Adsorption and Photocatalytic Properties of Modified Rectorite-Titanium Dioxide Composites

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Keywords: Rectorite; Modification; Titanium dioxide; Sol-gel method; Photocatalytic

Abstract: The rectorite (REC) is used as a raw material to modify REC with nitric acid. The modified REC-TiO2 composites were formed by sol-gel method on the surface of acidified REC sheets, and their adsorption properties and photocatalytic properties were studied. The results showed that the adsorption amount of methylene blue (MB) by REC, modified REC and modified REC-TiO2 composites increased with the increase of equilibrium concentration. The adsorption capacity of REC, modified REC and modified REC-TiO2 composites increased with the increase of temperature. The adsorption of MB on modified REC-titanium dioxide composites is endothermic. At 25 C, 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-titanium dioxide composites is 120.773 mg/g. The degradation rates of MB and 4-nitrophenol (4-NP) by modified REC-titanium dioxide composite under illumination were 99% and 98%, respectively. The degradation rates of MB and 4-NP of modified REC-TiO2 composites were 50% and 0.8% respectively under dark conditions. The degradation rates of MB and 4-NP of modified REC-TiO2 composites were improved under light conditions.

1. Introduction

At present, the wanton discharge of agricultural and industrial wastewater has caused serious environmental pollution, which has aroused widespread concern in society. In the process of industrialization and agriculture, the wastewater has not been properly treated, resulting in serious water pollution. Heavy metal ions are highly toxic, persistent and difficult to degrade, which will cause great harm to the health of human body, animals and plants [1].

Rectorite (REC) is a substance formed by alternately depositing montmorillonite and mica layers [2]. Because of its unique cation exchange performance, layered structure and adsorption performance, it is a good adsorbent. However, the adsorption capacity is limited and can be greatly increased by some chemical modification. Montmorillonite structure in REC is acidified. Through cation exchange in interlayer domain, the content of cations such as aluminum ion, magnesium ion, potassium ion, sodium ion, calcium ion and the like in the product are reduced, the specific surface area of cation dissolution is increased, a large number of broken bonds are generated by aluminum dehydroxylation in octahedron, so that the activity is enhanced [3], and the content of SiO2 is relatively increased [4]. However, the pH of the lowest point of the REC potential is lower than that of other materials of the same type. In view of the above situation, it is necessary to further study the REC material to increase its maximum adsorption capacity as an adsorbent, so that it has a very wide application and good development prospects in environmental protection.

In recent years, methods for controlling environmental pollution through semiconductor photocatalytic technology have been widely used [5], and this method has become a research boom in the field of governance. As a very promising semiconductor photocatalytic material, TiO2 is widely used in solar photovoltaic panels and photocatalytic pollution due to its good biochemical characteristics, high catalytic activity, good oxidation performance, low cost and no toxicity [6]. The fields of material management, photo-decomposition of water, hydrogen production, and antibacterial environmental protection are bound to lead the new direction of the environmental protection industry. Therefore, modified REC composites can be fabricated on the basis of acidified REC to improve its adsorption capacity and chemical activity. Modified REC was prepared by

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using nitric acid as acidifier and its structural layer was changed. Modified TiO2 composites were prepared by sol-gel method with butyl titanate as the titanium source. The modified REC-TiO2 composites were prepared by the sol-gel method. The modified REC composites had good adsorption and photocatalytic properties. Furthermore, infrared spectrum analysis, adsorption of methylene blue (MB), photocatalytic performance of methylene blue (MB) and p-nitrophenol (4-NP) were carried out on the modified REC-titanium dioxide composite.

At present, modified rectorite materials have been widely used in the preparation of catalytic materials, environmental protection materials, coatings, medical and health care materials, as well as in sewage treatment, the production of coatings suspension agent and the research of particle carriers, depending on their good adsorption and photocatalytic properties. However, the quantitative analysis of its internal substances, color modification, Nano-Research and so on are still insufficient. As a non-toxic and odorless environmental protection material, more attention should be paid to its development and utilization.

2. Reagents and Instruments

2.1 Reagents

Table 1 Laboratory reagents

Name	Manufacturer
REC (solid)	Hubei Zhongxiang Leto Stone Factory
65% nitric acid (liquid, AR)	Tianjin Damao Chemical Reagent Factory
Absolute ethanol (liquid, BR)	Laiyang kant chemical co., ltd
Butyl titanate (liquid, CP)	Guoyao Group Chemical Reagents Co., Ltd.
Glacial acetic acid (liquid, AR)	Tianjin Guangfu Fine Chemical Co., Ltd.
4-NP (solid, AR)	Tianjin Damao Chemical Reagent Factory
MB (solid, AR)	Tianjin Damao Chemical Reagent Factory
Ammonium nitrate (solid, AR)	Tianjin Damao Chemical Reagent Factory

2.2 Instruments

Table 2 Experimental Instruments

Instruments	Model	Manufacturer
NC ultrasonic cleaner	KQ3200DB	kun shan ultrasonic instruments co., ltd
Three-purpose ultraviolet analyzer	ZF-7	Shanghai Yuezhong Instrument and Equipment Co., Ltd.
Powerful electric mixer	JB90-D	Shanghai suoying instrument equipment co., ltd.
Ultraviolet-Visible Spectrophotometer	UV-752N	Shanghai Yuancheng Instrument Co., Ltd.
Water Bath Constant Temperature Oscillator	SHZ-82	Changzhou Nuoji Instrument Co., Ltd.
Intelligent Box Type High Temperature Furnace	DC-B5/11	Beijing Original Creation Technology Co., Ltd.
Digital display constant temperature water bath pot	HH-4	Guohua electric appliance co., ltd
Electronic balance	MP6001	Shanghai Shun Yu Heng Ping Scientific Instrument Co., Ltd.
Electrothermal blast dryer	101-1EBS	Beijing Yongguang Medical Instrument Factory
Low-speed desktop centrifuge	KA-1000	Shanghai Anting Scientific Instrument Factory
Electronic analytical balance	FA2004	Shanghai Shun Yu Heng Ping Scientific Instrument Co., Ltd.
Intelligent Box Type High Temperature Furnace	DC-B5/11	Beijing Original Creation Technology Co., Ltd.

3 Experimental Methods

3.1 Preparation of Solution

(1) Preparation of 0.1 mmol/L, 0.2 mmol/L, 0.3mmol/L, 0.4 mmol/L, 0.5mmol/L, 0.6mmol/L, 0.7mmol/L, 0.8mmol/LMB solution: Accurately weigh 0.0093g, 0.0187 g, 0.0280g, 0.0374 g, 0.0467g, 0.0561g, 0.0654g, 0.0748gMB solid with an electronic analytical balance, and place them into beakers respectively. After dissolution, move it into a labeled 250 mL volumetric flask, add deionized water to constant volume to the scale line, and shake well for later use.

(2) Preparation of 0.05 mmol/LMB solution: Take a 10 mL pipette, accurately remove 10.00mL of 0.5mmol/LMB solution, and transfer into a labeled 100 mL volumetric flask. Add deionized water to constant volume to the scale line and shake well for later use.

(3) Preparation of 0.01 mmol/LMB solution: Take a 10 mL pipette, accurately remove 10.00mL of 0.1mmol/LMB solution, and transfer into a labeled 100mL volumetric flask. Add deionized water to constant volume to the scale line and shake well for later use.

(4) Preparation of 10 mg/L4-NP solution: Accurately weigh 0.0025g4-NP solid with an electronic analytical balance and put it into a labeled 250 mL volumetric flask. Add absolute ethyl alcohol to constant volume, shake well after reaching the calibration line, and place in dark place away from light for later use.

(5) Preparation of 3 mol/L nitric acid solution: Accurately measure 52.0 mL of 65% nitric acid solution with a measuring cylinder and transfer it into a labeled 250 mL volumetric flask. Add deionized water to constant volume to the scale line and shake well for later use.

3.2 Preparation of Modified REC-TiO2 Composites

3.2.1 Preparation of Modified REC

Weigh 10.00 g REC with an electronic balance, put it into a 250mL beaker, add 100 ml of 3 mol/l nitric acid for pickling, and put it into a constant temperature water bath at 100℃. After mechanical stirring with a powerful electric stirrer for 3 h, the sample was washed with deionized water and centrifuged with a low-speed centrifuge, repeated several times until pH = 7. The modified REC was put into an electric blast drying oven at 105℃ and dried for 12 h to dry. The sample was ground in a mortar and passed through a 200 mesh sieve to obtain modified REC[7].

3.2.2 Preparation of modified REC-TiO2 composites by sol-gel method

40.0 mL absolute ethanol was accurately measured in a dosing cylinder and added to a 200 mL drying beaker. Butyl titanate of 15.0 mL was accurately measured in a dosing drum and slowly added along the beaker wall. The solution was mechanically stirred at room temperature for 15 minutes [8,9]. Accurate amount of 6.0 mL glacial acetic acid was taken, and the beaker was slowly dripped with a rubber head dropper (delaying the drastic hydrolysis of butyl titanate). The obtained solution was stirred vigorously with a strong electric mixer for 15 minutes until the solution was transparent. The modified REC was weighed by an electronic balance and added to the above transparent solution. The REC was stirred mechanically in a constant temperature water bath at 30 C. After 1 h of reaction, solution A was obtained.

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

Slowly drip solution b into solution a with a glue head dropper and mechanically stir [10] until the pH≈4 is ≈ 4, and put the mixed solution into a constant temperature water bath at 40 deg c [11]. Mechanically stirring for 0.5 h to form gel, sealing the semi-finished product with plastic wrap and standing for 12 h, washing with deionized water and centrifuging with a low-speed centrifuge, and repeating several times until the pH≈7 value is about 7. The sample was placed in an electric blast drying oven at 105 ° C and dried for 12 h to dry. Grinding with a mortar, passing through a 200 mesh sieve, and calcining for 3 h in a 300 ° C smart box type high temperature furnace to obtain a composite material of modified REC-TiO2 [12].

3.3 Structural Characterization and Property Testing of Modified REC-TiO2 Composites

3.3.1 Infrared Spectrum Analysis

The REC, modified REC and modified REC-TiO2 composite materials were put into an electric blast drying oven at 105℃ and dried for 2 h. The samples and potassium bromide were respectively mixed and ground in an agate mortar at a ratio of 1:100. After no visible particles were found, the samples were Tabletted by a Tabletting device and finally scanned by an infrared spectrometer. The resolution of the infrared spectrometer is 4cm-1, the analysis range is 400-4000cm-1, and the accuracy is 0.01cm-1[13]. The sample can be identified by analyzing the wavelength range of each absorption band and inferring the functional groups in the molecule.

3.3.2 Adsorption Experiment of Methylene Blue

(1) Drawing of Standard Curve

Accurately weigh 0.0005 g, 0.0010g, 0.0015g, 0.0020g and 0.0025g MB of solid with an electronic analytical balance, put them into different beakers, dissolve them and transfer them into labeled 250 mL volumetric flasks. Add deionized water to constant volume and shake well after the calibration line. Prepare MB solution of 2mg/L, 4mg/L, 6mg/L, 8mg/L and 10 mg/L. Measure its absorbance with an ultraviolet-visible spectrophotometer and record it. Draw the standard curve of concentration (C) and absorbance (A) of MB solution.

(2) Adsorption Kinetics

The composites of 0.0050g REC, modified REC and modified REC-titanium dioxide were accurately weighed by electronic analytical balance and added into three different MB solutions of 10.00mL 0.1mmol/L. It was oscillated in a water bath constant temperature oscillator at 25 C. Its absorbance was measured by ultraviolet-visible spectrophotometer every 15 minutes and recorded. After reaching the adsorption equilibrium, the measurement was stopped. The temperature was set to 35 and 45 respectively, and the above operations were repeated in turn.

(3) Adsorption Isotherm

10mL pipette was used to remove 10.00 mL MB solution from 0.01mmol/L, 0.05mmol/L, 0.1mmol/L, 0.2mmol/L, 0.3mmol/L, 0.4mmol/L, 0.5mmol/L, 0.6mmol/L, 0.7mmol/L, 0.8mmol/L MB solution respectively, 3 parts of each solution were removed and put into different labeled glass bottles. 10 parts of 0.0050 gREC, 10 parts of modified REC and 10 parts of modified REC-TiO2 composite materials are accurately weighed by an electronic analytical balance respectively and put into glass bottles filled with MB solutions with different concentrations. The glass bottle was placed in a 25℃ water bath thermostatic oscillator to oscillate at constant temperature until the adsorption reached saturation. The absorbance was measured with an ultraviolet-visible spectrophotometer and recorded [14].

3.3.3 Study on Photocatalytic Performance

Two parts of 0.0010 g modified REC-TiO2 _ 2 composite materials were accurately weighed by an electronic analytical balance, respectively added into 20 ml of 0.1 mmol/L MB solution, then shaken and shaken. One was irradiated under 365nm three-way uv analyzer, and the other was left standing in the dark [15]. The absorbance was measured and recorded every half hour, and stopped after continuous testing for 4 hours.

Accurately weigh two parts of 0.0020 g modified REC-TiO2 composite materials with an electronic analytical balance, add them into 10 ml of 10 mg/L 4-NP solution respectively, and shake well. One was irradiated under 253nm triple uv analyzer, and the other was left standing in the dark [16]. The absorbance was measured and recorded every half hour, and stopped after continuous testing for 4 hours.

4 Results and Discussion

4.1 Infrared Spectrum Analysis

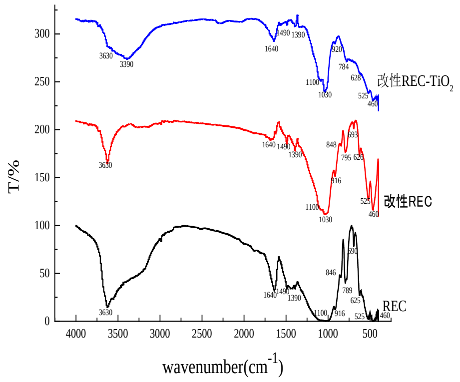

Fig. 1 Fourier transform infrared spectra of REC, modified REC and modified REC-TiO2 Composites

The Fourier infrared spectra of REC, modified REC and modified REC-TiO2 _ 2 composites are analyzed, and the absorption peaks appearing at wave numbers of 3630 cm-1 and 1640 cm-1 are the bending vibration absorption peaks of hydrogen bonds formed by interlayer absorption of water [17]; The absorption peak at wave number 3390 cm-1 is a tensile vibration absorption peak of -OH formed by silicon hydroxyl. The absorption peak appearing at the wave number of 1100 cm-1 is the stretching vibration absorption peak of Si-O-Si formed in the silicon-oxygen tetrahedral layer [18]; The absorption peak appearing at wave number 916 cm-1 is the tensile vibration absorption peak of -OH formed by aluminum hydroxyl. The absorption peak appearing at 525cm-1 wave number is a bending vibration absorption peak formed by silicon-oxygen bonds [19]; The absorption peak appearing at wave number 460 cm-1 is a bending vibration absorption peak formed by aluminosilicate bonds [20]. The absorption peak appearing at the wavenumber of 1390 cm-1 is the vibration absorption peak caused by the addition of nitric acid to the modified REC; the absorption peak appearing at the wavenumber of 920 cm-1 is the characteristic absorption of the supported TiO2 in the modified REC-TiO2 composite. Peak; when the TiO2 particles were loaded onto the modified REC sheet, the absorption peak at 3630 cm-1 was blue-shifted, indicating a strong interaction between the TiO2 particles and the modified REC.

4.2 Adsorption Experiment of Methylene Blue

4.2.1 Drawing Standard Curve

Table 3 Absorbance of MB solutions with different concentrations

c(mg/L)	0	2	4	6	8	10
A	0	0.311	0.623	0.935	1.245	1.542

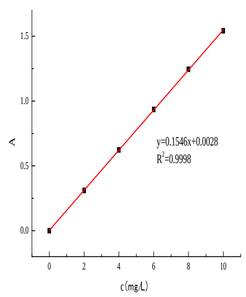

Fig. 2 MB standard Curve

According to the standard curve of MB absorbance changing with concentration, it can be concluded that when MB concentration is 0-10 mg/L, absorbance A has a good linear relationship with concentration C, the correlation is 0.9998, and the regression equation is: y=0.1546x+0.0028.

4.2.2 Adsorption Kinetics

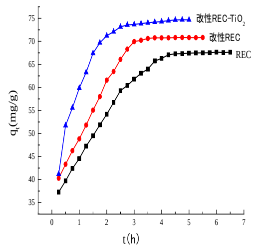

Fig. 3 Effect of contact time on MB adsorption

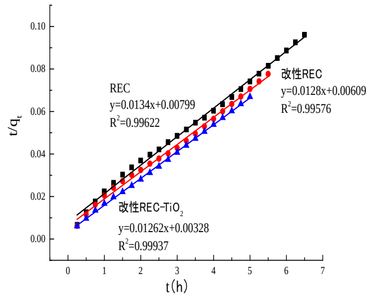

Fig. 4 Effect of time on adsorption of MB by REC, modified REC and modified REC-TiO2 composites

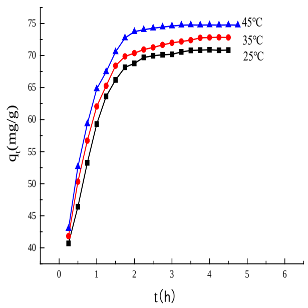

Fig. 5 Effect of temperature on MB adsorption

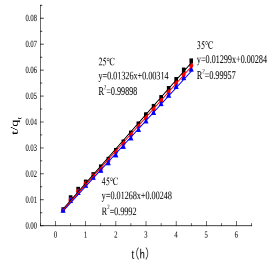

Fig. 6 Effect of temperature on adsorption of MB by modified REC-TiO2 composites

To study the kinetic mechanism of the adsorption process, quasi-secondary kinetic models are often used to simulate experimental results data [21]. According to the pseudo second-order kinetic equation:

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

Where k (mg/g.h) is the secondary adsorption rate constant [22], qt(mg/g) represents the adsorption amount of the adsorbent to MB at time t(h), and qe(mg/g) represents the adsorption amount of the adsorbent to MB at equilibrium time [23]. Relevant kinetic parameters obtained from experimental data are shown in Tables 4 and 5.

Table 4 Time-dependent kinetic parameters of adsorption of MB on REC, modified REC and modified REC-TiO2 composites

Sample	k(mg/g·h)	qe(mg/g)	R2
REC	0.013	74.627	0.996
Modified REC	0.027	78.125	0.996
Modified REC-TiO2	0.048	79.365	0.999

Table 5 Temperature kinetic parameters of MB adsorbed on modified REC-TiO2 composites

Modified REC-TiO2	k(mg/g·h)	qe(mg/g)	R2
25°C	0.027	75.414	0.999
35°C	0.037	76.982	0.999
45°C	0.062	78.864	0.999

The secondary kinetic model parameters of adsorption of MB by REC, modified REC and modified REC-TiO2 composites at different times are shown in Fig. 3-4. The data show that the second-order kinetic model of adsorbed MB [24] is linear, and its linear correlation coefficient is about 1. The second-order kinetic model parameters of adsorbed MB in modified REC-TiO2 composites at different temperatures are shown in Fig. 3-6. The data show that the second-order kinetic model of MB adsorption is linear, and the linear correlation coefficient is about 1.

As shown in Fig. 3-3, when the temperature is 25 °C, the equilibrium adsorption capacity of REC is 74.627mg/g, which is sTable after 6.5h; the equilibrium adsorption capacity of modified REC is 78.125mg/g, which is sTable after 5.5h. The equilibrium adsorption capacity of modified REC-TiO2 was 79.365 mg/g, which was sTable after 5.5 h. The adsorption performance of the modified REC-TiO2 composite is much higher than that of the modified REC and REC.

As shown in Fig. 3-5, when the temperature is 25 °C, the equilibrium adsorption capacity of the modified REC-TiO2 composite is 75.414 mg/g, which is sTable after 4.5 h; the modified REC-TiO2 composite at 35 °C. The equilibrium adsorption capacity was 76.982 mg/g, which was sTable after 4.5 h. When the temperature was 45 °C, the equilibrium adsorption capacity of the modified REC-TiO2 composite was 78.864 mg/g, which was sTable after 4.5 h. The adsorption capacity of modified REC-TiO2 composites increased with the increase of temperature, and finally reached the adsorption saturation state. The adsorption capacity of modified REC-TiO2 composites on MB at 45 °C is higher than that at 25 °C and 35 °C, indicating that the process of adsorbing MB by modified REC-TiO2 composites is an endothermic process.

4.2.3Adsorption Isotherm

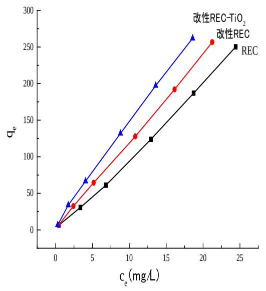

Fig. 7 Adsorption isotherm of MB adsorbed by REC, modified REC and modified REC-TiO2 composites

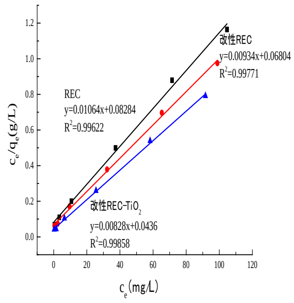

Fig. 8 Langmuir model for adsorption of MB by REC, modified REC and modified REC-TiO2 composites

The Langmuir model is used to fit the adsorption isotherm. The mathematical form is:

Where qe(mg/g) is the equilibrium adsorption amount, qmax is the maximum adsorption amount, and b(L/mg) is Langmuir constant [24]

$$\frac{c_e}{q_e} = \frac{1}{bq_{\max}} + \frac{c_e}{q_{\max}}$$

Table 6 Langmuir parameters of MB adsorption on REC, modified REC and modified REC-TiO2 Composites

Sample	b(L/mg)	qmax(mg/g)	R2
REC	0.128	93.985	0.996
Modified REC	0.137	107.066	0.998
Modified REC-TiO2	0.190	120.773	0.999

The Langmuir model parameters of MB adsorption on REC, modified REC and modified REC-TiO2 composites are shown in Fig. 3-8. The results show that the Langmuir model of MB adsorption is linear, and its linear correlation coefficient is about 1.

As shown in fig. 3-7, the adsorption capacity of MB by REC, modified REC and modified REC-TiO2 composites increases with the increase of equilibrium concentration. The maximum adsorption capacity of REC is 93.985mg/g at 25℃. The maximum adsorption capacity of modified REC is 107.006 mg/g; the maximum adsorption capacity of modified REC-TiO2 is 120.773 mg/g. It shows that the adsorption performance of modified REC-TiO2 composite is better than that of REC as it is and modified REC.

4.3 Study on Photocatalytic Performance

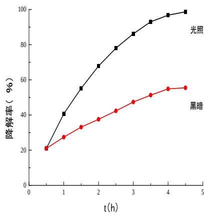

Fig. 9 Photocatalytic degradation of MB by modified REC-TiO2 composite

Under photocatalysis, titanium dioxide degraded MB by demethylation. At 662 nm wavelength, the absorbance of MB solution without adsorption decreased. The degradation rate of MB by modified REC-TiO2 composite was 99% under light and 50% under dark. Under the irradiation condition of ultraviolet lamp, the modified REC-titanium dioxide composites not only have adsorption effect on MB, but also have strong photodegradation effect, which makes the degradation rate of MB under the irradiation condition higher than that under the dark condition.

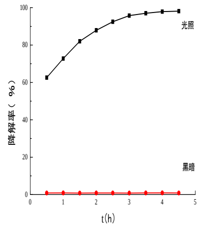

Fig. 10 Photocatalysis of 4-NP modified by modified REC-TiO2 composite

Under photocatalysis, 4-NP was removed by modified REC-titanium dioxide composite, rather than by its adsorption performance. Under illumination, the degradation rate of 4-NP by modified REC-titanium dioxide composite was 98%. In the dark, the degradation rate of 4-NP by modified REC-titanium dioxide composite was 0.8%. Under the irradiation of ultraviolet lamp, the modified REC-titanium dioxide composite has a strong photodegradation effect on 4-NP, which makes the degradation rate under irradiation higher than that under dark conditions.

5. Conclusion

The modified REC-titanium dioxide composites were prepared by nitric acid modified REC and titanium dioxide adhering to the surface of the modified REC sheet by butyl titanate. The loading of titanium dioxide particles in modified REC-TiO2 composite makes the adsorption rate of MB by modified REC-TiO2 faster than that of modified REC and REC. The adsorption of MB on modified REC-titanium dioxide composites is higher than that at 25 C and 35 C, indicating that the adsorption of MB on modified REC-titanium dioxide composites is an endothermic process. The adsorption capacity of MB on REC, modified REC and modified REC-TiO2 composites increased with the increase of equilibrium concentration. When the temperature is 25 °C, the maximum adsorption capacity of REC is 93.985 mg/g; the maximum adsorption capacity of modified REC is 107.006 mg/g; the maximum adsorption capacity of modified REC-TiO2 composite is 120.773 mg/g, indicating modification. The adsorption performance of REC-TiO2 composites is much higher than that of modified REC and REC. The adsorption capacity of REC, modified REC and modified REC-TiO2 composites increased with the increase of temperature, and finally reached the adsorption saturation state. Under degradation, the degradation rates of modified REC-TiO2 composites to MB and 4-NP were 99% and 98%, respectively. In the dark, the degradation rate of modified REC-TiO2 composites to MB and 4-NP was 50%. 0.8%, indicating that the light conditions are beneficial to improve the photocatalytic performance of modified REC-TiO2 composites for MB and 4-NP.

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