics

0.0050 g REC, modified REC and modified REC-TiO2 composite were accurately weighed by electronic analytical balance and added into three different parts of 10.00 mL 0.1 mmol / L MB solution. Put the oscillator into the water bath at a constant temperature to measure the absorbance, and record the absorbance with the water bath at 25 ℃ every 15 minutes. Set the temperature to 35 ℃ and 45 ℃, and repeat the above operation in turn.

2.2.3 Adsorption isotherm

Take 10.00 mL of MB solution from 0.01 mmol / L, 0.05 mmol / L, 0.1 mmol / L, 0.2 mmol / L, 0.3 mmol / L, 0.4 mmol / L, 0.5 mmol / L, 0.6 mmol / L, 0.7 mmol / L and 0.8 mmol / L MB solution respectively with a 10 ml pipette. Take 3 portions of each solution and put them into different labeled glass bottles. 0.0050 g REC, 10 parts of modified REC and 10 parts of modified REC-TiO_2 composite were accurately weighed by electronic analytical balance and put into glass bottles with different concentrations of MB solution. The glass bottle was placed in a water bath constant temperature oscillator at 25 ℃ and oscillated at constant temperature until the adsorption reached saturation. The absorbance was measured by ultraviolet visible spectrophotometer and recorded.

2.3 Study on Photocatalytic Performance

Two parts of 0.0010 g of modified REC-TiO_2 composite were accurately weighed with an electronic analytical balance and added into 20 mL of 0.1 mmol / L MB solution respectively, and then shaken up. One was irradiated by 365 nm triple UV analyzer, and the other was left in the dark . The absorbance was measured every half an hour and recorded. The test was stopped after 4 hours.

Two parts of 0.0020 g of modified REC-TiO_2 composite were accurately weighed with an electronic analytical balance and added into 10 mL of 10 mg / L 4-NP solution respectively, and then shaken up. One part was irradiated by 253 nm triple UV analyzer, and the other part was left in the dark . The absorbance was measured every half an hour and recorded. The test was stopped after 4 hours.

2.4 Infrared spectrum analysis

REC, modified REC and modified REC-TiO_2 composite materials were mixed with potassium bromide at the ratio of 1:100 in an agate mortar and ground, then pressed with a tablet press, and finally scanned with an infrared spectrometer. The resolution of the infrared spectrometer is 4 cm-1, the analysis range is 400-4000 cm^{-1}, and the accuracy is 0.01 cm^{-1}. Analysis of the wavelength range of each absorption band, infer that there should be some functional groups in the molecule, in order to identify the sample.

3 Results and discussion

3.1 Adsorption experiment of methylene blue

3.1.1 Adsorption kinetics

In order to study the kinetic mechanism of adsorption process, pseudo second order kinetic model is often used to simulate the experimental data [5].According to the pseudo second order kinetic equation: $\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$ (1)

Where k (mg / g · h) is the second-order adsorption rate constant [6], q_t (mg / g) is the adsorption capacity of MB at t (h), q_e (mg / g) is the adsorption capacity of MB at equilibrium time [7]. The kinetic parameters obtained from the experimental data are shown in Table 1 and Table 2.

Table 1. Second order kinetic parameters of MB adsorption by REC, modified REC and modified REC-TiO_2 composites with different time

Sample	k（mg/g·h）	q_e（mg/g）	R^2
REC	0.013	74.627	0.996
Modified REC	0.027	78.125	0.996
Modified REC-TiO_2	0.048	79.365	0.999

Table 2. Second order kinetic parameters of MB adsorption by modifiedREC-TiO_2 composite at different temperatures

Modified REC-TiO_2	k（mg/g·h）	q_e（mg/g）	R^2
25℃	0.027	75.414	0.999
35℃	0.037	76.982	0.999
45℃	0.062	78.864	0.999

3.2 Study on Photocatalytic Performance

Under the photocatalysis, TiO_2 can degrade MB by demethylation. At the wavelength of 662 nm, the absorbance of the unabsorbed MB solution decreases. The degradation rate of MB was 99% in light and 50% in dark. Under the condition of ultraviolet lamp irradiation, the modified REC-TiO_2 composite has strong photodegradation effect on MB in addition to adsorption effect, which makes the degradation rate under light condition higher than that under dark condition.

Under photocatalysis, the modified REC-TiO_2 composite can remove 4-NP, but not affected by its adsorption performance. The degradation rate of 4-NP was 98% in light and 0.8% in dark. Under the irradiation of UV lamp, the modified REC-TiO_2 composite has a strong photodegradation effect on 4-NP, which makes the degradation rate of 4-NP in the light condition higher than that in the dark.

3.3 Infrared spectrum analysis

The Fourier transform infrared spectra of REC, modified REC and modified REC-TiO_2 composites were analyzed. The results show that the absorption peaks at 3630 cm^{-1} and 1640 cm^{-1} are bending vibration absorption peaks of hydrogen bond formed by interlayer adsorbed water; the absorption peaks at 3390 cm^{-1} are Tensile vibration absorption peaks of -OH formed by silicon hydroxyl group; the absorption peaks at 1100 cm^{-1} are bending vibration absorption peaks The absorption peak at 916 cm^{-1} is the stretching vibration absorption peak of -OH formed by aluminum hydroxyl group; the absorption peak at 525 cm^{-1} is the bending vibration absorption peak formed by silicon oxygen bond; the absorption peak at 460 cm^{-1} is the stretching vibration absorption peak formed by aluminum hydroxyl group The absorption peak at cm^{-1} is the bending vibration absorption peak formed by the aluminosilicate bond. The results show that the absorption peak at 1390 cm^{-1} is the vibration absorption peak caused by the reaction of modified rec with nitric acid; the absorption peak at 920 cm^{-1} is the characteristic absorption peak of TiO_2 loaded in the modified REC-TiO_2 composite; when TiO_2 particles are loaded on the modified rec sheet, the absorption peak at 3630 cm^{-1} is the highest The blue shift of the absorption peak at cm^{-1} indicates that there is a strong interaction between TiO_2 particles and modified REC.

4 Conclusion

REC was modified by nitric acid and TiO_2 was attached to the surface of modified REC by butyl titanate to form modified REC-TiO_2 composite. The loading of TiO_2 particles in the modified REC-TiO_2 composite makes the adsorption rate of MB on the modified REC-TiO_2 faster than that on the modified rec and REC. The adsorption capacity of modified REC-TiO_2 composite for MB at 45 ℃ is higher than that at 25 ℃ and 35 ℃, indicating that the adsorption process of modified REC-TiO_2 composite for MB is endothermic. The MB adsorption capacity of rec, modified rec and modified REC-TiO_2 increased with the increase of equilibrium concentration. When the temperature was 25 ℃, the maximum adsorption capacity of rec was 93.985 mg / g; the maximum adsorption capacity of modified rec was 107.006 mg / g; the maximum adsorption capacity of modified REC-TiO_2 composite was 120.773 mg / g, indicating that the adsorption performance of modified REC-TiO_2 composite was much higher than that of modified rec and rec original sample. The adsorption capacity of REC, modifiedREC and modified REC-TiO_2 composite for MB increased with the increase of temperature, and finally reached the adsorption saturation state. The degradation rates of MB and 4-NP of the modified REC-TiO_2 composite were 99% and 98% respectively under light, and 50% and 0.8% respectively under dark, which indicated that the light condition was beneficial to improve the photocatalytic activity of the modified REC-TiO_2 composite.

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