Degradation of phenol by photocatalysis using TiO$_2$/montmorillonite composites under UV light

Huijuan Li$^1$ · Yeting Yao$^1$ · Xiaoyan Yang$^{1,2}$ · Xusheng Zhou$^1$ · Ran Lei$^1$ · Sufang He$^{2,3}$

Received: 2 September 2021 / Accepted: 1 May 2022 / Published online: 10 May 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

Abstract
Composites of titanium (IV) oxide combined with montmorillonite (MMT) with various TiO$_2$/MMT were prepared for photocatalysis application. The prepared samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), diffuse reflectance UV–visible spectroscopy, and X-ray photoelectron spectroscopy (XPS). The main influential factors such as the TiO$_2$/MMT dose, calcined temperature, and pH value of the solution were studied. The main intermediates of phenol degradation were determined by high performance liquid chromatography (HPLC). The results showed that the average size of TiO$_2$ nanoparticles was decreased from 22.51 to 10.66 nm through the immobilization on MMT. The components in the interlayer domain were replaced by titanium pillars, and the pillaring reaction proceeded in the interlayer domain, the basic skeleton of MMT was unchanged, and TiO$_2$ was dispersed on the surface of the MMT. When the initial concentration of phenol is 10 mg/L, the phenol solution pH is 6, and the UV light irradiation time is 240 min; the phenol degradation rate of 30%TiO$_2$/MMT composite is 89.8%, which is better than MMT (11.5%) and pure TiO$_2$ (58.8%). It shows that TiO$_2$ loaded on MMT improves its photocatalytic activity. The phenol reaction process detected by HPLC showed that it had undergone through hydroquinone and benzoquinone, and finally converted into maleic acid and carbon dioxide and small molecules. The possible photocatalysis mechanism is presented.

Keywords Montmorillonite · Titanium dioxide · Sol–gel method · Phenol degradation

Phenol and its derived compounds are one of the most toxic compounds and are used widely in petrochemical, chemical, and pharmaceutical industries. When they enter into the natural waters, they will cause serious pollution and great harm to the environment. Drinking water containing phenols may cause severe renal insufficiency, convulsions, and even death (Ruikun Wang et al. 2019). Phenol degradation techniques include adsorption, extraction, electrolysis, and photocatalytic oxidation (Muniandy and Adam 2014). Among them, TiO$_2$-based catalysts can handle higher concentrations of phenol-containing wastewater, mild reaction conditions, high treatment efficiency, and no secondary pollution, and they are widely used for photoelectric conversion, photochemical synthesis, and photocatalytic oxidation of environmental pollutants (Paulina Górska et al. 2009; Ali et al. 2012). However, poor adsorption, narrow absorption spectrum, and difficult recovery of nanoparticles of TiO$_2$ limit its application in water treatment (Sreenivasan Koliyat Parayil et al. 2012).

Montmorillonite (MMT) is a layered aluminosilicate mineral; its theoretical molecular formula is $\text{N}^{2+}_{x/3}\text{M}^{2+}_x\text{Si}_{8-x}\text{Al}_x\text{O}_{20}(\text{OH})_4\cdot n\text{H}_2\text{O}$. The unit is composed of two layers of silicon-oxygen tetrahedron with a layer of aluminum-oxygen octahedron. It belongs to a 2:1 type structure with swellable hydrous aluminosilicate. The special crystal structure makes montmorillonite have ion...
exchange capacity and dispersion suspension stability. It possesses layered structures, larger interlayer distance, specific surface area, and thermal stability, which can be obtained through physical and chemical methods such as pillarating, insertion replacement, and ion exchange (Ouachtak et al. 2021). Y. X. Liu studied the commercially available montmorillonite KSF as photoactive reagent and utilized for BPA photodegradation and found that the BPA degradation increased with the concentration of clays in the range of 0.5 to 5 g/L. The photodegradation rate of BPA is fitted well into the Langmuir–Hinshelwood equation (Y. X. Liu et al. 2008). K. Mogyorósi et al. prepared clay mineral–intercalated TiO₂ nanoparticles and found that calcination was not necessary for nanocomposite preparation that had high specific surface areas and well-crystallized anatase contents and thus could be used as an efficient photocatalyst (K. Mogyorósi et al. 2003). Daimei Chen et al. synthesized TiO₂-pillared montmorillonite and investigated it for methylene blue photocatalytic activity; the prepared TiO₂/MMT composites exhibited superior photocatalytic property, and the maximum removal efficiency was up to 98% within 90 min (Daimei Chen et al. 2012).

In this paper, TiO₂/MMT composites were prepared by a sol–gel method. The phenol solution was used as model degradation molecular. The effects of TiO₂ loading amount, calcination temperature, and solution pH on the degradation of phenol by TiO₂/MMT composites were investigated. FTIR, XRD, and SEM techniques were used to characterize the prepared composites.

Experimental

Materials

The montmorillonite (MMT) was supplied from Xinghe County, Inner Mongolia, China (purity 85%, major compositions: SiO₂, 78%; Al₂O₃, 11.63%; MgO, 3.71%; Fe₂O₃, 2.81%; and CaO is 2.03%). The other components of MMT are shown in Table 1: phenol, AR, Chengdu Kelong Chemical Reagent Factory; sodium chloride, AR, Chengdu Kelong Chemical Reagent Factory; 4-aminantipyrine, CR, Shanghai Qiangshun Chemical Reagent Co., Ltd.; potassium ferricyanide, CR, Shanghai Qiangshun Chemical Reagent Co., Ltd.

Sample preparation

1. Modification of montmorillonite (MMT)

Montmorillonite (Ca-MMT, 100 g) was dispersed into 1000 mL 1.0 mol/L NaCl solution and stirred for 2 h at 60 °C water bath. Then, the resulting suspension was separated by centrifugation and washed with distilled water until no Cl⁻ (using 0.1 mol/L AgNO₃ test), dried at 110 °C for 24 h, and ground; sodium montmorillonite (Na-MMT) can be obtained after 100 mesh.

2. Preparation of TiO₂

TiO₂ was synthesized through sol–gel method. Five milliliters of tetrabutyl titanate was dissolved in 7 mL anhydrous ethanol under vigorous stirring. At the same time, the above solution was dropwise added to a mixture with 15 mL ethanol, 8 mL deionized water, and 2 mL acetic acid to make a solution. Under vigorous stirring conditions, the viscosity of the mixed solution turns more and more and then changed into a sol. The product was aged for 24 h, dried at 110 °C for 24 h, and finally at different temperature for 4 h.

3. Preparation of TiO₂/MMT

The TiO₂ sol was mixed with a certain percent of modified Na-MMT aqueous suspension. In this mixed suspension, the beaker was rinsed with absolute ethanol and thoroughly stirred to prepare TiO₂/MMT. Aged for 24 h, the sol was dried at 110 °C for 24 h, and then placed in a muffle furnace (Shanghai Chongming Experimental Instrument Factory) and calcined at a certain temperature (300–600 °C) for 4 h; a modified TiO₂/MMT is obtained (named as w%TiO₂/MMT, which w is the mass percentage of TiO₂ and MMT; 40% TiO₂/MMT means that the TiO₂ mass is 0.4 and the MMT mass is 1.00).

Characterization

The as-prepared samples were characterized by different techniques. The crystalline phases of the TiO₂/MMT composites were investigated with X-ray diffraction (XRD, Rigaku D/Max 2000, Cu Kα radiation source with wavelength of λ = 0.15418 at 40 kV and 30 mA). The Fourier transform infrared (FT-IR) spectra were recorded on a Spectrum 100 spectrometer (BRUKER TENSOR27). Transmission electron microscopy (TEM, JEOL LEM-100CXII) and scanning electron microscope (SEM, S-3000 N, Hitachi, Japan) were used to observe the microstructure.

| Table 1 Compositions of MMT |
|-----------------------------|
| Composition | Content/wt% | Composition | Content/wt% |
| SiO₂       | 78.44        | SO₃          | 0.19        |
| Al₂O₃      | 11.63        | TiO₂         | 0.17        |
| MgO        | 3.71         | MnO          | 0.04        |
| Fe₂O₃      | 2.81         | P₂O₅         | 0.035       |
| CaO        | 2.03         | SrO          | 0.034       |
| K₂O        | 0.59         | ZnO          | 0.01        |
| Na₂O       | 0.26         | Rb₂O         | 0.008       |
of the as-prepared composites. Using BaSO$_4$ as the reflectance sample, the UV–Vis diffuse reflectance spectra were recorded with a HITACHI U-3010 spectrometer. The surface properties of the composites were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo, USA). The chemical states and the surface electronic states were analyzed based on binding energies.

**Photocatalytic degradation of phenol**

The photocatalytic activities of the produced TiO$_2$/MMT composites were measured by degrading phenol. In each experiment, 0.2 g photocatalyst was added to 100 mL solution (10 mg/L, the initial pH is 6; if the pH needs to change, adjust with acetic acid and ammonia). The mixed solution was stirred in the dark for 30 min in order to reach an adsorption–desorption equilibrium. Then, the suspension was irradiated with a UV light source (300 W, Optima wavelength 365 nm). During the irradiation period, an aliquot of 2.0 mL suspension was collected at regular 30-min intervals, and then centrifuged to remove the photocatalyst; the aliquots were immediately centrifuged and analyzed using UV–Vis spectrometer (UV-1800, Shimadzu).

In order to quantify the evolution of intermediate products, the extinction coefficients of maleic acid (MA), fumaric acid (FA), hydroquinone (HQ), catechol (CC), benzoquinone (BQ), and phenol (PhOH) were measured independently. The concentrations of phenolic compounds were calculated using high performance liquid chromatography (HPLC, PerkinElmer Altus 30) equipped with a Sinochrom ODS-BP column (3.5 μm; 4.6×250 mm) and a 220/240 pump, and also equipped with a Spectra 100 UV–Vis detector to identify the degradation products as an evaluation of the photocatalytic activity of the synthesized TiO$_2$/MMT composites. The mobile phase composition of methanol/NaH$_2$PO$_4$ (with 0.5 mol/L) ratio was 70:30. The mobile phase was delivered at a flow rate of 1.0 mL/min, and the detection wavelength was set at 254 nm. The 10-μL solutions were filtered on a 0.45-μm cellulosic filter before being injected into the HPLC chromatography.

**Results and discussion**

**XRD results**

The XRD pattern of the as-prepared pure MMT, TiO$_2$, and 30%TiO$_2$/MMT catalysts is shown in Fig. 1. For pure montmorillonite, the diffraction peak at 2$\theta = 19.77^\circ$, 21.85$^\circ$, and 26.76$^\circ$ is attributed to the Si–O–Si diffraction peak of Na-montmorillonite, the Si–O–Al, and the (101) of quartz, respectively. The original montmorillonite sample (MMT) shows a series of reflections at 2$\theta = 18.64^\circ$ with d003 = 0.448 nm and 2$\theta = 19.77^\circ$ with d100 = 0.449 nm, respectively. According to the JCPDS card (No. 00–003-0010), it is corresponding to Na-montmorillonite (Hongjuan Sun et al2015b, a). The diffraction peaks of TiO$_2$ at 2$\theta = 25.2^\circ$, 38.1$^\circ$, 47.7$^\circ$, and 54.4$^\circ$ correspond to those of anatase (101), (004), (105), and (204), respectively. At the same time, there is a rutile characteristic diffraction peak (2$\theta = 27.43^\circ$) for pure TiO$_2$ (600 °C, 4 h) and 30%TiO$_2$/MMT (700 °C, 4 h) which suggests that the montmorillonite as a carrier can increase TiO$_2$ phase transition temperature and make it still anatase phase after being calcined at 600 °C. The positions of the characteristic diffraction peaks of montmorillonite in the 30%TiO$_2$/MMT composite calcined at different temperatures have no obvious change, and the peak strength is weaker. It can be seen that the introduction of TiO$_2$ does not change the structure of montmorillonite. The diffraction peaks of TiO$_2$/MMT at 2$\theta = 26.76^\circ$
and 31.02° are obviously weakened or even disappeared compared with the original montmorillonite, which indicates that the original Si–O–Al bond was destroyed, and a new Si–O–Ti bond is constructed after replacing the aluminum ion in the interlayer (Djouadi et al. 2018). For the used 30% TiO2/MMT (600 °C, 4 h) composites, it can be seen that the diffraction peaks of MMT decreased and the TiO2 diffraction peaks increased compared as the fresh samples, which can be inferred as the TiO2/MMT composite dissociation as TiO2 and MMT to some extent, and the separated MMT dissolved in the reaction solution.

The average crystal size of the particles can be estimated from the widths of TiO2/MMT composite reflections by using the Scherrer formula,  

$$d = \frac{0.89 \cdot \lambda}{\beta \cdot \cos \theta},$$

where λ (1.5413 Å) is the wavelength, θ is the Bragg angle (°), d is the average crystallite size (nm), and β is the full width at half-maximum. The calculated data of the six TiO2-based catalysts are followed in Table 2.

It can be seen from Table 2 that the grain size of TiO2 reduces from 22.51 to 10.66 nm for pure TiO2 and 30% TiO2/MMT calcined at 600 °C for 4 h, indicating that the particle size of TiO2-pillared montmorillonite decreased effectively. And the crystalline size of TiO2 in 30% TiO2/MMT composites calcined at different temperatures also gradually increased with the temperature.

### SEM, TEM, and EDX images

Figure 2 displays the SEM images and EDX analysis of MMT, 30% TiO2/MMT, and used 30% TiO2/MMT composites, and also TEM images of pure TiO2 calcined at 600 °C for 4 h. The raw montmorillonite shows larger particle aggregates with a flower-like layer structure; the flaky structure is relatively close. According to the EDX results, the raw montmorillonite contains 13.4 wt.% of Si, 2.2 wt.% of Al, and 0.8 wt.% of Fe, and other elements such as O, C, and Mg are also presented in its structure. For the 30% TiO2/MMT (600 °C, 4 h) composite, the larger platelets and layer structure of montmorillonite can be observed clearly. Since the TiO2 nanoparticles were intercalated, the layer space was enlarged and the structural layers of montmorillonite were separated (R. Djellabi et al. 2014). Although the montmorillonite layers were still largely parallel, they lost long-range order in the c direction after TiO2 intercalation, which is consistent with the disappearance of the (001) reflection in the XRD patterns (Ping Zhang et al. 2014). And there are a lot of small aggregates, which are probably broken platelets and agglomerates of TiO2 crystallites caused by the hydrolysis of surface Ti(OC4H9)4 (Boualem Damardji et al. 2009). According to the EDS results, the material contains 9.3 wt.% of Si, 6.7 wt.% of Ti, 3.7 wt.% of Al, and 0.8 wt.% of Fe, and other elements such as O, C, and Mg are also presented in its structure. For the used 30% TiO2/MMT (600 °C, 4 h) composite, the layer structure of montmorillonite is also existed obviously, but the bulk of composites became smaller than the fresh ones because of reaction with stirring mix. Also, some particles are on the surface of the montmorillonite which may be the TiO2 nanoparticles. According to the EDX results, the material contains 1.6 wt.% of Si, 17.2 wt.% of Ti, and 1.0 wt.% of Al, and other elements such as O, C, and Ca are also presented in its structure. It can be seen that the Ti content increased, and the Si, Al, and other element contents decreased after reaction. We preferred that this phenomenon maybe caused by the acid produced in the reaction, which solved some metals such as Mg and Al and caused the Ti content to be increased, and also the photocatalytic activity can be kept.

### XPS analysis

X-ray photoelectron spectroscopy (XPS) measurements were carried out to probe surface composition and chemical state (up to 3 nm in depth) of the 30% TiO2/MMT and used 30% TiO2/MMT. The survey spectrum of the two photocatalysts indicates the presence of Si, Ti, O, and C elements (Fig. 3a). For the two samples, the O 1 s peaks at 531.5, 530.6, and 528.6 eV are attributed to physisorbed water, O atoms associated with surface Ti–OH species, and lattice oxygen with TiO2, respectively (Fig. 1c) [1]. The percentage of the three species in surface O species for fresh 30% TiO2/MMT was calculated to be 30.6, 37.4, and 32.0%, respectively. For the used 30% TiO2/MMT, the three species ratio was 20.6, 56.3, and 23.1%, calculated by XPS based on the ratio of the species peak area and the total O 1 s XPS spectrum area. It can be seen that the amount of O atoms associated with surface Ti–OH species on the used 30% TiO2/MMT is higher than the fresh one, suggesting that Ti–OH was produced in the photocatalysis reaction. Ti2p curves possess two peaks at 456.9 and 462.7 eV for the fresh and used 30% TiO2/MMT, allocating to 2p 3/2 and 2p 1/2 of Ti(IV) binding state, respectively (Fig. 3d). Ti2p peak in used 30% TiO2/MMT XPS spectrum gets stronger compared to that of the fresh one, implying more Ti–OH generation.

### Table 2

| Sample | d/ nm |
|--------|-------|
| TiO2 (600 °C, 4 h) | 22.51 |
| 30% TiO2/MMT (400 °C, 4 h) | 6.61 |
| 30% TiO2/MMT (500 °C, 4 h) | 7.68 |
| 30% TiO2/MMT (600 °C, 4 h) | 10.66 |
| 30% TiO2/MMT (700 °C, 4 h) | 29.50 |
| 30% TiO2/MMT (600 °C, 4 h) | 12.81 |
after reaction, which is in line with its EDX analysis (Han et al. 2019).

**FT-IR characterization**

Figure 4 presents FT-IR spectra of different samples of TiO₂, MMT, and TiO₂/MMT dried at 110 °C and calcined at 600 °C for 4 h, respectively. For the purified MMT, the broad band at 3422 cm⁻¹ is due to the stretching vibration of the hydroxyl group and the interlayer water molecules. And the weak peak at 3624 cm⁻¹ is attributed to –OH stretching vibration of Al–O–H. Bands at 1645 cm⁻¹ and 1468 cm⁻¹ are caused by the bending vibration of the hydroxyl group and the interlayer water molecules. The vibration peak at 1079 cm⁻¹ is caused by the antisymmetric stretching vibration of Si–O–Si in montmorillonite, which was caused by the strong hydration of Ca, Mg, and Al plasma strengthening the hydrogen bond between the surface of montmorillonite layer.
and water and weakening and dissolving the band of Si–O bond, resulting in the changing of Si–O and Si–O–Si into a single peak [16]. Bands at 845 cm$^{-1}$ and 794 cm$^{-1}$ attribute to the bending vibration peak of Mg$^{2+}$–OH and the hydroxyl vibration of MgAl–OH, respectively. And bands at 521 cm$^{-1}$, 474 cm$^{-1}$, and 916 cm$^{-1}$ are suggested to the bending vibration of Si–O–Al, Si–O–Si, and octahedral Al–O(OH)–Al in montmorillonite independently. The broad peak at 587 cm$^{-1}$ is attributed to Ti–O bond vibration, which indicates that TiO$_2$ is amorphous. After TiO$_2$-modified MMT, interlayer water and hydroxyl increased, which restricted the vibration of structural hydroxyl Al–OH. The peak at 3621 cm$^{-1}$ lost, and the two peaks at 1021 and 917 cm$^{-1}$ appeared; it shows that the composition of the interlayer of montmorillonite changed after TiO$_2$ was introduced, and the in-plane stretching vibration peaks of Ti–O–C and Si–O–Si were generated (Lingling Yuan et al. 2011; Chihiro Ooka et al. 2003). Also, at 796 cm$^{-1}$, the absorption of the hydroxyl vibration peak of MgAl–OH weakened, which may be related to the removal of hydroxyl as octahedron Ti hydrated ions into the interlayer. At the same time, the strength of 521 cm$^{-1}$ peak in the composite is obviously weakened and widened, which is the superposition of Ti–O and Si–O absorption peaks.

The results show that the strength of Si–O bond is also affected by titanium in lay. For the 30%TiO$_2$/MMT calcined at 600 °C for 2 h, 3422 cm$^{-1}$ and 916 cm$^{-1}$ disappear, while 1468 cm$^{-1}$ peak strength decreases, indicating that interlayer water lost. The vibration peak of Ti–O becomes narrow at 600 cm$^{-1}$, indicating the TiO$_2$ crystal phase formed. At the same time, the 1070 cm$^{-1}$ peak of 30%TiO$_2$/MMT changed into a single peak, which seems that the basic framework of MMT remained unchanged and retained its original structure. For the 30%TiO$_2$/MMT calcined at different temperatures, it can be seen that the peaks at 3625 cm$^{-1}$, 1030 cm$^{-1}$, and 845 cm$^{-1}$ gradually disappear, and the peaks of 3431 and 1648 cm$^{-1}$ gradually

![Fig. 3 XPS spectra of the fresh and used 30%TiO$_2$/MMT composites: (a) survey, (b) O1s spectrum for fresh 30%TiO$_2$/MMT, (c) O1s spectrum for used 30%TiO$_2$/MMT (d) Ti2p spectrum](image-url)
decrease, which is caused by the evaporation of interlayer water (V. Makrigianni et al. 2015).

UV–Vis spectra

Figure 5 shows diffuse reflectance UV–Vis spectra of 30%TiO2/MMT calcined from 400–700 °C. It can be seen from the Fig. 5 that the absorption band of pure TiO2 at 200–400 nm belongs to the electron coordinated by the titanium coordinated oxygen atom to the empty orbit of the central titanium atom, the characteristic absorption formed by OB2p → TiB3dz charge transfer, in which the tetrahedron at 248 nm. The characteristic peak of coordination titanium, the absorption peak around 337 nm was the absorption peak of octahedral coordination titanium (Aydin Has-sani et al. 2015). The peaks of 30%TiO2/MMT composites calcined at different temperatures around 433 and 504 nm are Fe–O absorption peaks of Fe2O3, because of the used montmorillonite content of 2.8% Fe2O3. At the same time, 30%TiO2/MMT composites calcined at different temperatures have a strong light absorption performance. The value of Eg was deliberated from the UV–visible pattern of the titled TiO2/MMT by extrapolating the line through the k axis, and it is exposed in Fig. 5. The wavelength maxima was 409.6 nm (pure TiO2), 427.1 nm (30%TiO2/MMT, 400 °C), 434.7 nm (30%TiO2/MMT, 500 °C), 418.4 nm (30%TiO2/MMT, 600 °C), and 451.5 nm (30%TiO2/MMT, 700 °C), respectively. Since the photoabsorption performance of the photocatalyst is positively related to the photocatalytic degradation activity of phenol, it was confirmed that the 30%TiO2/MMT (600 °C, 2 h) prepared by the sol–gel method has the best photocatalytic activity for phenol degradation.

Photocatalytic activity

Effect of TiO2 loading amount on TiO2/MMT

Figure 6 shows the phenol removal efficiency under UV light over MMT, TiO2, and different loading of TiO2 on TiO2/MMT calcined at 600 °C for 4 h. The results showed that the photolysis of phenol in the absence of photocatalyst is only 1.5%, which can be neglected. And the phenol degradation is 11.5% over MMT which shows that MMT has a certain adsorption capacity for phenol solution, but the adsorption activity was very low. It has 58.5% photocatalysis activity over pure TiO2. Also, for different amount loading of TiO2/MMT, the results indicated that the photodegradation efficiency of phenol increased with TiO2 content until 30%TiO2, then decreased after more TiO2 loading. Because TiO2 was the active center of the photocatalytic reaction, when its loading is less, the phenol degradation is low. When the loading of TiO2 was overdone, photo-generated electrons...
and holes were generated under light conditions, and the
photo-generated electrons and holes recombine to form a
composite band, which affects the formation of hydroxyl
active groups, reduces the utilization of ultraviolet light, and
causes reduced degradation efficiency. It was concluded that
the photocatalytic activity of 30%TiO2/MMT composites has
the best phenol degradation performance under ultraviolet
light.

Theoretically, the adsorption and degradation activity of
TiO2/MMT composites on phenol was the sum of the phe-
nol adsorption on montmorillonite and photodegradation
over pure TiO2. However, it can be seen from Fig. 6 that
the phenol adsorption rate of montmorillonite was 11.5%
and the degradation rate of TiO2 was 58.8% after 240 min
under UV light; the sum of the two was only 70.3%, which
is significantly lower than the 30%TiO2/MMT composite
(89.75%). On the one hand, the loading of montmorillonite
may increase the crystalline phase transition temperature of
TiO2 to a certain extent; it still maintains the anatase phase
structure at 600 °C. And it increases the degree of
TiO2 dispersion and makes its particles smaller, which contrib-
uted to improving the phenol degradation over TiO2/MMT
composites (Hongjuan Sun et al. 2015b, a).

Effect of calcined temperature

Figure 7 shows the phenol photocatalytic degradation over
30%TiO2/MMT composites calcined at different tempera-
tures (from 300 to 700 °C). For the 30%TiO2/MMT com-
posites calcined from 300 to 600 °C, it can be seen that the
degradation rate gradually increased with roasting tempera-
ture. When calcined at 600 °C, the phenol degradation rate
reached 89.75%, but it is only 15.08% when the roasting
temperature is 700 °C, which decreased significantly. In this
catalytic reaction system, the optimal calcination tempera-
ture of 30%TiO2/MMT photocatalytic composite is 600 °C.

The effect of the initial pH

The solution pH is one of the important parameters that
can markedly affect the photocatalytic process. In the
present work, the effect of the initial pH on the phenol
photocatalytic degradation efficiency was studied in the
pH range of 2–12 (Fig. 8). In this experiment, acetic acid
and ammonia are usually used to adjust the pH value
of the solution. The results indicated that the degree of

![Fig. 6 Phenol photocatalytic degradation over different photocatalysts calcined at 600 °C, 4h](image)

![Fig. 7 Phenol photocatalytic degradation rate over 30%TiO2/MMT composites calcined at different temperatures](image)

![Fig. 8 Phenol degradation activity of 30%TiO2/MMT composites in different pH reaction solutions](image)
Photodegradation efficiency increased with the pH values from 2 to 6 and then decreased. It can be seen from Fig. 8 that the photocatalytic performance of the reaction solution under slightly acidic conditions was significantly higher than that obtained under slightly alkaline conditions; the pH value will change the interfacial charge of the TiO₂/MMT, thereby changing the dispersion of the particles in the solution and affecting the adsorption behavior of the montmorillonite matrix on the catalyst surface. In the photocatalyst reaction, the electrons were excited from the valence band to the conduction band, forming electrons (e⁻) and holes (h⁺). The highly active holes consume OH⁻ in water during the reaction and oxidize them to have strong oxidative active -OH, then e⁻ and h⁺ undergo redox reactions with substances dispersed in water. As the pH value increases, the concentration of OH⁻ in the solution sharply increases, and then the concentration of -OH increased significantly, and the conduction electrons reacted with the adsorbed O₂ to form O₂⁻, which could also generate -OH with H₂O, so the degradation efficiency increased with the pH value. However, too high a concentration of -OH will cause a decrease in photocatalytic activity (Chunquan Li et al. 2021). Therefore, the photocatalytic effect was better under suitable pH conditions, which has a high photocatalytic degradation rate under acidic conditions.

The effect of 30%TiO₂/MMT (600 °C, 4 h) dosage

Catalyst dosage is an important parameter in heterogeneous photocatalytic reaction. In order to determine the effect of catalyst dosage on the phenol photodegradation, experiments were carried out by varying the amount of 30%TiO₂/MMT from 0.1 to 0.4 g (Fig. 9). Increasing the amount of photocatalyst from 0.1 to 0.2 g resulted in increasing the photodegradation efficiency from 42.25 to 89.96% at the reaction time of 240 min, respectively. Adding the catalyst dosage promoted the production of reactive species. However, more catalyst dosage would also induce greater aggregation of the catalysts and add the turbidity of the solution, reduce the degree of light penetration through the solution and thereby lead to a reduction in the phenol degradation efficiency. Therefore, 0.2 g 30%TiO₂/MMT photocatalysts is the best amount for phenol photocatalytic reaction (Shivatharsiny Rasalingama et al. 2014).

The recyclability and stability of the 30%TiO₂/MMT composite

To examine the recyclability and stability of 30%TiO₂/MMT (600 °C, 4 h), a cycle test of phenol degradation was carried out under optimal conditions. After each reaction cycle, the 30%TiO₂/MMT (600 °C, 4 h) photocatalyst
was separated from the solution after filtering and drying at 110 °C for 8 h; before each analysis, the results are shown in Fig. 10a. It can be seen that phenol photoactivities keep constant for the sixth cycle, about 88% phenol removal efficiency. Fig. 10b shows the pure TiO₂ and 30%TiO₂/MMT (600 °C, 4h) photocatalyst stability for phenol degradation under UV light irradiation for 48h (the reaction condition: C₀ = 10mg/L, catalyst: 0.2g/L). It can be seen that the relatively good degradation activity of the catalyst for phenol is 30%TiO₂/MMT photocatalytic composite, followed by pure TiO₂, but the photocatalytic activity of the four catalysts finally changes little and tends to reach higher. It can be seen that 30%TiO₂/MMT (600 °C, 4 h) had better repeatability and stability for phenol degradation.

HPLC analysis

HPLC was employed to identify the degradation products in order to evaluate the catalytic activities over the pure TiO₂ (600 °C, 4 h) and 30%TiO₂/MMT (600 °C, 4 h) photocatalysts (Fig. 11). Under our experimental conditions, benzoquinone (BQ), hydroquinone (HQ), maleic acid (MA), and fumaric acid (FA) have been identified as intermediates. It should be noted that the four compounds were produced in significant amounts during photocatalytic degradation with the two photocatalysts. For the pure TiO₂, the phenol concentration gradually decreased with the reaction time. It found that the four materials (HQ, BQ, MA, and FA) are the main aromatic compounds produced by phenol conversion. The highest concentration of the four materials is detected at 210 min and then decreased gradually; also, the MA and FA keep the higher concentration than BQ and HQ, which might be caused by that the BQ and HQ can turn into MA and FA or the phenol itself will be further converted into maleic acid and fumaric acid, and the residual phenol concentration was 27.17 mg/L after reaction for 420 min. During

Fig. 10  The recyclability (a) and stability (b) of phenol removal rate by UV light using 30%TiO₂/MMT (600 °C, 4 h) as photocatalyst. Reaction condition: [Phenol]₀ = 10 mg/L, [30%TiO₂/MMT (600 °C, 4 h)]₀ = 2.0 g/L, pH = 7.0

Fig. 11  HPLC chromatograms recorded during phenol decomposition under UV light on (a) TiO₂ and (b) 30%TiO₂/MMT photocatalysts
the phenol photocatalytic degradation over TiO$_2$, phenol is gradually degraded in the progress of the reaction, and most of it is directly mineralized into CO$_2$ and water (Asma Turki et al. 2015).

For the 30%TiO$_2$/MMT catalyst, with the extension of the photocatalytic reaction time, the phenol concentration in the residual solution decreased significantly. After 420 min reaction, the residual phenol concentration was 9.36 mg/L. Total benzoquinone (HQ), hydroquinone (BQ), maleic acid, and fumaric acid (FA + MA) was produced by the photocatalytic degradation system of 30%TiO$_2$/MMT. Compared with the pure TiO$_2$ system, 30%TiO$_2$/MMT had more phenol photo-degradation efficiency, and the total amount of intermediate products detected is larger than that in the TiO$_2$ system. The larger amount of HQ + BQ is due to the higher selectivity of 30%TiO$_2$/MMT in the phenol conversion. The loading of montmorillonite makes ·OH produced by TiO$_2$ easier to attack the para position of phenol. Hydroquinone is produced and further converted into p-benzoquinone. The amount of butadionic acid (FA + MA) detected in the reaction system of 30%TiO$_2$/MMT for phenol degradation was higher than that of pure TiO$_2$. Considering the production of HQ + BQ and FA + MA amount produced in this system, their concentration increased first and then decreased. It is speculated that the reaction course of the montmorillonite loading system may be the rapid phenol mineralization to produce CO$_2$ + H$_2$O. The amount of acid produced was small or is rapidly converted to CO$_2$ under these catalytic conditions [25].

The conversion of phenol calculated by liquid chromatography data was 45.7% (TiO$_2$) and 81.9% (30%TiO$_2$/MMT), respectively. It was found that the sum of the carbon content of the intermediate substances was much lower than the degradation rate caused by phenol. It is possible that a large amount of carbon was converted into carbon dioxide, leaving the reaction system. In addition, it can be seen from Fig. 10 that almost all the intermediate products of phenol degradation are converted into small molecular substances. With reference to high-performance liquid reaction data and a large amount of literature, it is concluded that under this experimental condition, the reaction mechanism of phenol degradation may be like this:

The good photocatalytic activity of the 30%TiO$_2$/MMT composites can be ascribed to the following reasons. The photocatalytic mechanism of 30%TiO$_2$/MMT composites is shown in Fig. 12. TiO$_2$ in the interlayer of MMT could increase the surface area of TiO$_2$/MMT composites, and adding the adsorption efficiency of phenol thus promotes the photodegradation efficiency of 30%TiO$_2$/MMT. Secondly, TiO$_2$ loaded on the surface of MMT improved its dispersion and enlarged the amount of exposed activates for reactions. When the composite photocatalyst is irradiated by sunlight, the electrons (e$^-$) in the valence band (VB) of TiO$_2$ will be excited by energy and transfer to the conduction band (CB) to generate photogenerated electrons, which will generate photogenerated holes (h$^+$). Photogenerated holes and electrons will combine with water and dissolved oxygen in water to form superoxide radical (-O$_2$)$^-$ and hydroxyl radical (-OH). The two radicals can oxidize phenol to HQ + BQ, and then convert into FA + MA, and finally mineralize into small molecules of H$_2$O and CO$_2$.

Conclusions

1. TiO$_2$/MMT composites were prepared by sol–gel method. The experiment results indicate 30%TiO$_2$/MMT (600 °C, 4 h) has relatively higher photocatalytic activities than other catalysts. A certain amount of TiO$_2$ (TiO$_2$/MMT = 30%) is highly dispersed on MMT sur-
face, and TiO₂ can cause the layer silicate of MMT to behave as barrier layer preventing TiO₂ powders from agglomeration and reduce its particle size from 22.51 to 7.68 nm. Besides, the best photoactivity of 30%TiO₂/MMT composites can be due to its smaller particle size, its layer structure, and the red shift of the onset absorption edge in the UV–Visible DRS.

2. The initial concentration of phenol was 10 mg/L, the initial pH of the solution was 6, the amount of catalyst used was 2 g/L, and the ultraviolet irradiation time was 240 min. Under the condition, the degradation rate of phenol was 89.8%. For phenol with an initial concentration of 50 mg/L, the phenol conversion detected by ultraviolet irradiation was 89.8%. For phenol with an initial concentration of 50 mg/L, the phenol conversion detected by ultraviolet irradiation was 89.8%.

The present study was supported by the Joint Project of Basic Agricultural Research Fund of Yunnan Province (2018FG001-051) and Open fund of Key Laboratory of State Forestry and Grassland Administration on Highly-Efficient Utilization of Forestry Biomass Resources in Southwest China (2021-KF02).

References

Chen Ke, Li J, Wang W, Zhang Y, Wang X, Haiquan Su (2011) The preparation of vanadium-doped TiO₂–montmorillonite nanocomposites and the photodegradation of sulforhodamine B under visible light irradiation [J]. Appl Surf Sci 257:7267–7285. https://doi.org/10.1016/j.apsusc.2011.03.104

Chen D, Zhu Q, Zhou F, Deng X, Li F (2012) Synthesis and photocatalytic performances of the TiO₂ pillared montmorillonite [J]. J Hazard Mater 235–236:186–193. https://doi.org/10.1016/j.jhazmat.2012.07.038

Damardji B, Khalaf H, Duclaux L, David B (2009) Preparation of TiO₂-pillared montmorillonite as photocatalyst Part I. Microwave calcination, characterisation, and adsorption of a textile azo dye [J]. Appl Clay Sci 44:201–205. https://doi.org/10.1016/j.clay.2008.12.010

Djellabi R, Ghorab MF, Cerrato G, Morandi S, Gatto S, Oldani V, Di Michele A, Bianchi CL (2014) Phototoxic TiO₂–montmorillonite composite for degradation of organic dyes in water [J]. J Photochem Photobiol, A 295:57–63. https://doi.org/10.1016/j.jphotochem.2014.08.017

Djouadi L, Khalaf H, Boukhatem H, Boutoumi H, Kezzime A, Santaballa JA, Canle M (2018) Degradation of aqueous ketoprofen by heterogeneous photocatalysis using Bi₂S₃/TiO₂–Montmorillonite nanocomposites under simulated solar irradiation [J]. Appl Clay Sci 166:27–37. https://doi.org/10.1016/j.clay.2018.09.008

Gór ska P, Zaleska A, Hupka J (2009) Photodegradation of phenol by UV/TiO₂ and Vis/N, C-TiO₂ processes: comparative mechanistic and kinetic studies [J]. Sep Purif Technol 68:90–96. https://doi.org/10.1016/j.seppur.2009.04.012

Gundogdu A, Celal Duran H, Senturk B, Soylak M, Ozdes D, Serencam H, Imamoglu M (2012) Adsorption of phenol from aqueous solution on a low-cost activated carbon produced from tea industry waste: equilibrium, kinetic, and thermodynamic study [J]. Chem Eng Data 57:2733–2743. https://doi.org/10.1016/j.cej.2010.03.059

Han Z, Choi C, Hong S, Wu T-S, Soo Y-L, Jung Y (2019) Activated TiO₂ with tuned vacancy for efficient electrochemical nitrogen reduction [J]. Appl Catal B: Environ 257:117896. https://doi.org/10.1016/j.apcatb.2019.117896

Hassani A, Khataee A, Karaca S (2015) Photocatalytic degradation of ciprofloxacin by synthesized TiO₂ nanoparticles on montmorillonite: effect of operation parameters and artificial neural network modeling [J]. J Mol Catal a: Chem 409:149–161. https://doi.org/10.1016/j.molcata.2015.08.020

Li C, Zhu N, Yang S, He X, Zheng S, Sun Z, Dionysiou DD (2021) A review of clay based photocatalysts: role of phyllosilicate mineral in interfacial assembly, microstructure control and performance regulation [J]. Chemosphere 273:129723. https://doi.org/10.1016/j.chemosphere.2021.129723

Liu YX, Zhang X, Guo L, Wu F, Deng NS (2008) Photodegradation of bisphenol A in the montmorillonite KSF suspended solutions [J]. Ind Eng Chem Res 47:7141–7146. https://doi.org/10.1021/ie800169c

Makrigianni V, Giannakas A, Daikopoulos C, Deligiannakis Y, Konstantinou I (2015) Prepar-tion, characterization and photocatalytic performance of peryloxy-tine-char/TiO₂ composites, toward phenol oxidation in aqueous solutions. Appl Catal B 174:244–252. https://doi.org/10.1016/j.apcatb.2015.03.007

Mogoryösi K, Dékány I, Fendler JH (2003) Preparation and characterization of clay mineral intercalated titanium dioxide nanoparticles [J]. Langmuir 19:2938–2946. https://doi.org/10.1021/la025969a

Muniandy L, Adam F (2014) Abdul Rahman Mohamed, Eng-Poh Ng, The synthesis and characterization of high purity mixed microporous/mesoporous activated carbon from rice husk using chemical activation with NaOH and KOH [J]. Microporous Mesoporous Mater 197:316–323. https://doi.org/10.1016/j.micromeso.2014.06.020

Ooka C, Yoshida H, Horio M, Suzuki K, Hattori T (2003) Adsorptive and photocatalytic performance of TiO₂ pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity [J]. Appl Catal B 41:313–321. https://doi.org/10.1016/S0926-3333(02)00169-8

Ouachitak H, El Guerdaoua A, Haounaïti R, Ahoulaira S, El Haouti R, Hafid N, Addi AA, Sljukic B, Santos DMF, LabdTaha M (2021) Highly efficient and fast batch adsorption of orange G dye from polluted water using superb organo-montmorillonite: Experimental study and molecular dynamics investigation. J Mol Liq 335:116560. https://doi.org/10.1016/j.molliq.2020.124125

Parayil SK, Kibombo HS, Wu C-M, Peng R, Baltrusaitis J, Koodali RT (2012) Enhanced photocatalytic water splitting activity of carbon-modified TiO₂ composite materials synthesized by a green synthetic approach [J]. Int J Hydrog Energy 37:8257–8267. https://doi.org/10.1016/j.ijhydene.2012.02.067

Rasalingama S, Kibombo HS, Chia-Ming Wu, Peng R, Baltrusaitis J, Koodali RT (2014) Competitive role of structural properties of titania–silica mixed oxides and a mechanistic study of the photocatalytic degradation of phenol [J]. Appl Catal B 148–149:394–405. https://doi.org/10.1016/j.apcatb.2013.11.025

Sun H, Peng T, Liu Bo, Xian H (2015) Effects of montmorillonite on phase transition and size of TiO₂ nanoparticles in TiO₂/montmorillonite nanocomposites [J]. Appl Clay Sci 114:440–446. https://doi.org/10.1016/j.claysci.2015.06.026

Turki A, Guillard C, Dappozze F, Kibibi Z (2015) GillesBerhault, Hafedh Kochkar, Phenol photocatalytic degradation over anisotropic TiO₂ nanomaterials: kinetic study, adsorption isotherms and
formal mechanisms [J]. Appl Catal B 163:404–413. https://doi.org/10.1016/j.apcatb.2014.08.010
Wang X, Huang S, Zhu L, Tian X, Li S, Tang H (2014) Correlation between the adsorption ability and reduction degree of graphene oxide and tuning of adsorption of phenolic compounds [J]. Carbon 69:101–112. https://doi.org/10.1016/j.carbon.2013.11.070
Wang R, Ma Q, Zhao Z, Ye X, Jin Q, Zhao Z, Liu Ji (2019) Adsorption of surfactants on coal surfaces in the coking wastewater environment: kinetics and effects on the slurrying properties of coking wastewater–coal slurry [J]. Ind Eng Chem Res 58(28):12825–12834. https://doi.org/10.1021/acs.iecr.9b01829

Yuan L, Huang D, Guo W, Yang Q, Jiang Yu (2011) TiO2/montmorillonite nanocomposite for removal of organic pollutant [J]. Appl Clay Sci 53:272–278. https://doi.org/10.1016/j.clay.2011.03.013
Zhang P, Mo Z, Han L, Zhu X, Wang Bo, Zhang C (2014) Preparation and photocatalytic performance of magnetic TiO2/montmorillonite/Fe3O4 nanocomposites [J]. Ind Eng Chem Res 53:8057–8061. https://doi.org/10.1021/ie5001696

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.