

Enhanced TiO₂ photocatalytic degradation of bisphenol E by β-cyclodextrin in suspended solutions

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Abstract

Enhancement of β-cyclodextrin (β-CD) on TiO₂ photocatalytic degradation of bisphenol E (BPE, bis(4-hydroxyphenyl)ethane) was investigated under a 250 W metal halide lamp ($\lambda \geq 365$ nm) in this work. In the system of photocatalytic degradation of BPE, the photodegradation rate of BPE in aqueous solutions containing β-CD and TiO₂ was obviously faster than that in aqueous solutions containing only TiO₂. After 40 min of irradiation, β-CD could increase the photodegradation efficiency by about 26% for 10 mg l⁻¹ BPE in the UV-vis/TiO₂ system and the photodegradation of 2.5–20.0 mg l⁻¹ BPE in aqueous solutions was found to follow pseudo-first-order law and the adsorption constant and the reaction rate constant of BPE in the system containing β-CD and TiO₂ are obviously higher than those in the system containing only TiO₂, the influence factors on photodegradation of BPE were studied and described in details, such as β-CD concentration, pH, BPE initial concentration and gas medium. The formation of CO₂ as a result of mineralization of BPE was observed during the photodegradation process. After 120 min of irradiation, the mineralization efficiency of BPE reached 61% in the presence of β-CD, whereas mineralization efficiency was only 23% in the absence of β-CD. The enhancement of photodegradation of BPE could be dependent on the enhancement of adsorption of BPE on TiO₂ surface and moderate inclusion-depth of BPE in the β-CD cavity.

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1. Introduction

Recently, endocrine disruptors (EDs) have been suggested to be associated with abnormal sexual development and abnormal feminizing responses of animals and the research of endocrine disruptors in the environment has received increasing attention [1]. BPE is a suspected endocrine disruptor, but as an important industrial chemical, BPE has also been used as the monomer for the production of polycarbonate plastics and epoxy resins. BPE was reported to have a 48-h EC₅₀ of 18 mg l⁻¹ against *Daphnia magna*, and the acute toxicity and estrogenic activity of BPE were comparable to that of bisphenol A (BPA) [2], thus, the development of methods to remove BPE is needed urgently. In recent 20 years, TiO₂ semiconductor photocatalysis is a well-established technique for the destruction of environ-

mental pollutants [3]. Ohko et al. reported TiO₂ photocatalytic degradation of bisphenol A and evaluated the estrogenic activity in the treated water during the photocatalytic reaction and concluded that TiO₂ photocatalysis could be a useful technology for the purification of water containing bisphenol A without generating any serious secondary pollution [4].

Cyclodextrins (CDs) are cyclic oligosaccharides of six to eight α-D-glucose units connected through glycosidic α-1,4 bonds, which are composed of hydrophobic internal cavity and hydrophilic external surface, this kind of special molecular structure allows them to form host/guest inclusion complex with various guest molecules with suitable polarity and dimension. In the field of environmental research, because of non-toxicity and biodegradability, CDs have been applied to promote degradation of hazardous pollutants discharged in the aqueous environments. Kamiya et al. investigated the inclusion effect of CDs on photodegradation rates of parathion and paraoxon and found β-CD a large inhibition effect on the parathion photodegradation rate but a large promotion effect on paraoxon photodegradation and

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γ -CD a considerable inhibition effect on the photodegradation rates of both parathion and paraoxon, α -CD exerts a small promotion effect on photodegradation rates of both parathion and paraoxon [5].

At present, many methods have been adopted for improving TiO_2 photocatalytic efficiency [6–10]. β -CD has been found to be able to improve the kinetics for charger transfer from the photoexcited semiconductor to electron acceptors retained in the β -CD cavity [11], so it is greatly significant to study on the effect of β -CD on the photodegradation behavior of organic substrates. In this work, a suspected endocrine disrupter BPE was used as a model compound, its photodegradation behavior based on β -CD modified TiO_2 was investigated for the first time under a 250 W metal halide lamp ($\lambda \geq 365$ nm) and formation and characterization of inclusion complex between β -CD and BPE were also studied. The effect of initial pH value, initial concentration of BPE, β -CD concentration and gas medium were evaluated and kinetics analysis was conducted, the mineralization efficiency of BPE was also determined during the photodegradation process. Supramolecular photodegradation system based on cyclodextrin is a kind of promising treatment method for some organic pollutants.

2. Materials and methods

2.1. Materials

Bisphenol E was purchased from Sigma–Aldrich (GC grade >99%). Its chemical structure is given in Fig. 1. α -CD and β -CD were purchased from Seebio Biotechnology Inc. (Shanghai, PR China) and Shuanxuan Microbe Medium Products Factory (Beijing, PR China), respectively, and used without further purification. Properties of α -CD and β -CD are listed in Table 1. The photocatalyst nano- TiO_2 (particle size 10–20 nm, surface area $120 \text{ m}^2 \text{ g}^{-1}$, crystal structure 100% anatase as determined by X-ray diffraction analysis) was purchased from High Technology Nano Co. Ltd. (Nanjing, PR China). Acetonitrile was of

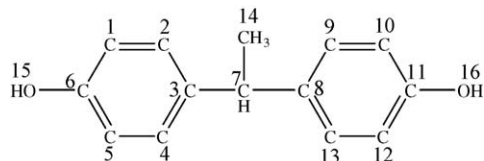


Fig. 1. Chemical structure of bisphenol E.

Table 1
Properties of cyclodextrin

Item	α -Cyclodextrin	β -Cyclodextrin
Glucose number	6	7
Molecular weight	972	1135
Solubility (0.01 g ml^{-1} (25°C))	14.5	1.85
Cavity diameter (\AA)	4.7–5.3	6.0–6.5
Cavity height (\AA)	7.9 ± 0.1	7.9 ± 0.1
Cavity volume (ml mol^{-1})	174	262

HPLC grade (Lingfeng Chemical Reagent Co., Shanghai, PR China). HCl and NaOH were used to adjust the pH values of solutions. All of the other reagents were analytic reagent grade. The double distilled water was used in the experiment.

2.2. Photodegradation experiment

Irradiation experiments were carried out in a cylindrical reactor, with a 250 W metal halide lamp ($\lambda \geq 365$ nm, Chenguang Illumination Instrument, Jinzhou, China) placed in cooling trap for maintaining constant temperature by water circulation. BPE and β -CD/BPE solutions containing TiO_2 were prepared in water, the pH values of reactant solutions were adjusted with HCl and NaOH depending on desired values and placed in photochemical reactor and purged with air at a fixed flow rate throughout the experiment. Prior to irradiation, the TiO_2 suspensions were equilibrated in the dark for 30 min. At different time intervals during the irradiation, samples were collected and centrifuged at 5000 rpm for 30 min in an LD5A-2A centrifuge (Beijing, PR China), and then the BPE concentration was determined by HPLC-UV.

2.3. Analysis and calculation

The UV absorbance spectra of BPE solution were recorded with spectrophotometer UV-1601 (Shimadzu, Japan). The characteristic absorbance peaks were at 227 and 280 nm, respectively. BPE in aqueous solution was detected by HPLC [Shimadzu LC-10ATVP pump, Shim-pack VP-DDS-C18 column ($4.6 \text{ mm} \times 150 \text{ mm}$, $5 \mu\text{m}$)] with a flow rate of 1.0 ml min^{-1} and UV detector (Waters 481 detector) at 280 nm. The mobile phase was acetonitrile/water mixture (50/50, v/v). The injection volume was $20 \mu\text{l}$. The retention time of BPE was about 4.8 min. The calibration curve equation for BPE detection was peak area = $15389.4C_{\text{BPE}} - 3444.5$ ($r = 0.9990$), where C_{BPE} was the concentration of BPE in the range of (0–10.0) mg l^{-1} . Measurements were carried out in triplicate for each experiment with errors less than 5%.

Carbon dioxide produced upon irradiation was determined as BaCO_3 [12] to inspect the mineralization efficiency of 200 ml BPE solution ($C_{\text{BPE}} = 10.0 \text{ mg l}^{-1}$) with and without β -CD at pH 6.0. CO_2 was removed from solution by oxygen and introduced into a concentrated $\text{Ba}(\text{OH})_2$ solution to produce BaCO_3 . The solutions were collected, BaCO_3 was allowed to precipitate and the excess of $\text{Ba}(\text{OH})_2$ was titrated with HCl solution with phenolphthalein as indicator. A blank experiment without BPE was performed under the same conditions.

The initial geometry of BPE and β -CD was constructed with the help of model in the Chemoffice (2004). The structures of BPE, β -CD and BPE/ β -CD were first optimized using molecular mechanics (MM) methods and then PM3 method was used, which is a semi-empirical method, but its performance is better than AM1 in biochemical systems because of its improved description of the interactions between non-bonded atoms, such as van der Waals, hydrogen bonding and hydrophobic forces. All calculations were carried out at P4 personal computer.

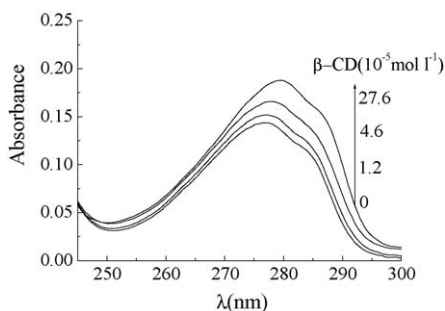


Fig. 2. UV absorbance spectra of BPE/ β -CD inclusion complex [BPE]=10.0 mg l⁻¹ and pH 6.0.

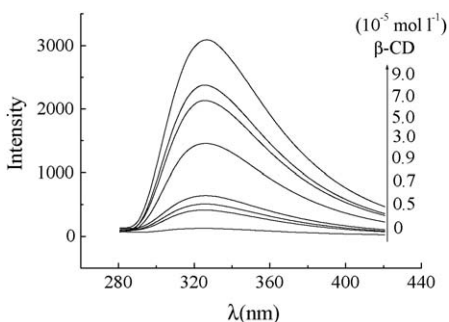


Fig. 3. Fluorescence spectra of BPE/ β -CD inclusion complex $\lambda_{\text{ex}}=276$ nm, $\lambda_{\text{em}}=325$ nm, [BPE]=10 mg l⁻¹ and pH 6.0.

2.4. Characterization of inclusion complex and determination of formation constant

β -CD can form host–guest inclusion complex with BPE. In this experiment, the inclusion complex was characterized with UV and fluorescence spectra. The results are shown in Figs. 2 and 3, respectively. Fig. 2 shows that the absorbance of inclusion complex increases with increasing of β -CD concentration and its maximum absorption wavelength shifts toward long wavelength. As can be seen in Fig. 3, the fluorescence intensity of BPE was also enlarged with increasing β -CD concentration. Based on the data of fluorescence spectra, a modified Benesi–Hildebrand equation was employed to calculate the formation constant K_f ($K_f=7.81 \times 10^3$ l mol⁻¹) and concluded that the molar ratio β -CD to BPE is 1:1.

3. Result and discussion

3.1. The control experiment

The BPE solutions were irradiated under metal halide lamp (250 W) with or without the addition of β -CD and TiO₂. The results are shown in Fig. 4. The concentration of BPE in aqueous solution in the absence of TiO₂ does not change after 60 min of irradiation, this is because that BPE and inclusion complex of BPE with β -CD in aqueous solutions have no absorption to the light with wavelength above 365 nm, no direct photolysis occurred in the experiment. The photodegradation of BPE occurred in solutions containing only TiO₂ and the photodegradation rate of BPE in aqueous solutions containing β -CD and

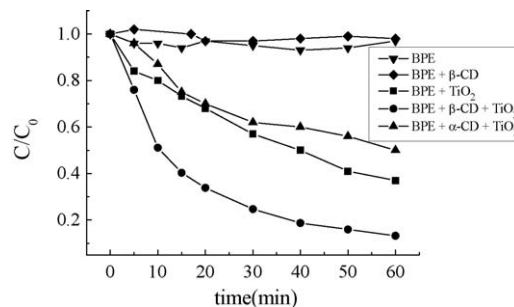


Fig. 4. BPE concentration change vs. time in the control experiments [BPE]=10.0 mg l⁻¹, [β -CD]= 4.6×10^{-5} mol l⁻¹ and [TiO₂]=1.0 g l⁻¹.

TiO₂ was obviously faster than that in aqueous solutions containing only TiO₂ and simultaneously, in order to prove whether β -CD could get degraded during the photocatalytic reaction of TiO₂, we carried out some experiments about β -CD in the UV–vis/TiO₂ system, the results are shown in Fig. 5. It is well known that no β -CD is degraded during the photochemical process. It is because β -CD was bonded onto TiO₂ surface and formed a stable supramolecular semiconductor receptor assembly unit [13], but α -CD exerted a small inhibition effect on the photodegradation of BPE, this is because α -CD has a small cavity and cannot form stable inclusion complex with BPE, which resulting in more free BPE molecules in the system and competitive adsorption between BPE and α -CD on the surface of TiO₂ will occur, therefore, the adsorbed BPE molecular on the surface of TiO₂ in the presence of α -CD is less than that in the absence of α -CD and the photodegradation rate of BPE in aqueous solution containing α -CD and TiO₂ is slower than that in aqueous solutions containing only TiO₂ correspondingly.

3.2. Effect of initial pH values

The effect of initial pH values on photodegradation of BPE was investigated and results are shown in Fig. 6. In the system containing TiO₂, the photodegradation rate of BPE decreased with increasing pH values from 3 to 12. This is due to the change of surface charge on TiO₂ solids from the positive to the negative causing the decrease of phenoxide anion adsorption onto solids. However, adding β -CD into the TiO₂ system caused the photodegradation rates to first increase then decrease with increasing pH values. The maximum reaction rate for BPE

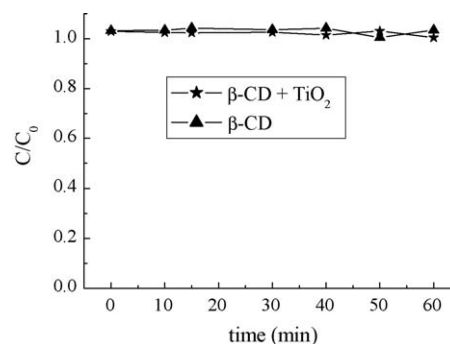


Fig. 5. β -CD concentration change vs. time during photochemical process [β -CD]= 4.6×10^{-5} mol l⁻¹ and [TiO₂]=1.0 g l⁻¹.

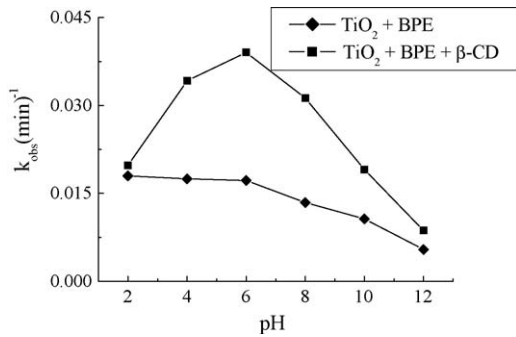


Fig. 6. Effect of the pH on photocatalytic oxidation of BPE [BPE] = 10 mg l⁻¹, [β -CD] = 4.6 \times 10⁻⁵ mol l⁻¹ and [TiO₂] = 1.0 g l⁻¹.

is at pH 6. This might have something to do with the inclusion of β -CD with BPE and the surface interaction between β -CD and TiO₂. Lu et al. studied the pH effect on β -CD adsorption amount on TiO₂ and found β -CD adsorption amount on TiO₂ is pH dependent with higher adsorption efficiency at pH values of 4–6, but lower adsorption efficiency in acidic and alkaline solution [6], so the better enhancement effect of photodegradation of BPE was obtained at pH 6 in the system containing TiO₂ and β -CD.

3.3. Effect of β -CD concentrations

Under the condition of pH 6.0, 10 mg l⁻¹ BPE and 1.0 g l⁻¹ TiO₂, the effects of β -CD concentration on photodegradation of BPE were investigated. The results are shown in Fig. 7. It is well shown that the photodegradation rates of BPE first increase then decrease with the β -CD concentration in the range of 0–18.4 \times 10⁻⁵ mol l⁻¹ and the maximum reaction rate is at β -CD concentration 4.6 \times 10⁻⁵ mol l⁻¹.

Early in 1994, Willner et al. reported the adsorption behavior β -CD on TiO₂, he suggested a monolayer adsorption process on TiO₂ and the adsorption isotherm of β -CD on TiO₂ is in accordance with Langmuir adsorption theory [13]. According to the adsorption model, we can know that equilibrium adsorption amount of β -CD on TiO₂ increases with increasing of β -CD concentration and has a maximum, so adsorption amount of BPE on TiO₂ increases with increasing of β -CD and the photodegradation rates of BPE increase, when β -CD reaches equilibrium adsorption on TiO₂ surface, no more β -CD can be adsorbed

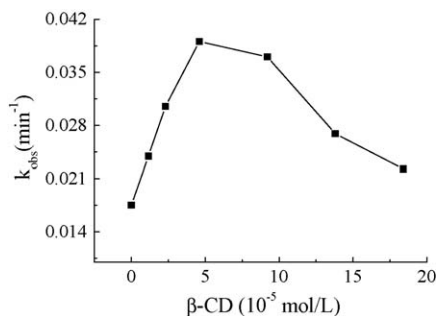


Fig. 7. Effect of the β -CD concentration on photocatalytic oxidation of BPE [BPE] = 10.0 mg l⁻¹, [TiO₂] = 1.0 g l⁻¹ and pH 6.0.

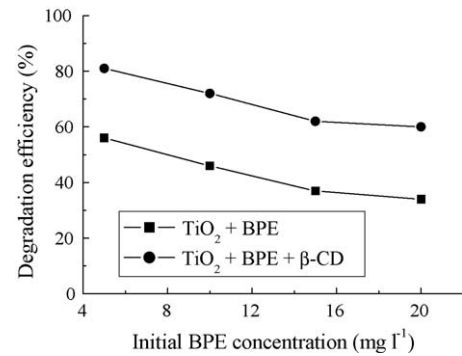


Fig. 8. Effect of initial concentration of BPE on the degradation efficiency [TiO₂] = 1.0 g l⁻¹, [β -CD] = 4.6 \times 10⁻⁵ mol l⁻¹, pH 6.0 and time = 40 min.

onto TiO₂, which results in competing toward hydroxyl radicals between unadsorbed β -CD and BPE during the photoreaction, so photodegradation rates of BPE decrease at higher β -CD concentration.

3.4. Effect of initial BPE concentration on degradation efficiency

To investigate the effects of BPE initial concentration on degradation efficiency, under the condition of pH 6.0, 4.6 \times 10⁻⁵ mol l⁻¹ β -CD and 1.0 g l⁻¹ TiO₂, the experiments were conducted at different BPE initial concentration of 5.0, 10.0, 15.0 and 20.0 mg l⁻¹. The results shown in Fig. 8 indicate that the higher initial BPE concentration, the lower BPE photodegradation efficiency is, and the photodegradation efficiency of BPE in aqueous solutions containing β -CD and TiO₂ was obviously higher than that in aqueous solutions containing only TiO₂. After 40 min of irradiation, β -CD could increase the photodegradation efficiency by about 26% for 10 mg l⁻¹ BPE in the UV–vis/TiO₂ system.

3.5. Effect of different gases on photodegradation BPE

The effect of different gases on photodegradation BPE was also investigated under the condition of pH 6.0, 10 mg l⁻¹ BPE, 1.0 g l⁻¹ TiO₂ and 4.6 \times 10⁻⁵ mol l⁻¹ β -CD. Results are shown in Fig. 9. It is well shown that the different gases have obvious effect on photodegradation of BPE. When nitrogen was used as

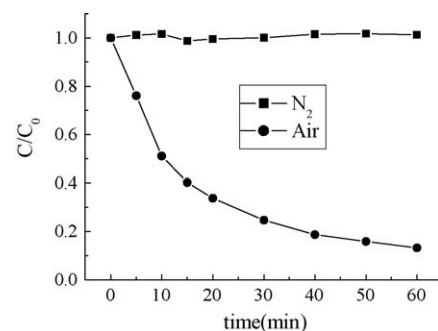


Fig. 9. Effect of the different gases on photocatalytic oxidation of BPE [BPE] = 10 mg l⁻¹, [β -CD] = 4.6 \times 10⁻⁵ mol l⁻¹, [TiO₂] = 1.0 g l⁻¹ and pH 6.0.

gas medium, no decrease of BPE concentration was observed during irradiation, which indicates that BPE cannot be degraded in the system purged nitrogen, whereas obvious photodegradation of BPE occurred in the system purged air, which indicates that photodegradation of BPE has something to do with oxygen in the air. This is because that molecular oxygen can react with conduction band electrons (e_{cb}^-) to yield superoxide radical anions ($O_2^{\bullet-}$) and hydroxyl radicals, which are active species in the photodegradation of organic material, and on the other hand electron-hole can easily recombine in the absence of oxygen.

3.6. Analysis of photodegradation kinetics

In this experiment, a semi-log plot of initial concentration of BPE versus irradiation time was linear indicating overall pseudo-first-order kinetics. The experiment was repeated with a range of initial concentrations from 2.5 to 20 mg l⁻¹. The initial rates for each concentration were determined from the pseudo-first-order rate constants and initial concentrations. The data were then fitted into the Langmuir–Hinshelwood kinetics rate model, which has been applied to the initial rates of photocatalytic degradation of many organic compounds [14]. The rate law is shown in Eq. (1), where R is the initial rate of disappearance of substrate and C is the initial concentration. k_{re} is the reaction rate constant and K_s is taken to be the Langmuir adsorption constant. However, the value of K_s is not directly equivalent to the Langmuir adsorption constant determined in the dark:

$$R = -\frac{dC}{dt} = \frac{k_{re}K_sC}{1 + K_sC} \quad (1)$$

The constants k_{re} and K_s were determined from a plot of $1/R$ versus $1/C$, with the slope equal to $1/k_{re}K_s$ and an intercept equal to $1/k_{re}$ and above calculation results are shown Table 2.

It could be seen that the initial rate of BPE photodegradation increased with increasing the initial concentration of BPE and because of higher reaction rate constant in the system containing β -CD and TiO_2 , the photodegradation rate of BPE in aqueous solutions containing β -CD and TiO_2 was obviously faster than that in aqueous solutions containing only TiO_2 .

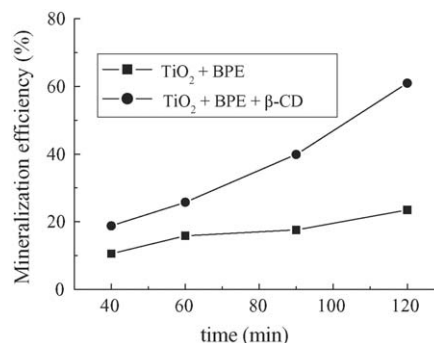


Fig. 10. Comparison of mineralization efficiency of BPE with β -CD and without β -CD [BPE] = 10.0 mg l⁻¹, [β -CD] = 4.6×10^{-5} mol l⁻¹, [TiO_2] = 1.0 g l⁻¹ and pH 6.0.

3.7. Effect of β -CD on mineralization of BPE

To investigate the effect of β -CD on the mineralization degree of BPE, the amount of CO_2 produced by the photocatalytic degradation reaction was measured. The results are shown in Fig. 10. It is well shown that the mineralization efficiency increases with increasing of irradiation time and the mineralization efficiency of BPE in the system containing β -CD and TiO_2 is obviously higher than that in the system containing only TiO_2 , after 120 min of irradiation, the mineralization efficiency of BPE reached 61% in the presence of β -CD, whereas the mineralization efficiency was only 23% in the absence of β -CD, which indicates the β -CD has obvious enhancement on the mineralization of BPE.

3.8. Result of HPLC chromatogram analysis

HPLC chromatograms of BPE with β -CD and without β -CD during photodegradation are shown in Fig. 11. It can be seen that the peaks area of BPE decreases with increasing reaction time and some obvious products with lower molecular weight and higher polarity formed at shorter retention time [15]. No other product peaks obviously occurred in HPLC chromatogram, this is because some products have lower absorption at wavelength 280 nm. Comparing groups (a and b), we find that peak area of

Table 2
Kinetics analysis of the photodegradation of BPE

System	BPE initial concentration C (mg l ⁻¹)	Initial rate R (mg l ⁻¹ min ⁻¹)	Kinetics equation	Reaction rate constant k_{re} (mg l ⁻¹ min ⁻¹)
TiO_2	2.5	0.06415	$R = \frac{0.0330C}{1+0.115C}, (r_1 = 0.9991)$	0.287
	5.0	0.1048		
	10.0	0.1535		
	15.0	0.1733		
	20.0	0.2108		
TiO_2/β -CD	2.5	0.1230	$R = \frac{0.0598C}{1+0.0878C}, (r_1 = 0.9990)$	0.682
	5.0	0.208		
	10.0	0.318		
	15.0	0.365		
	20.0	0.463		

r_1 represents correlation coefficient between $1/R$ and $1/C$.

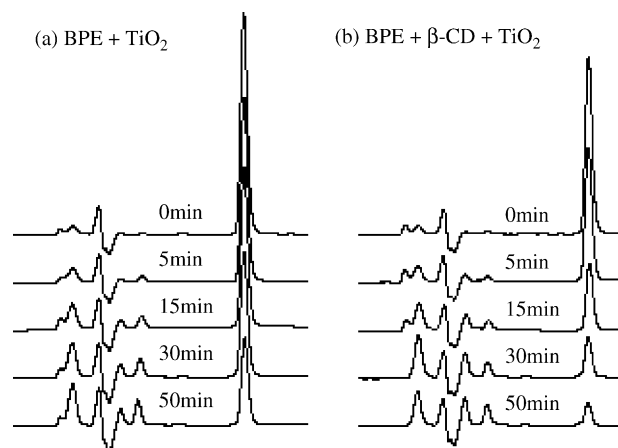


Fig. 11. HPLC chromatograms of BPE with β -CD and without β -CD during photodegradation (UV detector wavelength 280 nm) [BPE] = 10.0 mg l⁻¹, [β -CD] = 4.6 $\times 10^{-5}$ mol l⁻¹, [TiO₂] = 1.0 g l⁻¹ and pH 6.0.

BPE in the system containing β -CD and TiO₂ decreases obviously faster than that in the system containing only TiO₂ during photodegradation process. Moreover, at the beginning of irradiation, the peak area of BPE in the system containing β -CD and TiO₂ is obvious lower than that in the system containing only TiO₂, which indicates that more BPE molecules were adsorbed on the TiO₂ surface in the presence of β -CD, which results in enhancement effect of BPE photodegradation because of the inclusion of BPE with β -CD and the surface interaction between β -CD and TiO₂.

3.9. Preliminary study on the mechanism of the enhancement

From previous studies [6,13], we have known that β -CD can be bonded or adsorbed on TiO₂. To preliminary inspect the mechanism of the enhancement of BPE photodegradation, we first investigated the adsorption of BPE on TiO₂ surface in the presence or in the absence of β -CD in order to confirm that β -CD can enhance adsorption of BPE on TiO₂ surface. The adsorption of BPE on TiO₂ surface fits into Langmuir-type isotherm, which is described as follows [4]:

$$\frac{1}{M} = \frac{1}{\theta} + \frac{1}{\theta K_{ad} C} \quad (2)$$

where θ is the maximum adsorption amount of BPE on TiO₂ ($\mu\text{mol g}^{-1}$), K_{ad} the adsorption binding constant ($1 \mu\text{mol}^{-1}$), M the equilibrium adsorption amount of BPE on TiO₂ ($\mu\text{mol g}^{-1}$) and C is the equilibrium concentration of BPE in solutions ($\mu\text{mol l}^{-1}$). The results are listed in Table 3. From Table 3, it is well shown that the maximum adsorption amount and the

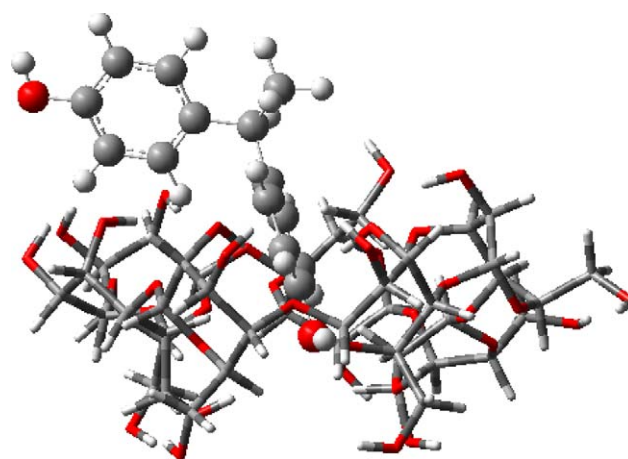


Fig. 12. Proposed structure of the BPE/ β -CD inclusion complex.

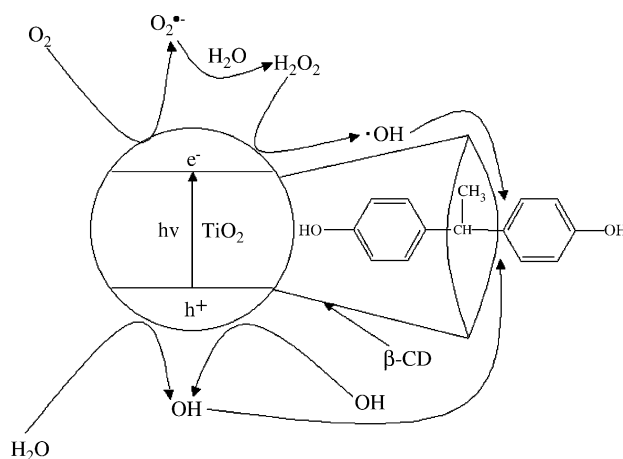


Fig. 13. Mechanism of the enhancement of BPE photodegradation.

adsorption constant of BPE in the system containing β -CD and TiO₂ are obviously higher than those in the system containing only TiO₂. Therefore, more BPE molecules can be adsorbed on TiO₂ surface because of inclusion with β -CD, which results in enhanced photochemical degradation of BPE.

On the other hand, based on the molecular modeling, the structure of BPE/ β -CD inclusion complex can be obtained. It is shown in Fig. 12. It is well known that BPE molecular can enter partly into the β -CD cavity, the remarkable enhancement effect of β -CD on the photodegradation of BPE could be dependent on the moderate inclusion-depth [5] which allows sufficient proximity of the reaction center of BPE (the position of C3 and C8 in the phenyl groups of BPE [16]) to catalytically active secondary hydroxyl groups of the β -CD cavity which can enhance the oxidation of excited BPE.

Table 3
Adsorption behavior of BPE in the aqueous solutions on the TiO₂ surface

	Adsorption equation	Maximum adsorption amount θ ($\mu\text{mol g}^{-1}$)	Adsorption constant K_{ad} ($1 \mu\text{mol}^{-1}$)
Without β -CD	$\frac{1}{M} = 0.2027 + \frac{47.36}{C}$, ($r_2 = 0.9997$)	4.93	4.28×10^{-3}
With β -CD	$\frac{1}{M} = 0.02906 + \frac{4.033}{C}$, ($r_2 = 0.9991$)	34.41	7.20×10^{-3}

r_2 represents correlation coefficient between $1/M$ and $1/C$.

Based on above results, we can draw a preliminary conclusion that the enhancement of photodegradation of BPE mainly results from the enhanced adsorption of BPE on the TiO₂ surface and moderate inclusion-depth of BPE in the β-CD cavity.

So, we propose a trinity interaction model of BPE–CD–TiO₂, which is described in Fig. 13. Since β-CD can include BPE in its cavity and be adsorbed onto the surface of TiO₂, it could play a role as “bridge” or “channel” for BPE to get onto the TiO₂ surface and accumulate to higher concentration which makes BPE degrade more easily in the presence of hydroxyl radicals photoproduced by TiO₂.

4. Conclusion

β-CD can enhance the photodegradation of BPE under the irradiation of a near UV light, the photodegradation rate of BPE depends on β-CD concentration, pH and BPE initial concentration. The photodegradation rate of BPE in aqueous solution containing β-CD and TiO₂ was obviously faster than that in aqueous solution containing only TiO₂, the reaction rate constant and the adsorption constant are 0.682 mg l⁻¹ min⁻¹, 7.20 × 10⁻³ l μmol⁻¹, respectively, in the system containing TiO₂ and β-CD, whereas they are 0.287 mg l⁻¹ min⁻¹, 4.28 × 10⁻³ l μmol⁻¹, respectively, in the system containing only TiO₂. The photodegradation efficiency of BPE decreased with increasing initial BPE concentration and the photodegradation efficiency of BPE in aqueous solution containing β-CD and TiO₂ was obviously higher than that in aqueous solution containing only TiO₂. After 40 min of irradiation, β-CD could increase the photodegradation efficiency by about 26% for 10 mg l⁻¹ BPE in the UV–vis/TiO₂ system at pH 6.0. After 120 min of irradiation, the mineralization efficiency of BPE reached 61% in the presence of β-CD, whereas mineralization efficiency was only 23% in the absence of β-CD. The enhancement of photodegradation of BPE mainly results from the enhancement of adsorption of BPE on TiO₂ and moderate inclusion-depth of BPE in the β-CD cavity.

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