Research on Photocatalytic Degradation of Methyl Orange by a β-Cyclodextrin/Titanium Dioxide Composite

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A photocatalytic composite of β-cyclodextrin/titanium dioxide (β-CD/TiO₂) was synthesized via the photoinduced assembly method in this work. The morphology of the composite was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively. The chemical composition was detected by Fourier transform infrared spectroscopy (FTIR). By means of phenolphthalein probe technique and back titration method, the contents of active β-CD (2.0%) and TiO₂ (0.0971±0.0006 g/0.1 g) in the prepared β-CD/TiO₂ composite were obtained. In order to investigate deeply the role of β-CD in TiO₂ photocatalytic system, 100 mL of 0.1 mmol L⁻¹ methyl orange (MO) aqueous solution was used as the organic pollutant, the photocatalytic activity of β-CD/TiO₂ and pure TiO₂ were assessed under the same conditions. The results showed that the degradation time of β-CD/TiO₂ was 43% shorter than that degraded by the aqueous solution containing only TiO₂. β-CD/TiO₂ demonstrated a better photocatalytic activity. The kinetics of photocatalytic degradation of MO by β-CD/TiO₂ and pure TiO₂ was studied. In addition, the degradation efficiency of MO by β-CD/TiO₂ was still above 85% after recycling for 5 times.

Keywords β-cyclodextrin, titanium dioxide, methyl orange, mechanism, photocatalytic degradation

Introduction

In recent years, the use of TiO₂ as photocatalytic semiconductor material is extensively and intensively studied for its non-toxic nature, photochemical stability and strong oxidizing power under ultraviolet light.¹⁻² The applications of TiO₂ and its modification to photocatalytic degradation of dyes³⁻⁴ various organic pollutants,⁵⁻⁶ and reduction of heavy metals⁷⁻⁸ have been reported by many researchers. However, the high electron-hole recombination rate makes TiO₂ a relatively inefficient photocatalyst.¹⁴

Cyclodextrins (CDs) are produced as a result of intramolecular transglycosylation reaction from degradation of starch by cyclodextrin glucanotransferase enzyme.¹⁵ The CD molecules are non-reducing cyclic oligosaccharides consisting of six to eight glucopyranose units linked by α-(1,4) bonds.¹⁶ The structure of CDs is similar a truncated cone with a hydrophobic inner cavity and a hydrophilic outer surface allowing to interact with a wide range of molecules and forming inclusion complexes through host-guest interactions.¹⁷⁻¹⁸

Recently, β-CD was added to the photocatalytic degradation systems in order to improve the photocatalytic degradation efficiency of TiO₂.¹⁹⁻²² It plays electron-donating and hole-capturing roles when linked to TiO₂, which restricts charge-hole recombination and makes further improvement of photocatalytic degradation efficiency.²² Furthermore, based on the hydrophobic inner cavity of β-CD, the charge transfer rate from the photoexcited semiconductor to electron acceptors is accelerated and the photocatalytic substrates are concentrated onto the TiO₂ surface.²⁴ However, few reports focus on photodegradation kinetics models for explaining the role of β-cyclodextrin in the photocatalytic degradation.

In this work, we proposed that β-CD can form inclusion complexes with the hydrophobic part of methyl orange (MO), and the negatively charged part was more easily to be adsorbed on the surface of TiO₂ for photocatalytic degradation. Meanwhile, three kinetics models were used to investigate the photocatalytic degradation process.

Experimental

Reagents

β-CD was purchased from TCI (Japan). TiO₂ (anatase, particle size < 25 nm, 99.8% metal basis), MO and ammonium hydroxide (NH₃·H₂O) were obtained from Shanghai Aladdin Co., Ltd. (China). Sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) were bought from Beijing Chemical Co., Ltd. (China). Ammonium sulfate [(NH₄)₂SO₄], sodium hydroxide (NaOH), phenolphthalein, hexamethylenetetramine, cresol red, zinc powder and xylene orange were all purchased from Tianjin Kernel Chemical Reagent Co., Ltd. (China). Ethylene diamine tetracetic acid disodium salt (EDTA) was supplied by Beijing Yili Chemical Reagent Co., Ltd.

Instruments

SEM (JSM-7500F, JEOL, Japan) was employed to analyze the surface morphology and composition of the synthesized samples. TEM (JEM2100, JEOL, Japan) was used for observing the ultrastructure changes of the samples. FTIR (IS10, Thermo Fisher Scientific, USA) was used to analyze the chemical composition in the specimens of β-CD, TiO₂ and β-CD/TiO₂. Photocatalytic degradation of MO by β-CD/TiO₂ was carried out under ultraviolet light using a 250-W high pressure mercury lamp and supplied by Jiguang special lighting electrical appliance factory (Shanghai, China). The progress of photocatalytic degradation was monitored by observing the disappearance of the absorption peak of MO at 463 nm by an ultraviolet and visible spectrophotometer (TU-1901, Beijing, China).

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Received June 8, 2017; accepted August 10, 2017.
Synthesis of a β-CD/TiO₂ composite

The photoinduced assembly method[22,26] was used for synthesis of a β-CD/TiO₂ composite in this procedure. In details, a β-CD/TiO₂ composite was synthesized by the addition of TiO₂ (2.0 g) and β-CD (1.8 g) into 100 mL of distilled water, then irradiated by a 250-W high-pressure mercury lamp for 30 min. The precipitation was centrifuged and washed with 100 mL of distilled water for 2–3 times until the pH could not be detected by phenolphthalein probe technology.[27,28] Then the product was dried in a vacuum oven at 50 °C for 12 h and the weight of product was recorded. The product was ground and well homogenized in the ball mill (100 mesh) before using.

Determination of the active β-CD by means of phenolphthalein probe technology

For evaluating the encapsulation ability of β-CD on TiO₂, Mäkelä et al.[27] put forward a method to measure β-cyclodextrin concentration based on the decolorization of phenolphthalein after embedding into the cavity of cyclodextrins. Also, our previous work of phenolphthalein probe technology was applied here.[19,20] The absorbance of the calibration solutions of CDs was measured at the wavelength of 553 nm at room temperature. The contents of β-CD (CcD) could be calculated by Eq. (1), where ΔA denotes the difference between the UV absorbance of dilute separation filtrates and that of β-CD blank (phenolphthalein solutions without addition of β-CD).

\[ \Delta A = 1.565c_{CD} + 0.011 \]  

Eq. (1)

The contents of active β-CD in a β-CD/TiO₂ composite were evaluated by Eq. (2), where c represents the active β-CD concentration of β-CD/TiO₂ composite (mol L⁻¹), cᵣ represents the β-CD concentration of β-CD/TiO₂ composite (mol L⁻¹), cᵢ represents the β-CD concentration of β-CD blank sample (inpregnated solution without addition of β-CD) (mol L⁻¹), M represents the β-CD molecular weight of 1135 g mol⁻¹, m denotes the weight of dry β-CD/TiO₂ composite (g).

[Active β-CD content (%) = \( \frac{(c - cᵢ) \times 0.1 \times M}{m} \times 100\% \)]  

Eq. (2)

Determination of TiO₂ by means of back titration method

In order to determine completely the contents of TiO₂ in β-CD/TiO₂ composite, a self-designed back titration method was used.

Firstly, 0.1 g of composite was placed in an oven until completely carbonized and then transferred to a muffle furnace and heated at 800 °C for 2 h to afford the white powder. After the heat treatment, the samples were cooled by quenching in air to room temperature and then 5 g of (NH₄)₂SO₄ and 10 mL of 98% (wt%) H₂SO₄ were added. The mixture was dissolved in 100 mL of distilled water after digestion.

Then, 10 mL of aqueous solution obtained from above was accurately moved into a 250 mL conical flask. 20 mL of 0.01 mol L⁻¹ EDTA standard solution and 2 drops of cresol red indicator were added. The pH of the solution was adjusted by adding 0.1 mol L⁻¹ NaOH solution drop by drop until the color change from red to yellow. The solution was boiled for 2 min and then cooled to room temperature. After adding 2–4 drops of xylenol orange, 1:1 (V/V) NH₄H₂O₂ was used to adjust the solution from yellow to reddish. 10 mL of hexamethylene tetramine tetramine buffer was added, and the solution changed bright yellow.

Excess EDTA was titrated by 0.01 mol L⁻¹ standard solution of zinc, using the sharp color change of indicator, from bright yellow to shallow brown red, shaken well and allowed to stand for 1–2 min to determine the endpoint. The amounts of TiO₂(m) were calculated by Eq. (3), where M represents the TiO₂ molecular weight of 79.87 g mol⁻¹, c is the concentration of zinc standard solution (0.01 mol L⁻¹),\( V \) denotes the back titration amounts of zinc standard solution (mL).

\[ m = M \times (0.0002 - cV) \]  

Eq. (3)

Photocatalytic experiment

Figure 1 showed the scheme of the self-designed photocatalytic reactor. In order to study the effect of β-CD/TiO₂ composite on photocatalytic degradation of MO, pure TiO₂ was used for comparison. Keeping the contents of TiO₂ constant, the photocatalytic materials of pure TiO₂ and β-CD/TiO₂ were tested, respectively.

Figure 1 Schematic diagram of photocatalytic reactor.

TiO₂ (0.0971 g) and β-CD/TiO₂ (0.1 g) were mixed with 100 mL of 0.1 mmol L⁻¹ MO solution in a 150 mL quartz test tube, respectively. Prior to irradiation, the reaction mixture remained in dark and stirred for 30 min to obtain adsorption equilibrium. Then the quartz test tubes were immediately irradiated with a 250-W high-pressure mercury lamp in our self-designed photocatalytic reactor (Figure 1). During the experiment, quartz test tubes were taken out of the reactor one by one at different time intervals. Before analysis, each sample in the tube was centrifuged. The reaction progress was monitored at 463 nm. Every solution was tested for three times.

In the UV-vis absorption spectra, the absorbance (A) and concentration (c, mol L⁻¹) were in accordance with Lambert-Beer law as shown in Eq. (4), where \( \varepsilon \) represents the molar absorption coefficient (L mol⁻¹ cm⁻¹) and b denotes the optical path length (cm).

\[ A = \varepsilon bc \]  

Eq. (4)

The photocatalytic degradation efficiency \( R[29-31] \) was evaluated by Eq. (5), where \( c₀ \) and \( c \) represent the concentration (mol L⁻¹) of MO before and after photocatalytic degradation, \( A₀ \) and \( A \) denote the absorbance of MO before and after photocatalytic degradation.

\[ R = (c₀ - c)c₀ \times 100\% = (A₀ - A)/A₀ \times 100\% \]  

Eq. (5)

The function of initial solution pH

In order to study the effect of initial solution pH on the degradation efficiency of MO by β-CD/TiO₂, the degradation efficiency under the pH=2, 4, 6, 8 and 10 were measured. In brief, 5 equiponderous β-CD/TiO₂ samples were mixed with isoconcentration solutions of MO (0.1 mmol L⁻¹) in our self-designed photocatalytic reactor, respectively. The pH was adjusted by HCl and NaOH, respectively. After 30 min of dark adsorption, the quartz test tubes were immediately irradiated with a 250-W high-pressure mercury lamp for 20 min under the same experiment conditions. Then the progress of photocatalytic degradation under different initial pH was monitored by observing the disappearance of the absorption peak of MO at 463 nm.

Recycle experiments

The regeneration performance of β-CD/TiO₂ was tested by carrying out 5 cycles of photocatalytic degradation experiments. The β-CD/TiO₂ was collected after the first photocatalytic degradation
experiment. After washing, drying and grinding, the composite was added into photocatalytic system and the procedures presented in "Photocatalytic experiment" were implemented.

Results and Discussion

Surface morphology study

SEM analysis of the β-CD/TiO₂ composite using β-CD and TiO₂ as references was investigated in this study and the images were listed in Figure 2. β-CD was seen to have a lamellar structure that existed in an amorphous form (Figure 2a). On the other hand, the unmodified TiO₂ demonstrated a nanoscale spherical shape and agglomerated together (Figure 2b). The surface of β-CD/TiO₂ (Figure 2c) could be observed with lots of irregularly shaped crystals, which showed no obvious difference on the morphology and particle size with pure TiO₂. Thus, the presence of β-CD in β-CD/TiO₂ could not be confirmed by SEM.

![Figure 2](Image)

Figure 2 SEM images of (a) β-CD (×10000); (b) TiO₂ (×10000); (c) β-CD/TiO₂ (×10000).

The FTIR spectra of β-CD, TiO₂ and β-CD/TiO₂ were shown in Figures 3a, 3b and 3c, respectively. By comparing the spectra, the existence of β-CD in the composite of β-CD/TiO₂ can be proved. In Figures 3a and 3c, there were three weak bands at 1154, 1078 and 1030 cm⁻¹, which were attributed to the stretching vibrations of C—O bond of CD. However, they cannot be observed in the Figure 3b.

![Figure 3](Image)

Figure 3 FTIR spectrum of (a) β-CD; (b) TiO₂; (c) β-CD/TiO₂ composite.

TEM analysis was applied for further examination. The particles of TiO₂ (Figure 4a) and β-CD/TiO₂ (Figure 4b) were all agglomerated together and both of the particle diameters were below 100 nanometers with spherical morphology. In Figure 4b, the dark-field imaging area of the particles increased significantly than that in Figure 4a, indicating that the aggregation effect of β-CD/TiO₂ was more obvious. It was also demonstrated that β-CD was loaded onto the surface of nano-TiO₂ instead of embedded in TiO₂.

![Figure 4](Image)

Figure 4 (a) TEM images of TiO₂; (b) TEM images of β-CD/TiO₂.

The components of active β-CD and TiO₂ in β-CD/TiO₂ composite

Due to the phenomenon of purple phenolphthalein solution became colorless in the presence of β-CD, the surface active β-CD contents on β-CD/TiO₂ had been determined by our previous research.[28,32] The purple phenolphthalein solution (pH=10.5) faded by mixing the β-CD/TiO₂ powder in dark. The solution was kept overnight to balance. The active β-CD contents on the surface of β-CD/TiO₂ were determined as 2.0% (wt%), which not only demonstrated a successful grafting of β-CD macromolecules but also verified the encapsulating ability of β-CD/TiO₂ composite.

The contents of TiO₂ in β-CD/TiO₂ composite were detected by means of back titration method. Gravimetric method was not applicable, because the co-existence of rutile and anatase phase led to the uncertainty of residue’s composition after the process of ashing (800 °C, 2 h). By means of back titration method, the contents of TiO₂ in β-CD/TiO₂ composite were detected as 0.971±0.0006 g/0.1 g (5 times of determination).

Photocatalytic performance analysis

The photocatalytic effects of TiO₂ and β-CD/TiO₂ on the degradation of MO under the 250-W high-pressure mercury lamp were studied, and the results are shown in Figure 5. Figure 5 was divided into two phases, one was dark-adsorbing for 30 min and the subsequent was photocatalytic degradation. The role of CD is multifunctional. In dark-adsorbing phase, β-CD plays a major role in adsorption as seen from the reduction of MO concentration in the solution in the presence of β-CD/TiO₂. During the photocatalytic degradation phase, both undegraded MO and the intermediate of N,N-dimethyl-aniline can be included by β-CD providing close proximity of MO to the catalyst. Furthermore, β-CD plays electron-donating and hole-capturing roles.[33]

Before photocatalytic reaction, the two materials were kept in MO solutions with isoconcentration and stirred in dark for 30 min to reach adsorption equilibrium, respectively. After dark adsorption, the c(0)/c values of MO by TiO₂ and β-CD/TiO₂ were 0.9960 and 0.8456, respectively. The interaction between TiO₂ and MO led to a little adsorption of MO (0.0040, 1−c(0)/c(∞)), which was much lower than that of β-CD/TiO₂ (0.1544). It meant that β-CD/TiO₂ exhibited an improved adsorption ability comparing to TiO₂, which demonstrated a relative strong binding affinity between β-CD and MO. This strong binding affinity had been proved by the work of Kompany-Zareh et al.[33]

After dark adsorption, MO was degraded and the possible pathways were likely to be as follows:[34]

\[ \text{TiO}_2 + hv \rightarrow h^+ + e^- \]
\[ e^- + O_2 \rightarrow O_2^- \]
\[ h^+ + H_2O \rightarrow \cdot OH + H^+ \]
\[ O_2^- + MO \rightarrow \text{degraded products} \]
\[ \cdot OH + MO \rightarrow \text{degraded products} \]
The photocatalytic degradation of MO was mainly caused by the superoxide anion free radicals (O$_2^-$) and the hydroxyl radicals (•OH), which were photinduced by TiO$_2$ under a 250-W high-pressure mercury lamp.$^{[16,37]}$

The degradation rates of MO by TiO$_2$ and β-CD/TiO$_2$ were calculated by Eq. (6), where $c_0$ and $c$ represent the concentration of MO before and after photocatalytic degradation (nmol L$^{-1}$), $t$ represents the photocatalytic degradation time of MO.

$$\text{Degradation rate} = \frac{dc}{dt}$$

In Figure 5, the degradation rate of MO by β-CD/TiO$_2$ was higher than by TiO$_2$, and the degradation time was shortened by the introduction of β-CD. The role of β-CD in photocatalytic reaction system is illustrated in Figure 6. The enhancement of degradation of MO was probably due to azo type of MO entering into the cavity of β-CD. The benzenesulfonate side uncovered interacted with TiO$_2$ more easily by electrostatic forces than without β-CD under the effect of electron-holes (h$^+$)$^{[18]}$. Furthermore, according to the literature,$^{[39,40]}$ the azo type of MO can be finally decomposed into CO$_2$ and H$_2$O in the presence of the hydroxyl radicals (•OH), as seen in Figure 7. The physical map that MO was degraded by TiO$_2$ and β-CD/TiO$_2$ at different time intervals was shown in Figure 8.

Based on the above results, we can draw the preliminary conclusion that the enhancement of photocatalytic degradation of MO could be dependent on the introduction of β-CD in two aspects. On the one hand, MO in this photocatalytic degradation system is included by the hydrophobic cavity of β-CD and the concentration of MO increased on the surface of TiO$_2$. On the other hand, β-CD plays electron-donating and hole-capturing roles when linked to TiO$_2$, which makes further improvement of photocatalytic degradation efficiency.$^{[41]}$

Three kinetic models can be applied to investigate the mechanism of the degradation process as shown in Figure 9. According to literature, the pseudo-zero order kinetic model is based on the assumption that the photocatalytic degradation rate is only controlled by the irradiation time.$^{[42,43]}$ While the pseudo-first order kinetic model and pseudo-second order kinetic model highlight that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.$^{[44,45]}$

The rate equations of the three different models were listed from Eq. (7) to Eq. (9), where $c_0$ is the initial concentration (nmol L$^{-1}$) of MO and $c$ represents its concentration (nmol L$^{-1}$) at time $t$ (min), $k_0$ (nmol L$^{-1}$ min$^{-1}$), $k_1$ (min$^{-1}$) and $k_2$ (L nmol$^{-1}$ min$^{-1}$) are the rate constants of pseudo-zero order kinetic model, pseudo-first order kinetic model and pseudo-second order kinetic model, respectively.

The pseudo-zero order equation:

$$c = c_0 - k_0t$$  (7)

The pseudo-first order equation:

$$\ln c = -k_1t + \ln c_0$$  (8)

The pseudo-second order equation:

$$\frac{t}{c} = \frac{1}{k_2c_0^2} + \frac{t}{c_0}$$  (9)
The contents of active assembly method and TiO
2 particles due to acidic environment, furthermore, β-CD could restrain the recombinati
on of photogenerated electron-hole pairs. Therefore, the anionic dye of MO was easily accumulat
ed on the surface of the TiO
2 particles. After dark-adsorbing for 30 min, the initial concentration of MO was raised, and this phe
nomenon can result in an enhancement of photocatalytic degradation efficiency.

The function of pH on the photocatalytic degradation efficiency

The degradation efficiency of MO by β-CD/TiO
2 under the different initial pH was shown in Figure 10. As shown in Figure 10, the photocatalytic degradation efficiency increased with decrease of the solution pH. The reason for the improvement of the degradation effi
ciency was attributed to the increase of the the positive charge on the surface of TiO
2 particles due to acidic environment, furthermore, β-CD could restrain the recombinati
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The regeneration performance of β-CD/TiO
2 was tested by 5 cycles of photocatalytic degradation experiments. The result of de
gradation efficiency in recycle experiment was shown in Figure 11. It could be seen that β-CD/TiO
2 still kept high degradation efficiency after 5 cycles. Photocatalytic degradation curves of recycle experi
ments by β-CD/TiO
2 were shown in Figure 12. The degradation effi
ciency of MO changed slightly, and the degradation rate basically remained unchanged. The pseudo-zero order kinetic model of recycle experiment was shown in Table 2. According to the fitted equation in this table, the sorption capacity is slightly decreased with the number of recycling. Therefore, β-CD/TiO
2 composite retained stable during the process, indicating a good regeneration property and a high pho
tocatalytic activity.

Conclusions

The β-CD/TiO
2 composite was synthesized by photoinduced as
sembly method and β-CD was loaded onto the surface of nano-TiO
2. The contents of active β-CD and TiO
2 in β-CD/TiO
2 were determined as 2.0% and 0.0971±0.0006 g/0.1 g, respectively. 100 mL of 0.1 mmol L
-1 MO could be completely degraded photocatalytically in 20

| Kinetic model          | TiO
2 | β-CD/TiO
2 |
|------------------------|-----|---------|
| Pseudo-zero order      | Fitted curve | $c = -0.022t + 0.7707$ | $c = -0.0417t + 0.8306$ |
|                        | $R^2$  | 0.8671  | 0.9926  |
| Pseudo-first order     | Fitted curve | $-\ln c = 0.0864t - 0.0965$ | $-\ln c = 0.1563t - 0.2848$ |
|                        | $R^2$  | 0.9853  | 0.8610  |
| Pseudo-second order    | Fitted curve | $t/c = 27.234t - 241.3$ | $t/c = 26.297t - 140.24$ |
|                        | $R^2$  | 0.7189  | 0.4773  |

Figure 9 kinetic model for the photocatalytic degradation of MO by pure TiO
2 and β-CD/TiO
2: (a) plots of pseudo-zero order kinetic model; (b) pseudo-first order kinetic model; (c) pseudo-second order kinetic model.

Figure 10 The degradation rate of MO by β-CD/TiO
2 under the different initial pH.

Recycle performance

The regeneration performance of β-CD/TiO
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**Table 2** Pseudo-zero order kinetic model of recycle experiment

| Recycle times | Fitted curve     | $R^2$ |
|---------------|------------------|-------|
| Recycle 1     | $c = -0.0417t + 0.8306$ | 0.9926 |
| Recycle 2     | $c = -0.0416t + 0.8416$ | 0.9900 |
| Recycle 3     | $c = -0.0411t + 0.8827$ | 0.9901 |
| Recycle 4     | $c = -0.0422t + 0.9478$ | 0.9899 |
| Recycle 5     | $c = -0.0397t + 0.9239$ | 0.9898 |

min by β-CD/TiO$_2$, the degradation time was 43% shorter than that by pure TiO$_2$. Thus, β-CD/TiO$_2$ demonstrates an excellent degradation performance. The kinetics of photocatalytic degradation of MO by β-CD/TiO$_2$ fitted the model of pseudo-zero order during the process. In addition, the composite of β-CD/TiO$_2$ showed a good photocatalytic activity and regeneration property after 5 recycle experiments.

**Acknowledgement**

This study is supported by the National Natural Science Fund of China (No. 51403030) and the Fundamental Research Funds for the Central Universities of China (No. 2572017CB23).

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