One-Pot Synthesis of TiO$_2$/Hectorite Composite and Its Photocatalytic Degradation of Methylene Blue

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Abstract: TiO$_2$/hectorite composite photocatalysts with different molar ratios of lithium, magnesium, and silicon were synthesized by a one-pot hydrothermal method. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), N$_2$ adsorption-desorption isotherms, and ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS). When the molar ratio of lithium, magnesium, and silicon was 1.32:5.34:8 (TH-2), the composite showed the highest UV photocatalytic degradation of methylene blue (MB). The apparent rate constant of TH-2 was 0.04361 min$^{-1}$, which was about 3.12 times that of EVONIK Degussa commercial TiO$_2$ of AEROXIDE P25. The improvement of photocatalytic efficiency of the composite was mainly due to its high specific surface area, light trapping ability, and effective separation of electrons ($e^-$) and holes ($h^+$). At the same time, the F element of hectorite is beneficial to the formation of TiF$_3$ in TiO$_2$, thus enhancing the photocatalytic activity. After five cycles, the removal rate of MB with TH-2 still reached 87.9%, indicating its excellent reusability.

Keywords: photocatalysis; TiO$_2$; hectorite; one-pot synthesis; degradation of organic dyes

1. Introduction

The development of the chemical industry has resulted in large-scale pollutant emission, which has brought about a series of environmental problems [1]. Organic dyes, in particular, are highly toxic and chemically stable, potentially teratogenic, and carcinogenic to humans [2]. As a “green” technology, photocatalysis has attracted widespread attention because it can efficiently degrade dyes to avoid its pollution to the environment [3,4].

Titanium dioxide (TiO$_2$) is considered one of the most promising photocatalysts because of its advantages of good chemical stability, nontoxicity, and low cost to degrade organic pollutants in the field of printing and dyeing [5,6]. However, TiO$_2$ has a wide band gap (3.0–3.2 eV) and excitation light is limited to ultraviolet light (4%), which greatly decreases its utilization efficiency of solar energy [7]. In addition, TiO$_2$ nanoparticles exhibit a low specific surface area, easy aggregation, and poor recycling, which limit its application range [8]. Therefore, improving the adsorption capacity and photocatalytic performance of TiO$_2$ is important.

Smectite clay is a layered silicate mineral with a high adsorption capacity and specific surface area, and some composite clay materials can change the phase of semiconductors or improve the separation of $e^-$ and $h^+$, which can be used to support TiO$_2$ [9]. The interlayer cations in the composite clays tend to capture electrons and oxidize the holes, thus reducing the charge recombination rate and improving the photocatalytic performance. Hectorite belongs to 2:1-type layered clay composed of a Si–O tetrahedron and a Mg–O octahedron arranged in 2:1 order in the vertical direction, and its molecular structure is $[\operatorname{Si}_x\operatorname{Al}_{1-x}\operatorname{O}_2\operatorname{OH}](\operatorname{Si}_x\operatorname{Al}_{1-x}\operatorname{O}_2\operatorname{OH})_z$ (M = Na, Li) [10,11]. Hectorite can facilitate the separation of composites and improve the recycling of catalysts [12]. Therefore, TiO$_2$/hectorite composite...
material with high photocatalytic performance can be prepared by utilizing the adsorption and ion exchange properties of hectorite to enhance the degradation rate of dye wastewater.

The composite of clay and TiO$_2$ has the advantages of small titanium crystal size, large porosity, and large specific surface area [13]. However, it is usually difficult for TiO$_2$ to enter the interlayer. Moreover, due to the wide band gap of TiO$_2$, TiO$_2$/clay composites have photocatalytic activity only under ultraviolet light [14]. Up until now, TiO$_2$/hectorite has been synthesized mainly by the hydrothermal method, sol-gel method, and hydrolysis method [15–17]. In previous studies, most of them reacted by mixing TiO$_2$ precursor solution with the suspension of hectorite directly. The process is complicated and takes a long time. Furthermore, it is difficult for TiO$_2$ to enter the interlayer of hectorite, which limits the photocatalytic activity [18]. Ma et al. synthesized TiO$_2$/hectorite and found the influence of titanium content on photocatalytic performance [19]. However, TiO$_2$ was usually only supported on the mineral surface, not in the interlayer space of hectorite. It is worth studying TiO$_2$/hectorite composite materials by utilizing the exchange ability of the interlayer cation to introduce titanium ions into the interlayer during the synthesis of TiO$_2$/hectorite. Therefore, we studied the synthesis of TiO$_2$/hectorite nanocomposites as photocatalysts at different molar ratios of lithium, magnesium, and silicon prepared by a simple one-pot hydrothermal method and utilization for the photodegradation of MB under UV light irradiation.

2. Results and Discussion

2.1. Characterization

2.1.1. X-ray Diffraction (XRD)

Figure 1 shows the XRD patterns of hectorite and TiO$_2$/hectorite (TH-1, TH-2, TH-3, TH-4, and TH-5). As for the hectorite, characteristic diffraction peaks of 20 approximately appear at 19.6, 28.0, 35.1, 53.3, 61.0, and 72.3° [20,21]. It can be observed that hectorite has low crystallinity and small particle size from the widened peaks. Some weak peaks of 20 appear at 29.0, 32.0, 38.7, 48.9, and 54.7°, which may be attributed to the residual starting materials and some intermediate products, such as lithium fluoride, lithium, and silicate [10].

![Figure 1. XRD patterns of hectorite: TH-1, TH-2, TH-3, TH-4, and TH-5.](image-url)

TiO$_2$ shows the characteristic diffraction peaks of the anatase phase (Joint Committee on Powder Diffraction Standards Card NO. 21-1272) at 25.3, 37.8, 48.06, 54.0, 55.07, and 62.8°, which correspond to the diffraction planes of (101), (004), (200), (015), (211), and (204) [10]. The same diffraction peaks are found for the TiO$_2$/hectorite photocatalysts with different molar ratios of Li, Mg, and Si. However, the characteristic peaks of hectorite...
become slightly weaker in comparison to the synthesized TiO$_2$/hectorite, indicating that the layered structure of hectorite is partially destroyed, but its skeleton structure is still maintained [22]. The crystallite size of TiO$_2$ can be calculated according to the Debye–Scherrer equation (Equation (1)) [23]:

$$D = \frac{K\lambda}{\beta \cos \theta},$$  

where the $K$ constant is the shape factor (value as 0.89), $\lambda$ is the wavelength, and $\beta$ is the half-peak width of the signal. The crystallite sizes of TiO$_2$ in TH-1, TH-2, TH-3, TH-4, and TH-5 are 11.3, 10.8, 11.2, 11.4, and 11.9 nm, respectively, according to the (101) peak by Equation (1), which are all smaller than that of P25 (21 nm) (Table 1). The appropriate particle size of TiO$_2$ is beneficial to increase the surface area, providing more photocatalytic active sites to improve the photocatalytic efficiency.

**Table 1.** Specific surface area ($S_{\text{BET}}$), pore size, pore volume, and crystal size of samples.

| Sample   | $S_{\text{BET}}$ (m$^2$/g) | Pore Size (nm) | Pore Volume (cm$^3$/g) | Crystal Size of TiO$_2$ (nm) |
|----------|----------------------------|----------------|------------------------|-------------------------------|
| TH-5     | 457.83                     | 3.21           | 0.32                   | 11.9                          |
| TH-4     | 412.34                     | 3.48           | 0.29                   | 11.4                          |
| TH-3     | 353.69                     | 3.52           | 0.20                   | 11.2                          |
| TH-2     | 491.97                     | 4.65           | 0.39                   | 10.8                          |
| TH-1     | 429.55                     | 3.69           | 0.19                   | 11.3                          |
| Hectorite| 260.27                     | 3.16           | 0.13                   | -                             |
| P25      | 50                         | -              | -                      | 21                            |

It has been found that for hectorite, magnesium from the magnesium oxide octahedron is more easily replaced by lithium ions, while silicon from silica the tetrahedron is difficult [20]. The number of lithium ions and magnesium ions have some effect on TiO$_2$/hectorite in the hydrothermal synthesis. With the increase in Li$^+$, the crystal size of TiO$_2$ decreases first and then increases gradually. Li$^+$ can accelerate the conversion of lithium silicate into hectorite, as well as increase the number of Li$^+$ replacing Mg$^{2+}$ on the lamella, enhancing the layer charge, so that more titanium ions have more chances to intercalate the interlayer to balance the negative charge. As for the samples, TiO$_2$ in TH-2 shows the best crystallinity. With the increase in the amount of lithium, diffraction peaks of TH-4 and TH-5 appear at 38.70, 44.99, and 65.48$^\circ$, corresponding to the diffraction of (111), (200), and (220) crystal planes of the cubic LiF crystal, suggesting the increase in residual LiF. In addition, the peaks at 48.9 and 54.7$^\circ$ are caused by the intermediate product lithium silicate.

2.1.2. Fourier Transform Infrared (FTIR) Spectroscopy

Figure 2 shows the FTIR spectra of the samples in the range of 4000 to 400 cm$^{-1}$. It can be obviously observed that there are similar peaks between hectorite and TiO$_2$/hectorite, indicating that the basic skeleton structure of hectorite is not damaged during the introduction of TiO$_2$. The absorption bands such as -OH stretching vibrations of crystalline water at 3620 cm$^{-1}$, Si–O stretching at around 1030 cm$^{-1}$, Mg–O at 650–670 cm$^{-1}$, and the vibration peak of Si–O–Si bonds at 470 cm$^{-1}$ can be observed, which are characteristics of hectorite [24,25]. The peaks at 1640 and 3460 cm$^{-1}$ are attributed to the bound water and the vibration of structural hydroxyl groups in the samples [26,27]. The bands of all the composite photocatalysts centered on 640 and 605 cm$^{-1}$ are typical for TiO$_2$ (anatase phase), corresponding to the stretching modes of Ti–OH and Ti–O bonds, respectively [28]. The bands between 700 and 500 cm$^{-1}$ are usually assigned to the stretching vibration modes characteristic of Ti–OH and Ti–O–Ti bonds. All samples have these peaks and thus all have TiO$_2$. 

#### Notes

- Debye–Scherrer equation: $D = \frac{K\lambda}{\beta \cos \theta}$
- Specific surface area ($S_{\text{BET}}$)
- Pore size, Pore volume
- Crystal size of TiO$_2$
composite photocatalysts centered on 640 and 605 cm\(^{-1}\) are typical for TiO\(_2\) (anatase phase), corresponding to the stretching modes of Ti–OH and Ti–O bonds, respectively\[28\]. The bands between 700 and 500 cm\(^{-1}\) are usually assigned to the stretching vibration modes characteristic of Ti–OH and Ti–O–Ti bonds. All samples have these peaks and thus all have TiO\(_2\).

**Figure 2.** FTIR spectra for hectorite, TH-1, TH-2, TH-3, TH-4, and TH-5.

### 2.1.3. Scanning Electron Microscopy (SEM)

The SEM images of hectorite, TH-1, TH-2, TH-3, TH-4, and TH-5 are shown in Figure 3. Figure 3a shows the typical structure of hectorite, which is a nanoscale layered structure and forms blocky particles with various sizes, rough surfaces, and different thicknesses\[15\]. SEM images of the five TiO\(_2\)/hectorite with different initial material ratios are given in Figure 3b–f. After the introduction of TiO\(_2\), the structure of TiO\(_2\)/hectorite is different from that of hectorite. The particle size of hectorite pillared by TiO\(_2\) is significantly reduced, showing a looser structure and disordered accumulation of flake structure, which can increase the specific surface area, enhance the adsorption ability, and improve the photocatalytic effect\[10\].

The lamellar structure of TiO\(_2\)/hectorite also shows that the ion leaching degree in the structure of hectorite is small and the skeleton is damaged to some degree, which is consistent with the XRD analysis results. The SEM images of TH-4 and TH-5 show a higher degree of agglomeration and lower nucleation of agglomerates in comparison with the TH-2 sample. In particular, the pattern of TH-5 gives an increase in irregular shape compared with other samples, which may be due to the excessive content of lithium ions inhibiting the entry of titanium ions into the layers of hectorite and agglomerating on the surface.

### 2.1.4. Transmission Electron Microscopy (TEM)

To further understand the structure of the composites, TEM was applied to characterize the microstructure. The TEM images of TH-1, TH-2, TH-3, TH-4, and TH-5 are shown in Figure 4. The black areas show that TiO\(_2\) is embedded in the interlayer of hectorite or supported on the surface, which is consistent with the XRD analysis results, indicating that some TiO\(_2\) enter the interlayer of hectorite. It can be seen from these images that TiO\(_2\) nanoparticles in TH-2 are well distributed in comparison with other samples, which is conducive to photocatalysis. Figure 4c shows that the distance (d) between two crystal faces of TiO\(_2\) is 0.353 nm, indicating the existence of an anatase phase structure of TiO\(_2\), corresponding to the (101) crystal plane of anatase\[29\]. The results suggest that the basic
structure of TiO$_2$ cannot be influenced by the hectorite, and the lattice plane of TiO$_2$ in contact with the hectorite surface is the (101) lattice plane.

Figure 3. Scanning electron microscopy (SEM) images: (a) hectorite, (b) TH-1, (c) TH-2, (d) TH-3, (e) TH-4, and (f) TH-5.
2.1.5. N₂ Adsorption-Desorption Isotherms

Figure 5 shows the N₂ adsorption-desorption isotherms and pore size distribution. According to the classification of IUPAC, the isotherms of all materials are regarded as type IV, corresponding to the mesoporous structure [30]. At the initial stage, N₂ adsorption capacities are greater than 0, indicating abundant micropores in the samples. Furthermore, the hysteresis loops of these samples belong to type H₃, which represent that the samples are lamellar particle materials with fissure structures [31].

The pore structure parameters including specific surface area (S_{BET}), pore volume, pore size, and crystal size are summarized in Table 1. Compared with hectorite, the surface area,
pore volume, and diameter of all composite samples increase, which would be beneficial to the adsorption and degradation of organic dyes. Among them, the TH-2 sample has the largest specific surface area of 491.97 m²/g, which is about twice that of hectorite and ten times that of commercial P25. The average pore size of TH-1~5 is larger than that of hectorite (3.16 nm), which proves that TiO₂ is successfully introduced into the interlayer of hectorite. At the same time, when the molar ratio of Li⁺ to Mg²⁺ is 1.32:5.34, most ions exchange between titanium ions and interlayer water molecules, Li⁺ is observed, and the interlayer spacing is largest. A higher specific surface area is beneficial to adsorption performance because it can provide more active sites, which can increase the contact area between organic pollutants and catalysts, thus increasing the photodegradation rate and improving the pollutant removal rate effectively ultimately.

Figure 5b is the pore size distribution curves calculated from Figure 5a. It can be observed that the pore size distribution curves of these samples are similar and the pore size is concentrated between 2 and 5 nm, which indicates again that hectorite and TiO₂/hectorite belong to the mesoporous structure. TH-2 displays a larger pore size distribution and the largest pore size, indicating that titanium ions have more chances to intercalate in the interlayer of hectorite under the condition. The pore size of TH-5 is larger than that of TH-4, which could be because of the increase in TiO₂ particles and their inhomogeneity [15].

2.1.6. Ultraviolet-Visible Diffuse Reflectance Spectra (UV-Vis DRS)

Figure 6 gives the UV-Vis DRS, and the optical absorption capacity of hectorite is weak in the wavelength range of 200~800 nm, which is probably attributed to its composition and particle size [10]. All the composite photocatalysts present an intense optical absorption under 425 nm compared with the single hectorite, indicating the electron Ti–O transformation and particle size [10]. The values of the band gap energies calculated from Equation (2) (Figure 6b) of hectorite (3.16 nm), which proves that TiO₂ has been successfully introduced into the interlayer of hectorite (3.16 nm), which proves that TiO₂ has been successfully introduced into the interlayer of hectorite under the condition. The pore size distribution curves of these samples are similar and the pore size is concentrated between 2 and 5 nm, which indicates again that hectorite and TiO₂/hectorite belong to the mesoporous structure. TH-2 displays a larger pore size distribution and the largest pore size, indicating that titanium ions have more chances to intercalate in the interlayer of hectorite under the condition. The pore size of TH-5 is larger than that of TH-4, which could be because of the increase in TiO₂ particles and their inhomogeneity [15].

Figure 6. UV-Vis diffuse reflectance spectra and band gaps: (a) reflectance spectra and (b) band gaps.
The values of the band gap energies calculated from Equation (2) (Figure 6b) of hectorite, TH-1, TH-2, TH-3, TH-4, and TH-5, are 3.33, 3.17, 3.06, 3.11, 3.14 and 3.22 eV, respectively. Except for TH-5, the band gaps of other composite photocatalysts are smaller than that of pure TiO$_2$ (3.2 eV). The TH-2 sample exhibits the strongest UV absorption capacity, thus providing a good opportunity to broaden the absorption band and improve the photocatalytic performance.

2.1.7. X-ray Photoelectron Spectroscopy (XPS)

The elemental states and surface components of the TH-2 sample were analyzed by XPS and are given in Figure 7. It mainly contains Ti, Si, Mg, F, C, and O, while the Li element in hectorite is not observed in TH-2 (Figure 7a). The phenomenon indicates that the ion exchange reaction has occurred in which Li ions are likely to be replaced by hydrogen ions or hydrate titanium ions during the reaction [10]. In addition, the leaching of Mg from the magnesia octahedron has a great influence on the skeleton structure.

The presence of a peak of F 1s for TH-2 with a binding energy at 685.2 eV is shown in Figure 7b, which is associated with the physical surface adsorption of F [34]. The UV-Vis DRS of TH-2 exhibits intense absorption in the UV region without an obvious redshift, which is consistent with the previous reports of F-doped TiO$_2$ [35,36]. In addition, the doping of the F element may contribute to the formation of oxygen holes.

![Figure 7. XPS spectra of TH-2 composite sample: (a) survey spectrum, (b) F 1s, (c) O 1s, and (d) Ti 2p.](image-url)
According to the spectrum of O 1s for TH-2 (Figure 7c), the peak at 530.1 eV demonstrates the existence of crystal lattice oxygen O$_2^-$ and the peak at 532.1 eV is mainly related to the Si–O bond from silicon lattice [32,37]. The surface adsorption of F (≡Ti–F) and surface –OH can proceed as follows (Equation (3)) [34], while it is difficult to see the peak of –OH as F occupies more space on the surface of the TiO$_2$/hectorite.

\[
≡ Ti – OH + F^- \leftrightarrow ≡ Ti – F + OH^- \quad pK_F = 6.2
\]  

Two strong peaks of Ti 2p at 458.8 eV and 464.6 eV are attributed to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ (Ti–O bond), respectively, indicating the existence of the Ti$^{4+}$ chemical state in the TH-2 photocatalyst [32]. Two peaks at 457.9 eV and 463.6 eV correspond to the Ti$^{3+}$ 2p$_{3/2}$ and Ti$^{3+}$ 2p$_{1/2}$, respectively, which confirms the formation of Ti$^{3+}$ [38,39]. As is well understood, Ti$^{3+}$ is generally considered to be beneficial for improving photocatalytic activity. The electron cloud density decreases with the binding energy [40,41]. Compared with pure TiO$_2$ (458.4 and 464.1 eV), the binding energy of Ti 2p$_{3/2}$ (458.8 eV) and Ti 2p$_{1/2}$ (464.6 eV) of TH-2 is much higher, which should be the formation of the Ti–O–Si bond between TiO$_2$ and hectorite [35,41,42]. The result indicates that the hectorite helps to promote the separation of e$^-$/h$^+$ pairs.

2.2. Photocatalytic Study

The photocatalytic performance of composite samples was studied in the degradation of MB with a 125 W high-pressure mercury lamp. The blank control group and P25 were used as comparisons. At low concentration, the photocatalytic degradation process conforms to the first-order kinetic equation, which can be fitted by the Langmuir-Hinshelword (L-H) model, as shown by Equation (4) [43,44].

\[
\ln \left( \frac{C_0}{C} \right) = kt,
\]  

where $C_0$ is the adsorption and desorption equilibrium concentration of MB, $C$ is the concentration of MB at time $t$, and $k$ is the photocatalytic kinetic constant. $k$ can be used to evaluate the photocatalytic performance, and the higher the value, the higher the catalytic efficiency. The photocatalytic performance of TH-1, TH-2, TH-3, TH-4, TH-5, and P25 was evaluated for MB degradation under UV light irradiation in Figure 8. On the one hand, Figure 8a shows the degradation curves at 10 ppm of MB for the samples TH-1, TH-2, TH-3, TH-4, TH-5, and P25, where their corresponding removal rates are 57.5%, 97.8%, 94.5%, 80.1%, 78%, and 60.7%, respectively. Without catalysis, the removal rate of MB is only 8.2%. The result of the photolysis does not show a significant reduction in MB, indicating that the irradiation with UV light by itself is not capable of degrading the dye. The composition of TiO$_2$ and hectorite clearly enhances the photocatalytic activity. Specifically, TH-2 and TH-3 show excellent photocatalytic activity, and photocatalysts are able to degrade 97.8% and 94.5% of MB within 60 min, while P25 and TH-1 only degrade MB by 60.7% and 57.5%, respectively. Although TH-1 has a higher surface area value than P25, its degradation is lower than that achieved by P25. The lower value from TH-1 can be attributed to the excess of defects present in the TH-1 sample, and P25 probably has a higher recombination of e$^-$/h$^+$ pairs by affecting the photodegradation. Therefore, its degradation is lower than those of TH-2, TH-3, TH-4, and TH-5. In particular, P25 (composed of ~30% rutile and 70% anatase) presents a better performance than TH-1, attributed to the transfer of electrons from Cb of anatase to those of rutile TiO$_2$ [32].
At the same time, the combination of TiO$_2$ prolongs their life, which improves the photoactivity. However, TH-1 could produce a defect valence band to the oxygen vacancy and Ti$^{3+}$, which impairs the photocatalytic MB degradation.

The photocatalytic performance of TH-1, TH-2, TH-3, TH-4, TH-5, and P25 was evaluated from the first-order kinetic fitting curve (Figure 8b), for the photodegradation of MB from highest to lowest, are shown in the order of TH-2 (0.04361 min$^{-1}$), TH-3 (0.03148 min$^{-1}$), TH-4 (0.0245 min$^{-1}$), TH-5 (0.02121 min$^{-1}$), P25 (0.01396 min$^{-1}$), and TH-1 (0.00898 min$^{-1}$) catalysts. The apparent rate constant of TH-2 is about 3.12 times that of P25. Based on these results, the removal rates of MB are increased by adding a quantity of TiO$_2$ in hectorite, and the highest degradation rate is achieved when the molar ratio of lithium, magnesium, and silicon is 1.32:5.34:8 (TH-2).

At the same time, the combination of TiO$_2$ and hectorite is beneficial to the generation of oxygen vacancies. These oxygen vacancies can trap the photogenerated species and prolong their lifetime, which improves the photoactivity. However, TH-1 could produce a defect excess and the formation of polycrystals by increasing the recombination of e$^-$/h$^+$ pairs, affecting the degradation of MB.

Based on the above result, the photocatalytic mechanism of TH-2 is given in Figure 9. First, TiO$_2$ in the interlayer of hectorite can increase the specific surface area to increase the adsorption capacity and contact of MB and the photocatalyst. Secondly, TiO$_2$ is uniformly dispersed on the hectorite to provide more active sites for the reaction. Thirdly, it is the most important that during the photocatalytic process, the electrons are stimulated from the valence band to the oxygen vacancy and Ti$^{3+}$ in TiO$_2$ under UV light irradiation, and the oxygen vacancy defect is beneficial to the adsorption of O$_2$, while the positive charge holes are left in the conduction band. At the same time, the negatively charged interlayer surface of hectorite is conducive to improving the photocatalytic activity, and the photogenerated holes can migrate to the surface quickly under the electronic attraction on the negatively charged interlayer surface.

In addition, photocatalytic activity is closely related to the behavior of photocarriers [45,46]. Subsequently, electrons (e$^-$) gathered on the surface of TiO$_2$ react with dissolved oxygen molecules in water to generate the superoxide radical anion ·O$_2^-$ and other high oxidation groups. As the conduction band has a more positive potential than that of ·OH/H$_2$O, the holes in the valence band react with water molecules (or surface hydroxyl groups) adsorbed on the surface of TiO$_2$ to form ·OH [34]. Furthermore, due to the adsorption of F on the surface of TiO$_2$, ·OH$_{free}$ is generated in the bulk solution. Finally, MB is oxidized into decomposed products by these active substances ·O$_2^-$ and ·OH.

**Figure 8.** (a) Photocatalytic degradation of MB under UV light; (b) the first-order kinetic fitting curve of the photocatalytic MB degradation.
Figure 9. Schematic illustration of a photocatalytic mechanism for the degradation process of MB under UV light toward TH-2 composite.

2.3. Reusability

Stability and reutilization are important to industrial application [47,48]. The reusability of the TH-2 composite is exhibited in Figure 10. After 5 cycles, the results show that the photoactivity can still achieve 87.9%, indicating the outstanding stability of TH-2. The decrease in catalytic activity may be mainly caused by the loss of surface area and the deposition of byproducts at the surface of the photocatalyst. It can result in the loss of active sites, agglomeration of nanoparticles, and reduction in crystallinity, which has been suggested by previous studies [49,50].

Figure 10. Reusability of TH-2 composite to the degradation of MB.

In addition, TiO$_2$/hectorite can be recovered from the mixture only by sedimentation, while P25 is difficult to precipitate due to its strong suspension force, indicating that the composite has good recyclability. It can be concluded that TiO$_2$/hectorite is an excellent catalyst material with stable activity and recoverability.
3. Materials and Methods

3.1. Materials

Tetrabutyl titanate (C_{16}H_{36}O_{4}Ti, TBOT, ≥99%) and anhydrous ethanol (C_{2}H_{6}O, ≥99.8%) were purchased from Aladdin Biochemical Technology Co., Ltd., Shanghai, China. Lithium fluoride (LiF), magnesium sulfate (MgSO_{4}), hydrochloric acid (HCl), sodium silicate (Na_{2}O·nSiO_{2}), sodium hydroxide (NaOH), and methylene blue (C_{16}H_{18}N_{3}ClS, MB) were all obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The Evonik Degussa P25 was provided by Evonik Industries AG, Frankfurt, Germany. Deionized water was used.

3.2. Synthesis of Photocatalysts

The TiO_{2}/hectorite nanocomposites were prepared through the one-pot hydrothermal method. First, a certain amount of LiF was added into 200 mL of distilled water with stirring to obtain an LiF dispersion. Secondly, a certain amount of MgSO_{4} was dissolved in 100 mL of distilled water, adding sodium hydroxide solution to obtain Mg(OH)_{2} precipitation. Then, the Mg(OH)_{2} was transferred to the LiF dispersion and stirred to form a uniform mixed slurry after being filtered and washed with deionized water. Subsequently, 18.46 g of sodium silicate (SiO_{2} 26% wt, Na_{2}O 8.2% wt) was added into 100 mL of distilled water with the dripping of hydrochloric acid to obtain SiO_{2}. Then, the SiO_{2} was transferred to the Mg(OH)_{2} and LiF mixed slurry and stirred to form a uniform mixed slurry (A) after being filtered and washed with deionized water.

Meanwhile, 1.1295 g of TBOT was dissolved in 10 mL of anhydrous ethanol with stirring for about 30 min to obtain a light yellow solution (B). Then, the dispersion mix A and solution B were put into the hydrothermal reaction kettle and reacted at 180 °C for 12 h. After the hydrothermal reaction, the solution was cooled to room temperature, centrifuged, washed, dried, ground, and finally sifted through 400 mesh to obtain a TiO_{2}/hectorite composite photocatalyst.

A starting mixture with different molar ratios of Li:Mg:Si (Si is 8) was prepared, as shown in Table 2. The five synthesized groups of catalysts were named TH-1, TH-2, TH-3, TH-4, and TH-5.

| Catalysts | Li:Mg:Si Molar Ratio of the Starting Mixture | Mass (g) |
|-----------|---------------------------------------------|----------|
|           | LiF | MgSO_{4} | Sodium Silicate |
| TH-1      | 0.72:5.64:8 | 0.1872 | 6.768 | 18.46 |
| TH-2      | 1.32:5.34:8 | 0.3432 | 6.408 | 18.46 |
| TH-3      | 1.92:5.04:8 | 0.4992 | 6.048 | 18.46 |
| TH-4      | 2.52:4.74:8 | 0.6552 | 5.688 | 18.46 |
| TH-5      | 3.12:4.44:8 | 0.8112 | 5.328 | 18.46 |

3.3. Characterizations

The crystallinity and structure of TiO_{2}/hectorite were obtained by the X’pert PRO Empyrean X-ray diffractometer (PANalytical, Almelo, The Netherlands) equipped with Cu-Kα radiation (λ = 0.15418 nm) at 45 kV and 40 mA. The scanning speed was 5°/min and the scanning range of 20 was 10–80°. The scanning electron microscopy (SEM) images were captured by a S-4800 scanning electron microscope (Hitachi, Tokyo, Japan) with an accelerated working voltage of 5 kV. TEM images were observed using a Tecnai F20 instrument (FEI Corp, Waltham, MA, USA) at 200 kV. The FTIR spectrum of these samples was recorded with a Nicolet iS5 FTIR spectrometer (Thermo Scientific, Madison, WI, USA) from 4000 to 400 cm^{-1}. The N_{2} adsorption-desorption isotherms were captured on a Micromeritics, ASAP 2460 nitrogen volumetric adsorption facility (Norcross, GA, USA) at liquid nitrogen temperature (77 K). The specific surface area and pore size were calculated by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda methods, respectively.
Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were recorded by using a UV-3600 spectrophotometer (Shimadzu, Tokyo, Japan) equipped with an integrating sphere, and BaSO$_4$ was used as the reference standard. X-ray photoelectron spectroscopy (XPS) was measured on a Thermo Scientific K-Alpha electron spectrometer (Thermo Fisher Scientific, Hillsboro, OR, USA) by using 12 kV Al-K$_\alpha$ X-ray radiation.

3.4. Photocatalytic Degradation

The photocatalysis of TiO$_2$/hectorite was studied by the degradation of MB in a photocatalytic reactor [10]. The photocatalytic degradation was performed under a 125 W high-pressure mercury lamp. The Mercury lamp was preheated for 30 min before reaction to ensure stable luminescence. The lamp was kept approximately 30 cm away from the solution.

Firstly, 3 mg of the TiO$_2$/hectorite catalyst was dispersed in 100 mL of 10 ppm MB solution. Then, the mixture was stirred magnetically for 30 min in the dark to achieve adsorption-desorption equilibrium. After that, with underexposure of UV light, 3 mL of suspension was taken every 10 min and filtered by a 0.45 µm membrane to remove photocatalyst. The absorbance of the filtrate was determined by a WF Z UV-2800H UV-vis spectrophotometer (Unico, Suite E Dayton, NJ, USA) at 664 nm to evaluate the photocatalytic efficiency. The removal rate of MB was calculated by Equation (5):

$$ R = \frac{C_0 - C_t}{C_0} \times 100, $$

where $C_0$ (mg/L) is the initial concentration of MB and $C_t$ (mg/L) corresponds to its concentration at time $t$.

After the photocatalytic degradation, the MB adsorbed on the material was completely degraded by irradiation under UV light. Then, the MB solution and photocatalytic materials were separated by centrifuge and dried at 120 °C for 2 h for recycling.

4. Conclusions

TiO$_2$ was introduced into the interlayer of hectorite by the one-pot hydrothermal method and the synthesized TiO$_2$/hectorite composites exhibited a higher UV photocatalytic activity than commercial P25. The number of titanium ions entering into the hectorite layer was changed by adjusting the molar ratio of lithium and magnesium in the raw material. The materials synthesized in this study showed anatase phase TiO$_2$, and the appropriate amount of lithium ion was beneficial to improve the crystallinity of the products according to XRD and FTIR analysis. SME and TEM studies indicated that TiO$_2$/hectorite showed a looser structure after being pillared by TiO$_2$ in comparison with hectorite, and the layer spacing of TiO$_2$ was 0.353 nm. In the N$_2$ adsorption-desorption analysis, TH-2 presented the largest specific surface area, the strongest adsorption capacity, and the best photocatalytic effect. UV-Vis DRS studies showed that the absorption band edge of TiO$_2$/hectorite was redshifted and its UV absorption capacity became stronger after TiO$_2$ incorporation, indicating the electron Ti–O transformation of TiO$_2$. XPS analysis indicated that Li or Na ions of hectorite were easily replaced by titanium ions or hydrogen ions during the preparation process, which can promote the separation of e$^-$-h$^+$ pairs.

The results showed that a suitable ratio of lithium to magnesium is beneficial to the improvement of the photocatalytic effect. When the molar ratio of lithium, magnesium, and silicon was TH-2 of 1.32:5.34:8, the TiO$_2$/hectorite photocatalyst had the highest removal rate of MB dye (97.8%). In addition, the TH-2 sample could be easily recycled and the removal rate of the MB still achieved 87.9% after five cycles, indicating good reusability. High specific surface area, strong light capture ability, and great e$^-$-h$^+$ separation efficiency are favorable for the promotion of photoactivity. The formation of oxygen vacancies and Ti$^{3+}$ can also promote the separation of photogenic e$^-$ and h$^+$. Therefore, TiO$_2$/hectorite has good photoactivity and reusability as a UV photocatalyst to be used in the field of photodegradation of organic pollutants.
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