



Photocatalytic degradation of 4,4'-biphenol in TiO₂ suspension in the presence of cyclodextrins: A trinity integrated mechanism

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ABSTRACT

Effect of cyclodextrins (CDs) on the photodegradation of 4,4'-biphenol (BIP) in TiO₂ suspension was examined using a 250 W metal halide lamp ($\lambda \geq 365$ nm) as irradiation light source. The adsorption of BIP on TiO₂ surface was also investigated in both conditions that CDs is absence or presence, as well as the inclusion complex of CDs with BIP. Results showed that, the behaviors of inclusion complex of BIP with CDs were the predominant factor in the photocatalytic reaction. A larger inclusion constant value (5600 M^{-1}) of BIP with β -CD followed by the enhancement of adsorption on TiO₂ surface leads to acceleration of photodegradation, while α -CD showed opposite effect on the photodegradation because of a much smaller inclusion constant (51 and 355 M^{-1} was obtained for α -CD/BIP and α -CD₂/BIP, respectively). The reaction constants were 1.35 , 1.17 and $2.48 \mu\text{M min}^{-1}$ for BIP in the absence of CDs, in the presence of α -CD and in the presence of β -CD, respectively. XRD analysis demonstrated that TiO₂ conserved their anatase crystal features after 5-h irradiation. A trinity interaction model of BIP photodegradation in TiO₂ suspension containing cyclodextrins was also proposed in this work. It would be beneficial to have a depth-in mechanism of CDs effect on reactant's photodegradation in TiO₂ suspension that would probably lead to a high efficiency and selectivity for the photodegradation of pollutants using TiO₂ as catalyst.

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1. Introduction

Titanium dioxide has been applied in many areas since Fujishima and Honda first discovered photochemical water splitting by a chemically modified n-TiO₂ electrode [1]. As in environmental protection, it is known that most organic pollutants can be completely decomposed to carbon dioxide and water when TiO₂ was used as the photocatalyst, mainly because of the photogenerated holes and hydroxyl radical [2–5]. However, TiO₂ was a relatively inefficient photocatalyst due to the recombination of charge-hole pair generated from the excited TiO₂. Furthermore, a large band gap (3.2 eV) resulted in the limited use of sunlight or visible light as an irradiation source. Therefore, the key pathways in TiO₂ modification were restricting charge-hole recombination and/or decrease band gap. Common modification methods include noble metal deposition, composite semiconductors, ion-doping, dye sensitization, surface reductive treatment and surface chelating [6].

In the recent two decades, cyclodextrin modified TiO₂ has attracted renewed interest since Willner et al. observed that β -CD could stabilize TiO₂ colloids and control the interfacial electron transfer processes [7]. Tachikawa et al. and Dimitrijevic et al. have

published excellent papers about the charge separation and redox reaction at the surface of cyclodextrin modified TiO₂ colloids. CDs could play electron-donating and molecular recognizing roles when linked to the semiconductor nano-particles [8,9]. Tachikawa et al. proposed direct and indirect one-electron oxidation processes of the substrate on the modified TiO₂ particulates. Feng et al. reported a formation of self-assembly photoactive TiO₂–cyclodextrin wires through a coordinate bond between oxygen atom from hydroxyl group on β -CD and surface titanium atom of TiO₂ particles [10]. In a new study, Du et al. revealed microscopic mechanisms for the separation and transfer of photogenerated electrons and holes [11].

It was found that the tailored TiO₂ could show a significant enhancement effect on the photocatalytic degradation of organic pollutants [12–14]. However, depending on the structure of the reactants and the reaction, complexation of one (or more) of the reactants by a cyclodextrin may lead to rate acceleration, no effect, or rate retardation. Which of these effects might occur depends on whether the transition state of the reaction is bound more strongly, the same, or less strongly than the initial state [15]. Therefore, for the same reactant, different cyclodextrin should give various results because of the different ability in the competition of adsorption on the TiO₂ surface and the different complexation constant. Furthermore, it is doubtful whether the results which were obtained from beforehand synthesized cyclodextrin modified TiO₂ colloids

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were fit for TiO₂ suspension. It is still not confirmed yet whether the inclusion complex of cyclodextrin with guests (reactants) or the adsorption was the key step in the photodegradation reaction. The influence of α - and β -CD on the photocatalytic degradation of 4,4'-biphenol (BIP) in TiO₂ suspended solution was investigated in this work. α - and β -CD was composed of 6 and 7 glucose units, respectively. BIP was chosen as the reactant because (a) BIP has a linear geometry which was different from the bisphenols that was obviously investigated with a bent structure. (b) All the phenols have strong absorption and emission bands in the UV-visible region, resulting in the convenience of studying their interaction with cyclodextrins without adding any chromophoric dyes. (c) BIP could form both 1:1 (α -CD/BIP) and 2:1 (α -CD₂/BIP) stoichiometry complex with α -CD while only 1:1 (β -CD/BIP) stoichiometry complex with β -CD [16–18]. A mechanism of the cyclodextrin effect was proposed.

2. Experimental

2.1. Materials

Analytic grade BIP was purchased from Alpha Aesar Chemicals Co. (purity $\geq 98\%$) and used without further purification. α -CD and β -CD were purchased from Wako Pure Chemical Inc. (HPLC, $\geq 97\%$). The photocatalyst nano-TiO₂ (particle size 10–20 nm, surface area 120 m² g⁻¹, crystal structure 100% anatase as determined by X-ray diffraction analysis) was purchased from High Technology Nano Co. Ltd. (Nanjing, PRC). Doubly distilled water was used in the experiments.

2.2. Photocatalytic experiments

A 250 W metal halide lamp (metal halide indium–thallium–sodium lamp, $\lambda \geq 365$ nm, Chenguang Illumination Instrument, Jinzhou, China) was used in the photocatalytic experiments, which was placed in a water circulation cooling trap to maintain the temperature constant at 15 ± 1 °C. Aqueous solutions of BIP with TiO₂ were placed in photochemical reactor and purged with air at a fixed flow rate throughout the experiments. The TiO₂ suspended solution containing BIP was equilibrated in dark for 1 h before irradiation. Samples were collected and centrifuged at 10,000 rpm for 1 h in a 5415D centrifuge (Eppendorf, Germany) at different time intervals during the irradiation. Unless otherwise specified, all the experiments were carried out at neutral pH value.

2.3. Analysis

The BIP concentrations were analyzed by HPLC (LC-10AT, Shimadzu) with a flow rate of 1.0 ml min⁻¹ and UV absorbance detection at 278 nm. The injection volume to a Kromasil 100-5 C-18 column (4.6 mm \times 250 mm, 5 μ m) was 20 μ l. The mobile phase was CH₃OH/H₂O mixture (70/30, v/v).

2.4. Inclusion complex of CDs with BIP

In this study, the characterization of the complex was demonstrated by steady-state fluorescence study. All steady-state fluorescence spectra were recorded with a Hitachi FL-4500 fluorescence spectrometer. Excitation wavelength was fixed at 276 nm, while the emission wavelength varied from 290 to 400 nm. The sample chamber was modified to accommodate a thermostated cuvette holder, where the temperatures were maintained by a temperature circulator. Prior to fluorescence measurement, all the working solutions were equilibrated for 4 h.

2.5. Adsorption experiments

The adsorption studies were performed in dark with aqueous suspensions containing 10–100 μ M of BIP and 2 g l⁻¹ catalysts in continuously stirred 250 ml glass vessels for 12 h. Langmuir isotherms were used to quantify the adsorption of BIP on TiO₂ surface in both absence and presence of CDs. K_L and θ were determined by means of a non-linear regression fit of the Langmuir equation (Eq. (1)):

$$q_e = \frac{\theta K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the amount of solute adsorbed by gram of TiO₂, K_L is Langmuir equilibrium constant and θ is the adsorption maximum capacity of the solute on the TiO₂ surface and C_e is the solute concentration in the equilibrium.

2.6. Properties and characterization of modified TiO₂

1 g l⁻¹ TiO₂ and 5 g l⁻¹ different cyclodextrin suspended solution was irradiated under a 250 W metal halide lamp for 5 h. The suspended solution was centrifuged, whereafter, the solid phase was washed ten times with water. Bare TiO₂ and TiO₂ with cyclodextrin without irradiation were used as reference in XRD (Rigaku Dmax-rA, Japan) analysis.

3. Results and discussion

3.1. Inclusion complex of CDs with BIP

Since Benesi–Hildebrand method was initially put forward by Benesi and Hildebrand in 1949 [19], it has been widely used for determining the stoichiometry and equilibrium constant of the binding interactions. The 1:1 form of Benesi–Hildebrand equation (Eq. (2)) is used for determining the equilibrium constant of BIP with β -CD,

$$\frac{1}{F - F_0} = \frac{1}{k} + \frac{1}{kK[G]_0[CD]_0} \quad (2)$$

where F and F_0 are fluorescence intensity of the BIP in the presence and in the absence of cyclodextrin, respectively. $[G]_0$ and $[CD]_0$ are the initial concentration of the BIP and cyclodextrin, respectively. k is a constant, which depends on the fluorescence spectrometer.

Eq. (3) is used to determine the inclusion constant of BIP with α -CD [20]:

$$\frac{F}{F_0} = \frac{1 + F_1/F_0 K_1 [CD]_0 + F_2/F_0 K_1 K_2 [CD]_0^2}{1 + K_1 [CD]_0 + K_1 K_2 [CD]_0^2} \quad (3)$$

where F_1/F_0 and F_2/F_0 are the fluorescence of the 1:1 and 2:1 complexes, respectively, which are relative to the amount of free BIP, K_1 is the equilibrium constant for 1:1 complex formation, and K_2 is the equilibrium constant for the addition of a second host to a 1:1 complex to form a 2:1 complex.

A 1:1 inclusion complex of β -CD/BIP and both α -CD/BIP and α -CD₂/BIP complex was formed (Fig. 1) and the inclusion constant is 5600, 51(K_1) and 355(K_2) M⁻¹ for β -CD/BIP, α -CD/BIP and α -CD₂/BIP, respectively. All the inclusion constants are slightly larger than the reference because our work was carried out at a lower temperature and the inclusion complex is exothermic reaction. The inclusion constant is smaller than bisphenol A and other bent bisphenol compounds because of a more difficult dethreading process for bent molecules.

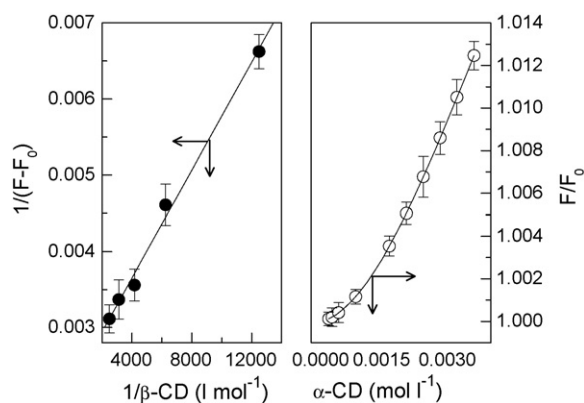


Fig. 1. Simulation of 1:1 Benesi–Hildebrand equation for β -CD/BIP complex and simulation of 1:2 Benesi–Hildebrand equation for α -CD/BIP complex. The concentration of BIP in β -CD and α -CD solution was 4 and 8 μ M, respectively.

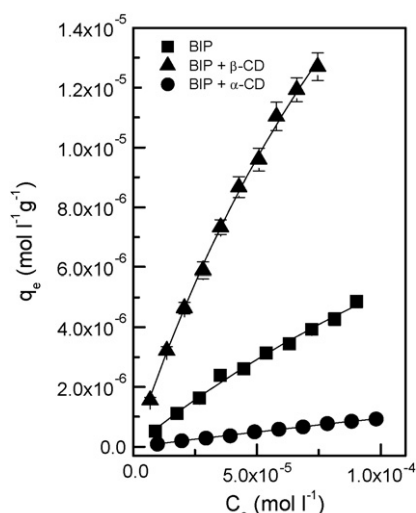


Fig. 2. Langmuir-type simulation plots for BIP (■), β -CD/BIP (▲) and α -CD/BIP (●) in aqueous solution. Black curves were obtained by means of a non-linear regression fit of the Langmuir equation. The ratio of BIP to CD was fixed at 1:1, $\text{TiO}_2 = 2 \text{ g l}^{-1}$.

3.2. Adsorption of CDs, BIP and the inclusion complex on TiO_2 surface

In TiO_2 suspension, not only cyclodextrin and BIP could adsorb on TiO_2 surface, inclusion complex of CDs with BIP also should be taken into account. Results of non-linear regression fit of the Langmuir equation are shown in Fig. 2. The results of adsorption constants and inclusion complex constants are listed in Table 1. It is clearly shown that both the maximum adsorption amount and the adsorption constant of BIP in the system containing β -CD and TiO_2 are obviously higher than those in the system containing only TiO_2 . Therefore, more BIP molecules are adsorbed on TiO_2 surface while in the presence of β -CD. The adsorption constant of BIP is

Table 1
Langmuir equilibrium constant (K_{ad}), adsorption maximum capacity (θ) and inclusion constants (K) for BIP obtained from Benesi–Hildebrand and Langmuir plots as shown in Figs. 1 and 2.

Substrate	K_{ad} (M^{-1})	θ ($\mu\text{M g}^{-1}$)	K (M^{-1})
BIP	3294 ± 901	20 ± 5	/
BIP/ α -CD	553 ± 274	20 ± 10	51 ± 4 (K_1) 355 ± 20 (K_2)
BIP/ β -CD	6216 ± 624	40 ± 3	5600 ± 550

553 M^{-1} in the presence of α -CD, which is quite smaller than that of without CDs or in the presence of β -CD.

It is suggested that hydroxyl group played an important role in adsorption on TiO_2 surface [21] and it is reasonable that CDs has higher affinity on TiO_2 surface than that of BIP. For the adsorption of BIP on TiO_2 in the presence of β -CD, since the inclusion constant is much bigger than the adsorption constant, large parts of BIP molecules are supposed to form inclusion complex with β -CD, resulting in the collective adsorption on TiO_2 surface together. While in the presence of α -CD, because of much smaller inclusion constants and lower affinity than α -CD, a retardation of BIP adsorption on TiO_2 was observed.

In our previous work [13], DRFT-IR spectrum has shown the peaks at 1645 and 2361 cm^{-1} assigned as $\text{C}=\text{O}$ and $-\text{CH}_2$ groups, respectively, which indicates that β -CD can associate with TiO_2 surface and cannot be washed off by water. Formation of both $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds were also observed by Feng's FT-IR experiments of TiO_2 -CD wires. We suggested the formation of hydrogen bond by active hydroxyl group outer surface of β -CD and TiO_2 because there were no new peaks in XPS analysis. In this study, we investigated XRD analysis using bare TiO_2 and TiO_2 with cyclodextrin without irradiation as reference. The peaks at $2\theta = 25.2$, 37.8 and 47.6 confirms that there is only anatase phase and the results also demonstrated that the anatase TiO_2 conserved their anatase crystal features no matter in adding α -CD or β -CD (Fig. 3). The same results were obtained by Feng et al. even after the suspension was irradiated for 1–2 weeks [10]. Take $\lambda = 0.154 \text{ nm}$ and half-peak breadth = 0.671 to Scherrer-equation we can get a particle size of 12 nm . In a recently work [11], Du et al. found both nondissociative and dissociative adsorption configurations should be present under thermal equilibrium by means of first-principles calculations of

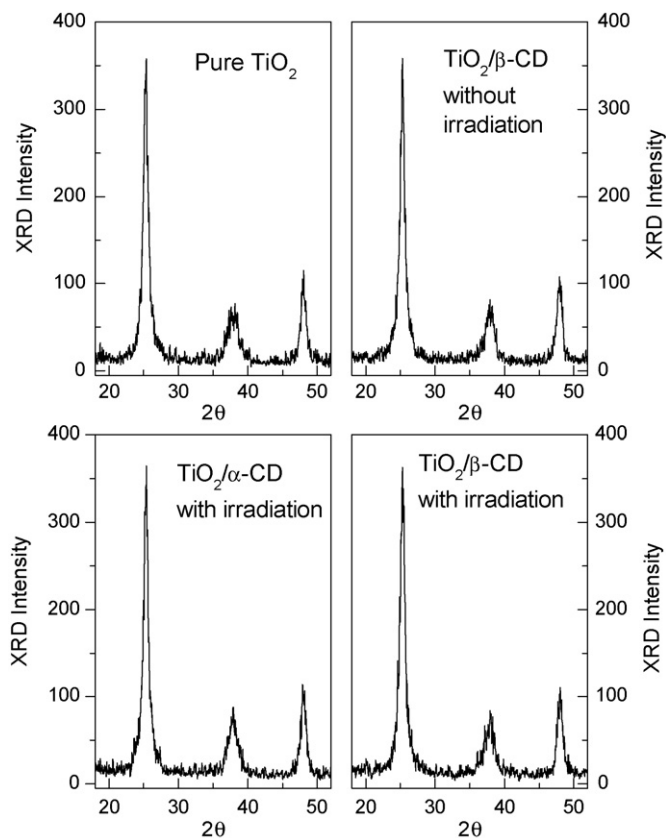


Fig. 3. XRD experiment of pure TiO_2 (top left), TiO_2/β -CD prepared without irradiation (top right), TiO_2/α -CD (down left) and TiO_2/β -CD (down right) prepared with 5 h irradiation using a 250 W metal halide lamp as the light source.

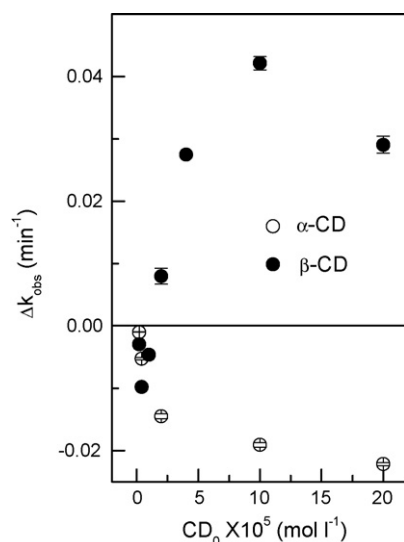


Fig. 4. Effect of CDs/BIP ratio on the photodegradation rate. $[BIP]_0 = 20 \mu\text{M}$, $TiO_2 = 0.5 \text{ g l}^{-1}$. CDs/BIP ratio was in a range from 1:10 to 10:1. $\Delta k_{\text{obs}} = k_{\text{obs}} - k_{\text{obs}0}$, where k_{obs} and $k_{\text{obs}0}$ are pseudo-first-order kinetics rate of photodegradation of BIP in the presence and absence of cyclodextrin, respectively.

glucose, as a prototype of polyhydroxyl carbohydrates and alcohols on TiO_2 surfaces. They also suggested the probability for desorption decreases roughly exponentially with the number of glucose units in the cyclodextrins. We also found that there was almost no β -CD decomposed after 80 min irradiation [13].

3.3. CDs/BIP ratio effect on the photodegradation of BIP photocatalytic degradation

As shown in Fig. 4, different CDs have various influences on the photodegradation of BIP in TiO_2 suspended solution. α -CD showed rate retardation in the whole CD/BIP ratio range from 1:10 to 10:1 with a fixed BIP initial concentration of $20 \mu\text{M}$. β -CD also showed an inhibitive effect on the photodegradation of BIP when the concentration of β -CD was low ($<20 \mu\text{M}$ in this study). Whereas, when the concentration increased, β -CD obviously led to rate acceleration, with a maximum rate at the concentration of $100 \mu\text{M}$. If the concentration of β -CD continued increasing, the observed reaction rate slowed down again. The retardation of BIP photodegradation in lower β -CD concentration was probably because that there was no enhancement of BIP adsorption on the TiO_2 surface after 1 h equilibrium (Fig. 5) and the competition reaction on TiO_2 surface between β -CD and BIP. It can be seen that the equilibrium concentration hardly has any change no matter how many α -CD therein. As for β -CD, when the concentration was lower than $4 \mu\text{M}$, the equilibrium concentration was quite close to the initial concentration. The equilibrium concentration decreased sharply with increasing β -CD until to a BIP/CD ratio of 1:5. However, more CD does not lead to more adsorption amount. Therefore, the optimized ratio of BIP to β -CD was 1:5 in this study because superfluous β -CD will result in the competing toward hydroxyl radicals.

Willner et al. suggested a monolayer adsorption process of β -CD on TiO_2 surface and the adsorption isotherm of β -CD on TiO_2 was in accordance with Langmuir adsorption theory [22]. It was reasonable to consider that α -CD has analogical adsorption behavior because of the quite similar structure comparing with β -CD. With the increment of β -CD concentration, the host guest inclusion complexes formed by β -CD and BIP molecules became more and more tightly in the solution. The amount of free guest molecules in the solution was reduced, while the interaction between the inclusion complexes and TiO_2 was enhanced. Therefore the photodegrada-

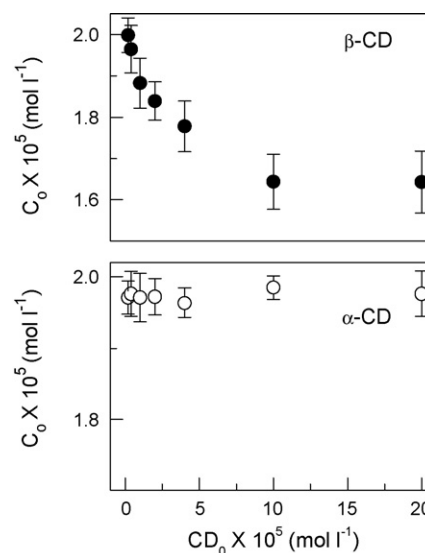


Fig. 5. Concentration of BIP after 1 h equilibrium in 0.5 g l^{-1} TiO_2 suspension containing various amount of β -CD (●) and α -CD (○). The initial concentration of BIP was $20 \mu\text{M}$.

tion of the BIP molecules in the inclusion complexes by TiO_2 was promoted. However, as β -CD/BIP ratio was increased up to five, photodegradation rate of BIP would no longer increase. The reason was that no more β -CD can be adsorbed onto TiO_2 when β -CD reaches equilibrium adsorption on surface of TiO_2 , resulting in competing toward hydroxyl radicals between unadsorbed β -CD and BIP during the photoreaction. Consequentially, photodegradation rates of BIP decrease at higher β -CD concentration. With regard to α -CD, increment of CD concentration only resulted in the competing toward hydroxyl radicals between unadsorbed α -CD and BIP, since the inclusion constant is much smaller.

3.4. Kinetic study of BIP photodegradation

In this experiment, a semi-log plot of concentration of BIP in the absence and in the presence of cyclodextrin versus irradiation time is linear, indicating overall pseudo-first-order kinetics. The experiment was repeated in the range of initial concentrations from 20.0 to $80.0 \mu\text{M}$ (Fig. 6). The initial rates for each concentration were determined from the pseudo-first-order rate constants and initial concentrations. The initial rate of BIP photodegradation increased with increasing the initial concentration of BIP and because of lower reaction rate constant in the system containing α -CD and TiO_2 , the photodegradation rate of BIP in aqueous solutions containing α -CD and TiO_2 was obviously slower than that in aqueous solutions containing only TiO_2 . With a catalyst of 0.5 g l^{-1} and BIP initial concentration of $20 \mu\text{M}$, R_0 is 0.7738 , 0.4458 and $1.686 \mu\text{mol l}^{-1} \text{ min}^{-1}$ for BIP in the absence of CDs, in the presence of α -CD and in the presence of β -CD, respectively. R_0 is increased to 1.174 , 0.8371 and $2.228 \mu\text{mol l}^{-1} \text{ min}^{-1}$ while the initial concentration was $80 \mu\text{M}$. The data were then fitted to the Langmuir–Hinshelwood kinetics rate model, which has been applied to the initial rates of photocatalytic degradation of many organic compounds [3,23,24]. The rate law is shown in Eq. (4),

$$R_0 = -\frac{dC}{dt} = \frac{k_{\text{re}}K_s C_0}{1 + K_s C_0} \quad (4)$$

where R_0 is the initial rate of disappearance of substrate and C_0 is the initial concentration of BIP. k_{re} is the reaction rate constant and K_s is taken to be the Langmuir adsorption constant.

Calculation results of k_{re} and K_s in the condition of absence and presence of CDs are listed in Table 2. It was noticeable that the

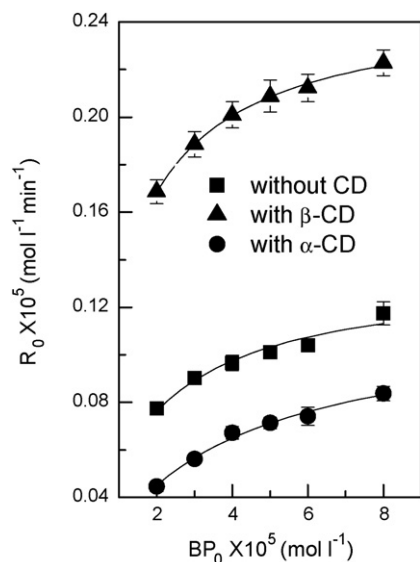


Fig. 6. Langmuir–Hinshelwood type simulation plots for BIP (■), BIP/β-CD (▲) and BIP/α-CD (●) in aqueous solution. Black curves were obtained by means of a non-linear regression fit of the Langmuir–Hinshelwood equation. BIP concentration varies from 20 to 80 μM, [CD] = 40 μM, TiO₂ = 0.5 g l⁻¹.

Table 2

Reaction rate constant (k_{re}) and K_s for BIP, BIP/β-CD and BIP/α-CD in aqueous solution obtained from Langmuir–Hinshelwood type plots simulation.

Substrate	k_{re} (μM min ⁻¹)	K_s (μM ⁻¹)
BIP	1.35	0.065
BIP/α-CD	1.17	0.032
BIP/β-CD	2.48	0.106

photodegradation rate of BIP in aqueous solutions containing β-CD and TiO₂ was obviously faster than that in aqueous solutions containing only TiO₂. It also can be seen that faster degradation rate accompanied with larger K_s value.

3.5. Mechanism of the effect of CDs on BIP photodegradation

As shown below, where reactions (a) and (d) account for the induced degradation of BIP and the complex CD-BIP, respectively by excitation of TiO₂, and the inclusion complex reaction (c) and the reaction between cyclodextrin and TiO₂ (b) was also taken into

account.



Since CDs have higher affinity on TiO₂ surface than BIP, CD molecules could adsorb on TiO₂ surface and occupy the reaction sites. Cyclodextrin would capture holes on active TiO₂ surface resulting in the formation of stable TiO₂/CD complex. So reaction (c), the inclusion complex reaction of cyclodextrin with reactants, should be the key step in photocatalytic degradation in TiO₂ suspension containing CDs, for β-CD/BIP, the inclusion constant is large (5600 M⁻¹), large parts of BIP forms inclusion complex, resulting in the indirect photodegradation to be the main reaction channel. Since the inclusion constant was much smaller, retardation of BIP degradation happened in a prerequisite condition that there was no or little direct photodegradation attributed to the occupied surface by α-CD. On the other hand, Tachikawa et al. observed the exclusion of aromatic radical cations from cyclodextrin nanocavity by pulse radiolysis resulting in the reaction of the radical in bulk solution [25]. Therefore, it was more difficult for BIP radical to be excluded from α-CD cavity while it formed α-CD₂/BIP at higher α-CD concentration. A trinity interaction model was proposed in Fig. 7.

As shown in Fig. 4, optimized ratio of β-CD to BIP was 5:1 in this study, which was quite close to the four azo dyes carried out in the previous study [13]. But for the bent bisphenol molecules, k_{obs} is the greatest at a ratio of 1:1. The effect of ratio of CDs/BIP on the photodegradation also could be explained by reaction (c). The inclusion constant of β-CD with BIP, Orange II and bisphenol A was 5600, 5000 [26] and 80,000 M⁻¹ [16], respectively. Most BPA could transform into inclusion complex even when the concentration of β-CD was low, leading to the indirect photodegradation reaction.

However, all-important works in the future should quantify direct photodegradation and indirect photodegradation in TiO₂ suspension containing cyclodextrin. Since cyclodextrin molecule could form various stoichiometry inclusion complexes with different guests, their photodegradation behaviors also should be investigated. All these works have already begun in our lab. It would be beneficial to have a depth-in mechanism of CDs effect on reactant's photodegradation in TiO₂ suspension that would probably lead to a high efficiency and selectivity photodegradation of pollutants using TiO₂ as catalyst.

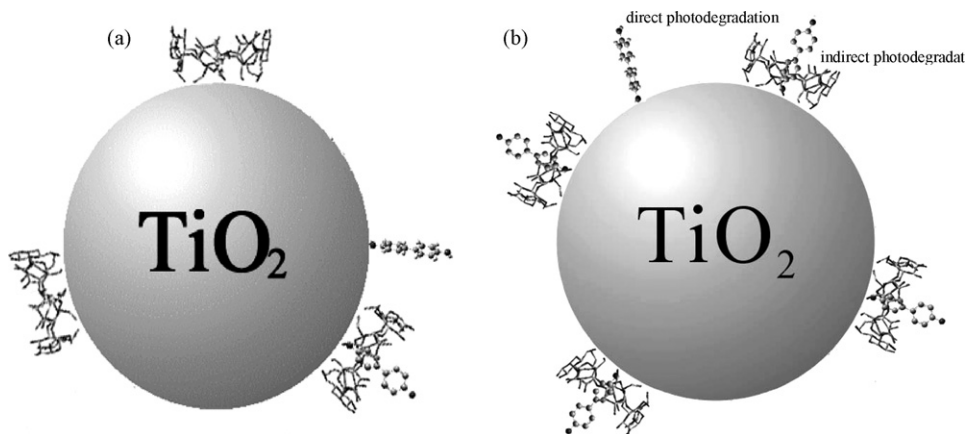


Fig. 7. A trinity interaction model of BIP photodegradation in TiO₂ suspension containing cyclodextrin (a) for α-CD and (b) for β-CD.

4. Conclusion

In this work, we carried out a detailed study of the effect of α -CD and β -CD on the photodegradation of BIP in TiO_2 suspension. We obtained equilibrium constant (K_{ad}), adsorption maximum capacity (θ) for BIP adsorbed on TiO_2 surface. K_{ad} values were 3294, 553 and 6216 M^{-1} for BIP in the absence of any CD, in the presence of α -CD or β -CD, respectively. α -CD showed rate retardation effect on BIP photodegradation in TiO_2 suspension, while great enhancement of BIP photodegradation was found in the presence of β -CD. Although, inhibition given by lower β -CD concentration does exist. XRD analysis demonstrated that TiO_2 conserved their anatase crystal features during the irradiation.

We think that inclusion of CD complex with reactant was the key step in TiO_2 photodegradation containing cyclodextrins. Inclusion constants of 51, 355 and 5600 M^{-1} were obtained for α -CD/BIP, α -CD₂/BIP and β -CD/BIP, respectively. Most BIP molecules could form inclusion complex with β -CD even at a low CD concentration, which results in the indirect photodegradation on TiO_2 surface. Theoretically, the value of α -CD/BIP should be large enough to make sure that BIP could transform into inclusion complex with α -CD, but superfluous α -CD would also conduce to the competition reaction with hydroxyl radical. Hence, α -CD showed rate retardation of BIP photodegradation in TiO_2 suspension, the reaction rate was decreased with increasing α -CD concentration. Furthermore, value of inclusion constant was also the deciding factor in the optimized amount of CD. A trinity interaction model of BIP photodegradation in TiO_2 suspension containing cyclodextrin was also proposed in this work.

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