Activated Carbon Loaded Ti3+ Self-Doped TiO2 Composite Material Was Prepared By Microwave Method and Degradation of Rhodamine B Under UV-Light

Yingjie Xu
Kunming University of Science and Technology

Qi Zhang
Kunming University of Science and Technology

Guiyu Jiang
Kunming University of Science and Technology

Hongying Xia (hyxia81@163.com)
Kunming University of Science and Technology

Wuchen Cai
Kunming University of Science and Technology

Hen Yan
Kunming University of Science and Technology

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Activated carbon loaded Ti$^{3+}$ self-doped TiO$_2$ composite material was prepared by microwave method and degradation of Rhodamine B under UV-light

Yingjie Xu$^{a,b,c,d}$, Qi Zhang$^{a,b,c,d}$, Guiyu Jiang$^{a,b,c,d}$, Hongying Xia$^{a,b,c,d,\ast}$, Wuchen Cai$^{a,b,c,d}$, Heng Yan$^{a,b,c,d}$

$^a$ State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, 650093, Yunnan, China

$^b$ Yunnan Provincial Key Laboratory of Intensification Metallurgy, Kunming University of Science and Technology, Kunming 650093, Yunnan, China

$^c$ Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming 650093, Yunnan, China

$^d$ Faculty of Metallurgy and Energy Engineering Kunming University of Science and Technology, Kunming 650093, Yunnan, China

Abstract: In this work, the AC loaded Ti$^{3+}$ self-doped TiO$_2$ composite material was synthesized by the microwave method. Through XRD, XPS, SEM, RT-IR, UV-vis and other characterization methods to analyze the crystallinity, valence, morphology and other properties of the composite material. There is a synergistic effect between AC and TiO$_2$, C—O—Ti and O—Ti—C bonds are formed between them. And promote the formation of anatase, make TiO$_2$ form a mixed crystal form, and improve the efficiency of electron-hole separation. The doping of Ti$^{3+}$ produces the Jahn-Teller effect, which reduces the band gap energy of the composite material to 2.2~2.4eV. The adsorption-catalysis experiment showed that the TiO$_2$/Ti$^{3+}$/AC composite prepared under microwave conditions has a removal rate of more than 96% for Rh-B, and the removal rate of pure TiO$_2$/Ti$^{3+}$ is only 50.44%. In addition, the effects of different preparation methods on the removal rate of Rh-B were compared. And it was found that the maximum removal rate of composite materials prepared under conventional conditions was 90.58%, which was significantly lower than the efficiency under microwave conditions. At the same time, the change in the adsorption capacity of AC was explored, and it was found that the saturated adsorption capacity of the 283K composite material was 161.67mg/g. When the temperature was 323K, the maximum adsorption capacity was 250.93mg/g, and the pure AC was only 115.47mg/g. Therefore, the composite material prepared by the microwave method can be regarded as an efficient and economical material for wastewater treatment.

Keywords: photocatalysis; Synergy effect; spent activated carbon; microwave

1 Introduction

In recent years, with the rapid development of industry, the pollution problem caused by industrial wastewater has become increasingly prominent, which has attracted widespread attention. Therefore, environmental protection and treatment have become an urgent problem to be solved.$^{[1,2]}$
Photocatalytic oxidation has been found to be a highly efficient and pollution-free environmental treatment technology by many scholars. Pollutants in water can be degraded and removed by photocatalysts, which is of great significance for environmental treatment and resource regeneration. TiO$_2$ is considered as an ideal catalyst, because it can produce hydroxyl radical (·OH). Which leads to oxidation under light irradiation and can effectively degrade organic pollutants into carbon dioxide and water. However, TiO$_2$ has a large band gap width and poor adsorption capacity. In addition, the photogenerated electrons and holes are easy to compound and dissipate in the form of heat during the migration process. Which reduces the utilization of photogenerated electrons and seriously limits the practical application of photocatalysis. Therefore, in order to improve the degradation effect of TiO$_2$, which has been modified by many scholars at home and abroad. For example: Dozzi and Shibuya doped Pt group metals in TiO$_2$, the research results showed that the doping of Pt group metals leads to a red shift in the absorption spectrum. And the doping hindered the recombination of electrons and holes, which effectively improved the oxidation capacity of holes. Xu and Kamaljeet Singh doped rare earth elements, which were shown to convert near-infrared and visible light into visible and ultraviolet light. It can also act as a hole trapping agent and become an electron trap to inhibit the recombination of electrons and holes, therefore enhancing the photocatalytic performance. Besides, the non-metallic element N, C, B etc. have been used by some scholars to improve TiO$_2$ photocatalytic performance. Because non-metallic elements enter the TiO$_2$ lattice, distorting the TiO$_2$ lattice, narrowing the band gap and enhanced photocatalytic properties. However, doping of these elements may replace Ti ions in the TiO$_2$ lattice, causing crystal instability and increased carrier capture, leading to a reduction in photocatalytic properties.

In these methods, Ti$^{3+}$ self-doped TiO$_2$ and loaded on activated carbon can effectively improve the photocatalytic performance. The reason is that activated carbon has a large special surface area and pore size. As a carrier, it can exhibit strong adsorption capacity, also provide more active sites for the photocatalyst. At the same time, it can be modified with the photocatalyst, enhance the adsorption capacity of activated carbon, reduce the band gap of TiO$_2$, and enhance the catalytic ability in the visible light region. Meanwhile, doping of Ti$^{3+}$ shows Jahn-Teller effect, to further decrease the energy of the system, splitting into band gap states below the Fermi level and excited above the Fermi level. When TiO$_2$ is doped with Ti$^{3+}$, due to the width of the Ti$^{3+}$ band gap state and the excited state itself, the transition from the band gap state to the excited state will broaden the absorption spectrum of TiO$_2$. Furthermore doping of Ti$^{3+}$ can hinder carbon replacement of Ti ions in TiO$_2$, accelerate the migration of optoelectronics-hole, thus improving photocatalytic performance.

In this paper, tetrabutyl titanate was used as a raw material, sodium borohydride was used as a reducing agent, and paracetamol waste activated carbon was used as a carrier. A microwave calcination method was used to successfully synthesize a composite photocatalytic material of activated carbon supported Ti$^{3+}$ self-doped TiO$_2$. Rh-B dye is used as a raw material to simulate degradation. Compared with pure activated carbon, it is found that the activated carbon in the composite material has better adsorption performance than pure activated carbon. Under ultraviolet light irradiation, the catalytic performance of the composite material is significantly better than that of pure TiO$_2$. At the same time, the adsorption-catalytic performance of the composite material prepared under microwave conditions and conventional conditions is compared. And the results show that the performance under microwave is far better than that under conventional conditions. Due to microwave the heating is uniform and efficient, and the inside and outside of the object can
be heated at the same time. In addition, a variety of characterization techniques have been used to conduct in-depth research on composite materials.

2 Experiment

2.1 Materials

Anhydrous ethanol (EtOH, A.R.) (Tianjin Zhiyuan Chemical Reagent Co., Ltd, China), tetrabutyl titanate (TBOT, C.P.)(Shanghai Macklin Biochemical Co., Ltd, China), nitric acid (HNO₃, 0.4M)( Cologne chemistry of Chengdu, China), sodium borohydride (NaBH₄, C.P.(Fuchen Chemical of Tianjin, China), spent activated carbon (SAC)(Suzhou NO.5 Pharmaceutical Factory Co., Ltd), among which the spent activated carbon is taken from activated carbon that has adsorbed paracetamol in a pharmaceutical factory, the whole process of the experiment was carried out with deionized water.

2.2 Preparation of AC loaded Ti⁴⁺ self-doped TiO₂

20ml EtOH, 7ml TBOT and \( m(TiO₂):m(SAC)=1:7 \) of SAC were mixed to obtain mixture A, 10ml EtOH and 8ml HNO₃ were mixed to obtain solution B. Under the action of a magnetic stirrer, solution B was dropped into mixture A, wait until a colloid is formed. Then, 0.13g, 0.3g, 0.4, 0.5g of NaBH₄ were added to the above mixture, stirred for 2h to ensure that the reaction was complete and the product was uniformly loaded on the AC. After that, filtered and dried, transferred the filter residue to a quartz tube, N₂ was used as a protective gas, and heated at 500°C for 2h under microwave conditions to obtain a composite material containing impurities. Heated for 3h under normal conditions, and the other methods was the same.

Putted the prepared composite material containing impurities into a beaker, added 250ml (1M) of HCl, stirred for 12h under the action of a magnetic stirrer. Then filtered, and washed the filter residue with deionized water until it was neutral. Afterwards, dried for 8h at 60°C, and ground to nanometer level. The flow chart of composite material been prepared was shown in Fig.1.

2.3 Sample characterization technology

Use Cu-Kα as X-ray light source, X-ray diffractometer (XRD) (D8 ADVANCE) with \( \lambda=0.15416\text{nm}, \) voltage \( \leq 40\text{KV}, \) current \( \leq 40\text{mA} \) for phase analysis. The field emission scanning electron microscope is used to observe the morphology of the sample (FE-SEM) (JEOL JSM-7800F). The ultraviolet-visible (UV-VIS) absorption spectrum was recorded in an ultraviolet-visible spectrophotometer (Shimadzu, UV-2600), and the data collection range was 200-800nm. Perform spectral measurement in X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, ESCALAB Xi+), using X-rays as excitation source, monochromatic Al target X-ray source and double anode Al/Mg target X-ray source, you can Provide chemical information about the sample surface and interface 1-10nm, with C1s (284.6eV) as a reference. Use Fourier transform infrared spectrometer (MB3600-CH20) to detect the type of functional group of the product.

2.4 Measurement of photocatalyst catalytic activity

First, 0.1g TiO₂/Ti⁴⁺/AC was added into the 200ml Rh-B solution at the consistence of 150mg/L, and after stirred for 80min under dark conditions to clear up the effect of adsorption. Afterward, irradiated the above mixture under ultraviolet light, and took a small amount of supernatant every 30 minutes and filtered with a 0.22um filter plug. The filtrate was analyzed with an ultraviolet spectrophotometer (Shimadzu, UV-2600), and the degradation rate (δ) of Rh-B was calculated by equation (2.1):

\[
\delta = (C_0 - C_t)/C_0
\]

\( C_0 \) (mg/L) and \( C_t \) (mg/L) are the initial concentration of Rh-B dye and the concentration at a
certain moment, respectively.

2.5 Measurement of adsorption properties

For study the adsorption performance of AC after modified, first, 0.1g TiO$_2$/Ti$^{3+}$/AC was added into the several Erlenmeyer flasks which contained 100ml Rh-B dye, the concentration of dye is 100~300mg/L. And then the mixed solution is heated at 303~323K by a constant temperature gas bath oscillator at a shaking speed of 300 revolutions per minute until the adsorption equilibrium. After reached the adsorption equilibrium, the supernatant was taken and the concentration of residual Rh-B was detected by spectrophotometer. The equilibrium adsorption capacity, $q_e$ (mg/g), of TiO$_2$/Ti$^{3+}$/AC is calculated by Equation (2.2)

$$q_e = \frac{(C_0 - C_e)V}{M}$$

The $C_0$(mg/L) is the initial concentration, $C_e$(mg/L) is the concentration at the adsorption equilibrium, $V$(L) is the volume of the adsorbate, and $M$(g) represents the mass of the adsorbent. The Langmuir, Freundlich and Temkin isotherm models were used to judge the nature of the adsorption process. The specific parameters are listed in Table 1.

The kinetic research method is similar to the adsorption isotherm method. At room temperature, add 0.1g composite material to 200ml Rh-B solution with a concentration of 50~200mg/L. Take the supernatant every 10min, filter it with a 0.22um filter plug, and detect the remaining concentration by an ultraviolet spectrophotometer. The amount of Rh-B adsorbed by the composite material $q_t$(mg/g) is calculated by equation (2.3):

$$q_t = \frac{(C_0 - C_t)V}{M}$$

$C_t$ is the concentration of Rh-B solution at a certain moment. The mechanism followed by the adsorption process were studied through pseudo-first order, pseudo-second order and intraparticle diffusion models. The model parameters are listed in Table 2.

3 Results and discussion

3.1 XRD Analysis

XRD pattern of the composites with different NaBH$_4$ content are presented in Fig. 2. With the different addition of NaBH$_4$, the quality of TiO$_2$ in the composite material is different, resulting in different amounts of anatase and rutile, which is consistent with Fig.2. The sample behaves as anatase TiO$_2$ at 25.3°, 37.8°, 47.7°, and 62.6°, 27.4°, 35.9°, 39.1°, 41.1°, 43.9°, 54.1°, 56.5°, 63.9°, 68.8° and 69.6° Both showed obvious rutile TiO$_2$. Pure TiO$_2$/Ti$^{3+}$ shows the rutile peak as the main peak, while the active carbon load shows the anatase peak as the main peak. The peak intensity of TiO$_2$/Ti$^{3+}$/AC at 27.4° is obviously weakened. It can be found that the addition of activated carbon promotes the formation of anatase. This is consistent with the research results of Jang et al. [36] and Ren et al. [37]. At the same time, in this study, it was found that microwave calcination reduced the anatase to rutile transformation temperature to 500°C. However, in the study of Lei et al. [38], only a small amount of rutile appeared when calcined at 500°C. Yang et al. [39] did not find rutile formation in the TiO$_2$ film prepared at 500°C through XRD observation. Yang et al. [40] studied the influence of 300~800°C on the crystal form transformation, and the results showed that the anatase to rutile transformation occurs when the temperature is higher than 700°C, which is obviously different from this study. This study found that the mixed crystal composite material formed by the anatase type and the rutile type has obvious mixed crystal effect. Its photocatalytic efficiency is higher than the single crystal TiO$_2$. On the one hand, the existence of two crystal types can undergo interband transition simultaneously during photocatalysis. However, there are differences between the conduction band levels, which promote photogenerated electrons to gather in the conduction
belt of anatase, and the resulting holes are in the valence band of rutile, separating the photogenerated flow ions and improving the quantum efficiency. On the other hand, the optical quantum energy is small, only the diamond type transition phenomenon, the transition process of electronic transport to the sharp titanium guide belt, thus making the photocarrier separation. Therefore, the hybrid TiO$_2$ not only improves the electron-hole separation rate, reduces the probability of composite, but also broadens the absorption wavelength, and thus enhances the photocatalytic performance.\cite{41, 42}

Scherrer formula:

$$D = \frac{K\gamma}{B\cos\theta}$$  \hspace{1cm} (3.1)

Where K is the Scherrer constant, if B is the half-height width of the diffraction peak, then $K=0.89$; if B is the integral height and width of the diffraction peak, then $K=1$; D is the average thickness of the crystal grain perpendicular to the crystal plane direction (Å); B is the half-height width of the measured sample diffraction peak; $\theta$ is the Bragg diffraction angle; $\gamma$ is the X-ray wavelength, generally 1.54056 Å.

According to the calculation of Scherrer formula, the average grain size of TiO$_2$/Ti$^{3+}$/AC is 32.1nm, and the grain size of pure TiO$_2$/Ti$^{3+}$ is 57.8nm. As we all know, rutile TiO$_2$ is an R-type tetragonal crystal system with a dense lattice structure. Therefore, a large number of rutile TiO$_2$ should have a smaller grain size, but in this work, the result is the opposite. This is because activated carbon and TiO$_2$ have an interface effect that inhibits the growth of crystal grains\cite{43-45}. Even though anatase has a larger grain size than rutile, the final composite material has a grain size smaller than that of pure TiO$_2$/Ti$^{3+}$ due to the action of activated carbon.

3.2 XPS Analysis

Fig.3 shows the XPS spectrum of 0.13g-TiO$_2$/Ti$^{3+}$/AC. As Fig.3a shown, the wide scan XPS of the TiO$_2$/Ti$^{3+}$/AC indicates C, O and Ti existence. A semi-quantitative analysis of Fig.3b found that C-C, C-O and C=O accounted for more than 75%, which is approximately consistent with the load. Two new characteristic peaks at 283eV and 287.6eV were ascribed to the O-Ti-C and C-O-Ti. The emergence of new chemical bonds indicates that high-temperature calcination has caused some changes in the interface between AC and TiO$_2$. The results indicated that the existence of the synergistic effect between each other, which is propitious to the raising photocatalytic performance of the TiO$_2$. As shown in Fig.3c, the peak at 532.8eV is ascribed to the Ti-OH\cite{47}, indicating that oxygen vacancies are formed here\cite{48, 49}. The presence of -OH contributes to catalyst degradation of dyes. As Fig.3d shown, Ti2p is presented in the form of Ti2p1/2 and Ti2p3/2 at different binding energies. The peak at the 458.2eV and 463.4eV correspond to Ti2p3/2 and Ti2p1/2 of Ti$^{3+}$ respectively. The peak centered at 459.2eV is assigned to Ti2p3/2 of Ti$^{4+}$, and the peak centered at 465.2eV belongs to Ti2p1/2 of Ti$^{4+}$. The binding energies of Ti2p are reduced by 1.0eV and 1.8eV which belongs to Ti$^{4+}$, respectively, which indicates that a small amount of Ti$^{4+}$ is deoxidized to Ti$^{3+}$, which is similar to the results of Zhou\cite{50} and Su\cite{51} et al.

3.3 FT-IR Analysis

FT-IR spectrum in the range of 500–4000cm$^{-1}$ of the synthesized composite material was analyzed, and as shown in Fig.4. Appears in the range of 500–700cm$^{-1}$, which is attributed to the stretching vibration of the Ti-O-Ti bond\cite{52}. In the range of 1000–1250cm$^{-1}$, the TiO$_2$/Ti$^{3+}$/AC has an extra peak, which is attributed to Fig.3b, forming a C-O-Ti bond at 1100cm$^{-1}$\cite{46}. The absorption peaks at 1380cm$^{-1}$ and 1650cm$^{-1}$ belong to the C-O and C=O bond. Especially, the peak of pure
TiO$_2$/Ti$^{3+}$ also appears at 1650 cm$^{-1}$, which is attributed to the CO$_2$ in the air$^{[53,54]}$. This is the same as the group shown in Fig.3b, verifying that the above-mentioned chemical bond does exist in the composite material. The absorption peak at 3400 cm$^{-1}$ always exists, which belongs to -OH, but the absorption peak of supported materials is generally weaker, indicating that -OH is reduced. Pure TiO$_2$/Ti$^{3+}$ contains more -OH groups than composite materials. The loading of AC makes reduction of -OH groups on the anatase surface, this is similar to the results of Zheng et al$^{[55]}$.

3.4 SEM and EDS Analysis

Fig.5 shows a typical SEM image of the composite material. As shown in Fig.5a and b, the pure TiO$_2$/Ti$^{3+}$ produced mainly exists in a spherical structure$^{[56]}$. The results shown in Fig.2, indicate that the rutile has a spherical structure at this time, and the particles are agglomerated with each other. According to the molecular collision theory$^{[57]}$, the prerequisite of chemical reaction is whether the reactant molecules can contact and collide with each other, and not every collision will cause chemical reaction. Only when the energy between molecules reaches the critical value and the collision in a fixed direction can chemical reaction occur$^{[58]}$. The agglomeration of particles leads to a decrease in the specific surface area of the TiO$_2$/Ti$^{3+}$ particles, which hinders the effective collision between the catalyst and the dye molecules, which is very unfavorable for photocatalysis. Fig.5c and d are SEM images of the catalyst blocked on the AC. The presence of the catalyst can be clearly seen on the surface of the AC. The shape of the composite catalyst is more complex, with spherical$^{[59]}$ and irregular shapes$^{[60]}$, which is attributed to the presence of a large amount of rutile and anatase in the composite material. In addition, it has also been observed that TiO$_2$/Ti$^{3+}$ is dispersed on the surface of the support. For the photocatalyst, AC as a support not only provides a larger specific surface area, provides active sites for TiO$_2$/Ti$^{3+}$. At the same time, it also inhibits the growth of crystal grains and promotes the formation of anatase. These behaviors are particularly beneficial to the removal of dyes. Fig.6 shows that the typical EDS spectrum is derived from TiO$_2$/Ti$^{3+}$/AC, as the spectrum shows that the photocatalyst is uniformly distributed on the AC surface. It reveals the existence of C, O and Ti elements in the composite material. According to the mass specific gravity analysis C: O: Ti=11:2.5:1, it shows that the EDS result is close to the actual addition amount.

3.5 UV-VIS Analysis

UV-vis diffuse reflectance spectroscopy was used to test the response range of the composite material with the addition amount of 0.13g~0.5g NaBH$_4$, as shown in Fig.7. Usually the band gap energy of TiO$_2$ is 3.0~3.2 eV, which can only absorb 3%~5% of ultraviolet light$^{[61]}$. The doping of Ti$^{3+}$ can effectively reduce the band gap energy of TiO$_2$, which has been reported by many studies$^{[62-65]}$. As shown in Fig.7a, the response range of the prepared conforming material to light has been widened to 450~500 nm. This show that the doping and loading of substances promotes the photocatalytic performance of TiO$_2$, due to the Jahn-Teller effect produced by Ti$^{3+}$ and the synergy between AC and TiO$_2$, which effectively reduces the band gap energy of TiO$_2$$^{[32]}$. Fig.7b shows that the band gap energy of 0.13g NaBH$_4$ is 2.2 eV, and the band gap energy of 2.4 eV belongs to 0.4g NaBH$_4$. The band gap energy of this study is compared with pure TiO$_2$ and pure TiO$_2$/Ti$^{3+}$$^{[66-68]}$ produced by other scholars, the band gap energy has changed significantly. Meanwhile, it was found that the addition of 0.13g NaBH$_4$ has the smallest band gap energy, which is because of with the addition of NaBH$_4$ increases, a large amount of intermediate products are produced to cover the surface of the catalyst, which prevents the catalyst from being reduced$^{[69]}$. But it was found that the band gap
energy decreased between 0.4~0.5g NaBH₄ addition amount, which may be due to the excessive viscosity of the system, which caused the excessive NaBH₄ to fail to react completely. During the subsequent pickling, the hydrolysis produced part of Ti³⁺.

### 3.6 Photocatalysis Experiment

To test the photocatalytic degradation potential of the TiO₂/Ti³⁺/AC, Rh-B dye was used to simulate pollutants for degradation. As shown in Fig.8, SAC, regenerated AC and pure TiO₂/Ti³⁺ were used as reference materials to compare the adsorption-photocatalytic performance of the modified conforming materials. First, put all the samples under dark conditions to make the composite material reach adsorption equilibrium to eliminate the influence of adsorption on the catalytic process. Then, the photocatalytic degradation experiment was carried out under ultraviolet light irradiation. Fig.8 shows that AC and SAC have almost no catalytic ability during the degradation process. Under ultraviolet light, the removal rates of AC and SAC to rhodamine B dye are 6.59% and 1.81%, respectively. The removal rate of Rh-B dye by pure TiO₂/Ti³⁺ and 0.13~0.5g-TiO₂/Ti³⁺/AC gradually increased with time. By comparing AC, TiO₂ and 0.13~0.5g-TiO₂/Ti³⁺/AC composite materials on the changes in the removal rate of Rh-B dye, it is found that the removal rate of Rh-B by composite materials is generally higher than that of the other two, which is attributed to the synergy between TiO₂ and AC. Particular, it is found that the degradation rate of the composite material with 0.13g NaBH₄ addition amount is the largest within 120min. This is because of when the NaBH₄ addition amount is less than 0.13g, the reduced Ti³⁺ is less and the effect of doping modification on TiO₂ is poor. When the amount of NaBH₄ is 0.2~0.5g, the reduction reaction will be terminated prematurely due to the large amount of intermediate products produced during the reduction process.

Table 3 shows the kinetic parameters of the three materials for catalytic degradation of Rh-B dye under ultraviolet light. It is observed that the pseudo-first-order kinetic model of R² is greater than the pseudo-second-order kinetic model, indicating that the degradation process conforms to the pseudo-first-order kinetic model. Fig.9 shows the linear fitting of pseudo-first-order catalytic kinetics of 0.13g-TiO₂/Ti³⁺/AC, pure TiO₂/Ti³⁺ and AC under ultraviolet light. The pseudo-first-order dynamics model is equation 3.2:

\[
\ln \frac{C_0}{C_t} = Kt
\]  

(3.2)

The photocatalytic degradation rate of 0.13g-TiO₂/Ti³⁺/AC for rhodamine B is 0.00895, pure TiO₂/Ti³⁺ is 0.00245, and AC is 0.00012. After AC loaded with TiO₂/Ti³⁺, the degradation rate was increased by 3.65 times compared with unloaded, due to the synergistic effect between TiO₂ and AC that enhanced the photocatalytic performance. AC as an adsorption center, increasing the concentration of dye molecules around the photocatalyst, increasing the active sites on the TiO₂ surface, and promoting the separation of photogenerated electrons and holes [31,32,70]. Fig.10 shows the removal rate of Rh-B by the catalyst produced under microwave conditions and conventional conditions. By comparing the photocatalytic degradation rate of the composite material produced by the muffle furnace and the microwave oven, it is found that the composite material produced by the microwave method has a removal rate of more than 96% of Rh-B. While the conventional method is only 90%, which is attributed to the heating characteristics of the microwave. Fig.11 vividly shows the photocatalytic degradation mechanism of composite materials, the prepared catalyst produced oxygen vacancies during the preparation process. When exposed to light, photoelectrons were excited, and Ti³⁺ combined with the oxygen vacancies and existed in the form
of \([\text{O}_{2}^-\text{Ti}^{3+}]^{-29}\). In order to achieve the purpose of inhibiting the recombination of electron pairs and holes, and improve the photocatalytic performance.

As shown in Table 4, the TiO\(_2\) composite material produced in this study was compared with the previously reported TiO\(_2\) composite material for the removal rate of Rh-B. The results show that compared with other reports, under the optimal experimental scheme, the composite material produced in this study has a removal rate of more than 96% for Rh-B, showing excellent adsorption-catalytic performance.

At the same time, repetitive experiments by three times were carried out on the composite material. The results showed that the second time compared with the first time, the removal rate of Rh-B only decreased by 2%, while the total removal rate decreased by only 6% after three repeated experiments. At this time, the removal rate of Rh-B by the composite material still exceeds 90%, indicating that the synthesized composite material has the characteristics of high efficiency and recyclability.

### 3.7 Adsorption Experiment

Use Langmuir, freundlich, Temkin isotherm models to judge the nature of the adsorption process. Under the condition of no ultraviolet light, the adsorption performance of the prepared composite material was evaluated according to the adsorption of Rh-B dye. The linear fitting parameters of the adsorption isotherm experiment have been listed in Table 5. According to the fitting results, the Langmuir isotherm model has the greatest degree of fit, indicating that the adsorption isotherm process can be well explained by the Langmuir isotherm equation. In addition to this, the maximum adsorption amount was observed increasing with increasing temperature, shown in Fig.12. Indicating that the process of AC adsorption of Rh-B is heat absorbing, and a similar phenomenon was found by Karthikeyan\(^{[75]}\) and Amalraj\(^{[76]}\) in their study. This phenomenon can be explained as an increased temperature, increasing the molecular kinetic energy of the whole system, and the dye molecules accelerate without irregular movement, resulting in the enhanced adsorption capacity of activated carbon\(^{[77]}\).

In Fig.8, during the dark treatment adsorption process, the adsorption rate of the supported composite material on Rh-B is significantly higher than that of AC. This is due to the synergistic effect between TiO\(_2\)/Ti\(^{3+}\) and AC. It also shows that the catalyst is almost dispersed in AC surface did not cause a large amount of blockage of AC pores. The adsorption mechanism followed in the adsorption process of composite materials is studied through pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Table 6 lists the model parameters and experimental data. \(R^2\) is used to judge the degree of fit of the adsorption process to the model. It can be seen from Table 6 that the pseudo-second-order kinetic model has the best fit, and the error between \(q_{e,\text{cal}}\) and \(q_{e,\text{exp}}\) is the smallest. Therefore, the pseudo-second-order kinetic model can be used to explain the adsorption mechanism, as shown in Fig.13. \(K\) gradually decreases with the initial concentration of the dye, indicating that the active sites of the composite surface decrease as the initial concentration increases. At 150–200mg, the \(K\) site is large to the minimum critical value. The adsorption kinetic data of pure TiO\(_2\)/Ti\(^{3+}\), AC and modified AC are listed in Table 7. After SAC was desorbed with hydrochloric acid and heated by microwave at 873K, the equilibrium adsorption capacity of Rh-B was 115.466mg/g, while the equilibrium adsorption capacity of the composite material was 157.7699mg/g. Which proved the existence of AC and TiO\(_2\)/Ti\(^{3+}\), the synergistic effect increases the number of active sites on AC.

### 4 Conclusion

Nano-TiO\(_2\)/Ti\(^{3+}\) was supported uniformly on activated carbon, which was produced by a
microwave calcination method under neutrality condition. XRD, XPS, FT-IR and UV-vis analysis shows that the obtained composite material is modified by Ti$^{3+}$ to promote the separation of photogenerated carriers, and the synergistic effect to form C-O-Ti and O-Ti-C bonds, which significantly enhances the adsorption capacity and photocatalytic performance. Rhodamine B dye is used as a degradation product under ultraviolet light. Through dark adsorption and photocatalysis, the removal rate of Rhodamine B by the composite material exceeds 96%, and the efficiency is only reduced by 6% when it is recycled for three times. The modified activated carbon has a maximum capacity of 250.93mg/g for rhodamine B at 323K.

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6 Conflict of Interest Statement:
Each contributing author has no conflict of interest.

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Figure 1

Production process of activated carbon supported Ti3+ self-doped TiO2 catalyst.
Figure 2

XRD patterns of composite materials under microwave condition.
Figure 3

XPS spectrum of TiO2/Ti3+/AC composite. Wide scan XPS spectra(a), C1s spectrum(b), O1s spectrum(c), Ti2p spectrum(d).
Figure 4

FT-IR spectrum of TiO2/Ti3+/AC composite.
Figure 5

Pure TiO2/Ti3+(a)(b), catalyst supported on activated carbon(c)(d).
Figure 6

EDS diagram of 0.13g-TiO2/Ti3+/AC under microwave.

Figure 7

UV-vis diffuse reflectance spectra of 0.13g-TiO2/Ti3+/AC (a), the Kubelka–Munk function photon energy diagrams of best and worst (b).
Figure 8

SAC, regenerated AC, pure TiO$_2$/Ti$^{3+}$ and 0.13~0.5g TiO$_2$/Ti$^{3+}$/AC on the degradation of Rh-B.
Figure 9

The first-order linear fitting of the degradation of rhodamine B dyes by three materials under ultraviolet light.
Figure 10

Removal rate of Rh-B by composite materials under microwave and conventional conditions.
Figure 11

AC supported Ti3+ self-doped TiO2 photocatalytic degradation mechanism diagram.
Figure 12

Langmuir isotherms for Rh-B adsorption onto TiO2/Ti3+/AC at the temperature of 303~323K.
Figure 13

Pseudo-second-order linear fitting for adsorption of Rh-B onto TiO2/Ti3+/AC at 283K.

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