

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

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Abstract

Enhancement of β -cyclodextrin (β -CD) on TiO₂ photocatalytic degradation of bisphenol A (BPA) was investigated under a 250 W metal halide lamp ($\lambda \geq 365$ nm) in this work. In the system of photocatalytic degradation of BPA, the photodegradation rate of BPA in aqueous solutions containing β -CD and TiO₂ was obviously faster than that in aqueous solutions containing only TiO₂. After 60 min of irradiation, β -CD could increase the photodegradation efficiency by about 23% for 10 mg l⁻¹ BPA in the UV-vis/TiO₂ system, the photodegradation of 2.5–20.0 mg l⁻¹ BPA in aqueous solutions was found to follow pseudo-first-order law, and the adsorption constant and the reaction rate constant of BPA 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 BPA were studied and described in details, such as β -CD concentration, pH, BPA initial concentration and gas medium. The formation of CO₂ as a result of mineralization of BPA was observed during the photodegradation process. After 120 min of irradiation, the mineralization efficiency of BPA reached 100% in the presence of β -CD, whereas mineralization efficiency was only 36.7% in the absence of β -CD. The enhancement of photodegradation of BPA mainly results from the enhancement of adsorption of BPA on TiO₂ surface and the lower bond energy between some atoms in BPA molecule after inclusion interactions with β -CD.

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1. Introduction

The research of endocrine disrupters in the environment has received increasing attention in recent years [1]. Bisphenol A (BPA) is a representative endocrine disrupter, but as an important industrial chemical, BPA has been widely used as the monomer for the production of polycarbonate plastics, such as baby bottles and as a major component of epoxy resin for lining of food cans and dental sealants [2]. Global production of bisphenol A is over a million tonnes per year, with an estimated European annual production of 504,000 tonnes [3], in Japan, over 200,000 tonnes of BPA is estimated to be produced every year [4]. It was reported that BPA could be

released from polycarbonate flasks during autoclaving and lacquer coating in food cans [5], and it is well known that BPA causes not only strong estrogenic endocrine disrupting effect [6] but also various disease including carcinogenesis [7,8]. BPA has an acute toxicity in the range of about 1–10 mg l⁻¹ for a number of freshwater and marine species [9]. Thus, the development of methods to remove BPA is needed urgently. Biological [10] and chemical [11–17] procedures have been used for degradation and treatment of BPA. However, there are some disadvantages in treatment time and treatment efficiency. In recent 20 years, TiO₂ semiconductor photocatalysis is a well-established technique for the destruction of environmental pollutants [18]. Ohko et al. reported TiO₂ photocatalytic degradation of BPA and evaluated the estrogenic activity in the treated water during the photocatalytic reaction and concluded that TiO₂ photocatalysis could

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be a useful technology for the purification of water containing BPA without generating any serious secondary pollution [19].

Cyclodextrins (CDs) are cyclic oligosaccharides of six to eight α -D-glucose units connected through glycosidic α -1,4 bonds and 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 of a large inhibition effect on the parathion photodegradation rate but a large promotion effect on paraoxon photodegradation and 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 [20].

At present, many methods have been adopted for improving TiO_2 photocatalytic efficiency [21–25]. β -CD has been found to be able to improve the charge transfer from the photoexcited semiconductor to electron acceptors retained in the β -CD cavity and concentrate some organic substrates on TiO_2 surface [26], so it is greatly significant to study the effect of β -CD on the photodegradation behavior of organic substrates. In this work, a representative endocrine disrupter BPA 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 BPA were also studied. The effect of initial pH value, initial concentration of BPA, β -CD concentration and gas medium were evaluated and kinetics analysis was conducted, the mineralization efficiency of BPA 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

Chemically pure BPA was purchased from Damao Chemicals Co. (Tianjin, PRC) and used without further purification. Its chemical structure is given in Fig. 1. α -CD and β -CD were purchased from Seebio Biotechnology Inc. (Shanghai, PRC) and Shuanxuan Microbe Medium Products Factory (Beijing, PRC), 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

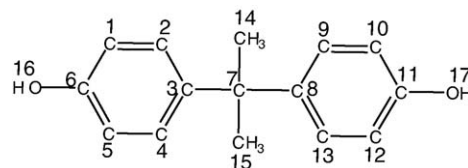


Fig. 1. Chemical structure of bisphenol A.

High Technology Nano Co. Ltd. (Nanjing, PRC). Acetonitrile was HPLC grade (Lingfeng Chemical Reagent Co., Shanghai, PRC). 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, Chengguang Illumination Instrument, Jinzhou, China) placed in cooling trap for maintaining constant temperature by water circulation. BPA and β -CD/BPA 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 10 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, PRC), and then the BPA concentration was determined by HPLC–UV.

2.3. Analysis and calculation

The UV absorbance spectra of BPA solution were recorded with spectrophotometer UV-1601 (Shimadzu, Japan). The characteristic absorbance peaks were at 225 and 280 nm, respectively. BPA 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 (Shimadzu UV–vis 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 BPA was about 6.0 min. The calibration curve equa-

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
Water (wt%)	10.2	13.2–14.5
pK_a (25°C)	12.332	12.202
Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) (25°C)	3.443	3.224

tion for BPA detection was peak area = 7735.8 C_{BPA} - 742.6 ($r = 0.9996$), where C_{BPA} was the concentration of BPA in the range of 0–10.0 mg l^{-1} . Measurements were made in triplicate in each experiment with errors less than 5%.

Carbon dioxide produced upon irradiation was determined as BaCO_3 [27] to inspect the mineralization efficiency of 200 ml BPA solution ($C_{\text{BPA}} = 10.0 \text{ mg l}^{-1}$) 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 BPA was performed under the same conditions.

The initial geometry of BPA and β -CD were constructed with the help of model in the Chemoffice (2004). The structure of BPA, β -CD and BPA/ 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. Finally B3LYP was used, which is one kind of density functional theory (DFT) in Gaussian98 package, at the STO-3G level. All calculations were carried out at P4 personal computer.

2.4. Characterization of inclusion complex and determination of formation constant

β -CD can form host/guest inclusion complex with BPA [28]. 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 BPA was also enlarged with increasing β -CD concentration. Based on the data of fluorescence spectra, a modified Bensi–Hildebrand equation was employed to

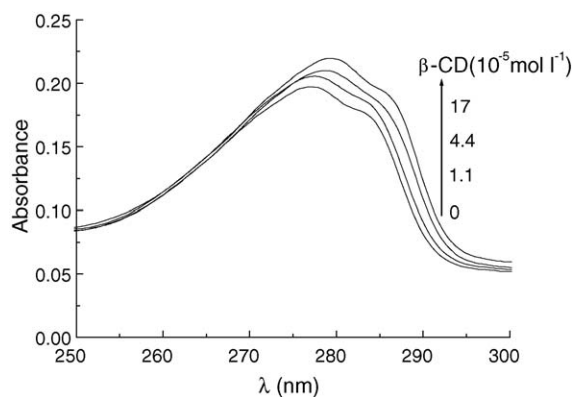


Fig. 2. UV absorbance spectra of BPA/ β -CD inclusion complex where $[\text{BPA}] = 10.0 \text{ mg l}^{-1}$, pH 6.0.

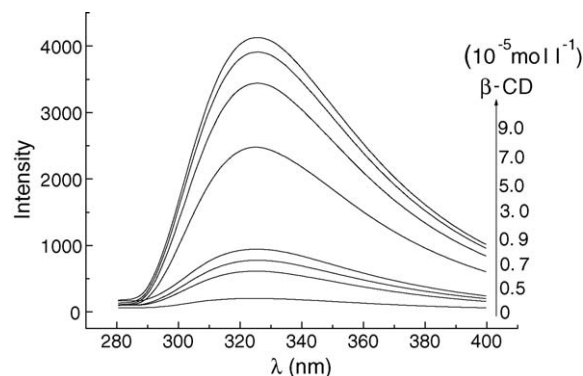


Fig. 3. The fluorescence spectra of BPA/ β -CD inclusion complex where $\lambda_{\text{ex}} = 276 \text{ nm}$, $\lambda_{\text{em}} = 325 \text{ nm}$, $[\text{BPA}] = 10 \text{ mg l}^{-1}$, pH 6.0.

calculate the formation constant K_f ($K_f = 5.80 \times 10^3 \text{ l mol}^{-1}$) and concluded that the molar ratio β -CD to BPA is 1:1.

2.5. Error

The data are presented as means from triplicate experiments. The errors are below 5%.

3. Result and discussion

3.1. The control experiment

The BPA solutions were irradiated under metal halide lamp (250 W) with or without the addition of β -CD and TiO_2 . The results are shown in Fig. 4. The concentration of BPA in aqueous solution in the absence of TiO_2 does not change after 60 min of irradiation, this is because BPA and inclusion complex of BPA 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 BPA occurred in solutions containing only TiO_2 , and the photodegradation rate of BPA in aqueous solutions containing β -CD and TiO_2 was obviously faster than that in aqueous solutions containing only TiO_2 , no β -CD was degraded dur-

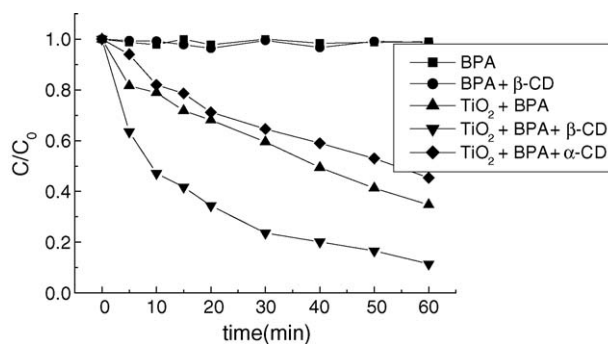


Fig. 4. BPA concentration change vs. time in the control experiments where $[\text{BPA}] = 10 \text{ mg l}^{-1}$, $[\beta\text{-CD}] = 4.4 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{TiO}_2] = 1.0 \text{ g l}^{-1}$, $[\alpha\text{-CD}] = 4.4 \times 10^{-5} \text{ mol l}^{-1}$, pH 6.0.

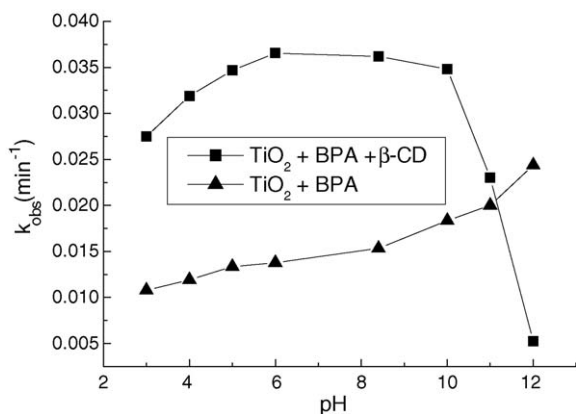


Fig. 5. Effect of the pH on photocatalytic oxidation rates of BPA where [BPA] = 10 mg l⁻¹, [β-CD] = 4.4 × 10⁻⁵ mol l⁻¹, [TiO₂] = 1.0 g l⁻¹.

ing the photochemical process because β-CD was bonded onto TiO₂ surface and formed a stable supramolecular semiconductor receptor assembly unit [21,26], but α-CD exerted a small inhibition effect on the photodegradation of BPA, this is because that α-CD has a small cavity and can not form stable inclusion complex with BPA.

3.2. Effect of initial pH values

The effect of initial pH values on photodegradation of BPA was investigated and results are shown in Fig. 5. In the system containing TiO₂, the pseudo-first-order rate constants (k_{obs}) of BPA increase with increasing pH values from 3 to 12. This is because that BPA can form phenolicoxide anion in alkaline solution and be easily oxidised, on the other hand, with the increasing pH, the hydroxyl radicals produced on TiO₂ surface increase, they can attack the benzene ring more easily. So the photodegradation rate of BPA gradually increases with increasing of pH. However, adding β-CD into the TiO₂ system causes the pseudo-first-order rate constants (k_{obs}) to first increase then decrease with increasing pH values. The maximum pseudo-first-order rate constant (k_{obs}) of BPA is at pH 6. This might have something to do with the inclusion of β-CD with BPA 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 [21], so the better enhancement effect of photodegradation of BPA 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 BPA and 1.0 g l⁻¹ TiO₂, the effects of β-CD concentration on photodegradation of BPA were investigated, the results are shown in Fig. 6. It is well shown that the pseudo-first-order rate constants (k_{obs}) of BPA first increase then decrease with the β-CD

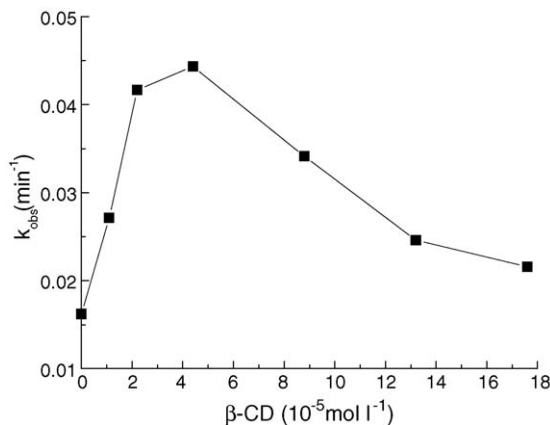


Fig. 6. Effect of the β-CD concentration on photocatalytic oxidation rates of BPA where [BPA] = 10 mg l⁻¹, [TiO₂] = 1.0 g l⁻¹, pH 6.0.

concentration in the range of 0–17.6 × 10⁻⁵ mol l⁻¹ and the pseudo-first-order rate constant of BPA was the greatest at β-CD concentration of 4.4 × 10⁻⁵ mol l⁻¹.

Early in 1994, Willner et al. reported the adsorption behavior of 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 [26]. 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 BPA on TiO₂ increases with increasing of β-CD and the photodegradation rates of BPA increase, when β-CD reaches equilibrium adsorption on TiO₂ surface, no more β-CD can be adsorbed onto TiO₂, which results in competing toward hydroxyl radicals between unadsorbed β-CD and BPA during the photoreaction, so photodegradation rates of BPA decrease at higher β-CD concentration.

3.4. Effect of initial BPA concentration on degradation efficiency

To investigate the effects of BPA initial concentration on degradation efficiency, under the condition of pH 6.0, 4.4 × 10⁻⁵ mol l⁻¹ β-CD and 1.0 g l⁻¹ TiO₂, the experiments were conducted at different BPA initial concentration of 5.0, 10.0, 15.0 and 20.0 mg l⁻¹. The results shown in Fig. 7 indicate that higher the initial BPA concentration, the lower BPA photodegradation efficiency is, and the photodegradation efficiency of BPA in aqueous solutions containing β-CD and TiO₂ was obviously higher than that in aqueous solutions containing only TiO₂. After 60 min of irradiation, β-CD could increase the photodegradation efficiency by about 23% for 10 mg l⁻¹ BPA in the UV-vis/TiO₂ system.

3.5. Effect of different gases on photodegradation of BPA

The effect of different gases on photodegradation of BPA was also investigated under the condition of pH 6.0, 10 mg l⁻¹ BPA, 1.0 g l⁻¹ TiO₂ and 4.4 × 10⁻⁵ mol l⁻¹ β-CD. Results

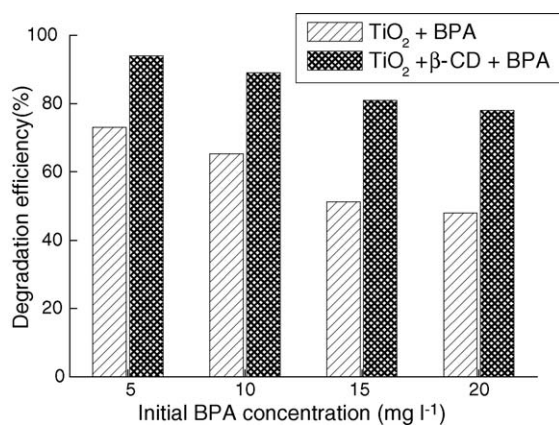


Fig. 7. Effect of initial concentration of BPA on the degradation efficiency where $[\text{TiO}_2]=1.0 \text{ g l}^{-1}$, $[\beta\text{-CD}]=4.4 \times 10^{-5} \text{ mol l}^{-1}$, pH 6.0, time = 60 min.

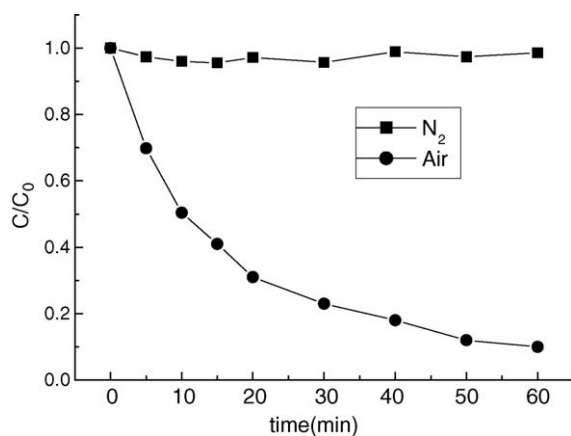


Fig. 8. Effect of the different gas on photocatalytic oxidation of BPA where $[\text{BPA}]=10 \text{ mg l}^{-1}$, $[\beta\text{-CD}]=4.4 \times 10^{-5} \text{ mol l}^{-1}$, $[\text{TiO}_2]=1.0 \text{ g l}^{-1}$, pH 6.0.

are shown in Fig. 8. It is well shown that the different gases have obvious effect on photodegradation of BPA. When nitrogen was used as gas medium, no decrease of BPA concentration was observed during irradiation, which indicates that BPA cannot be degraded in the system purged nitro-

gen, whereas obvious photodegradation of BPA occurred in the system purged air, which indicates that photodegradation of BPA 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 ($\text{O}_2^{\bullet-}$) 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 BPA 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 to the Langmuir–Hinshelwood kinetics rate model, which has been applied to the initial rates of photocatalytic degradation of many organic compounds [29]. 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.

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

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

It could be seen that the initial rate of BPA photodegradation increased with increasing the initial concentration of BPA and because of higher reaction rate constant in the system containing $\beta\text{-CD}$ and TiO_2 , the photodegradation rate of BPA in aqueous solutions containing $\beta\text{-CD}$ and TiO_2 was obviously faster than that in aqueous solutions containing only TiO_2 .

Table 2
Kinetics analysis of the photodegradation of BPA

System	BPA 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	0.0911	$R = \frac{0.0320C}{1 + 0.0915C}$ ($r_1 = 0.9901$)	0.350
	5.0	0.109		
	10.0	0.178		
	15.0	0.190		
	20.0	0.228		
TiO ₂ /β-CD	2.5	0.194	$R = \frac{0.0993C}{1 + 0.120C}$ ($r_1 = 0.9968$)	0.831
	5.0	0.298		
	10.0	0.446		
	15.0	0.520		
	20.0	0.645		

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

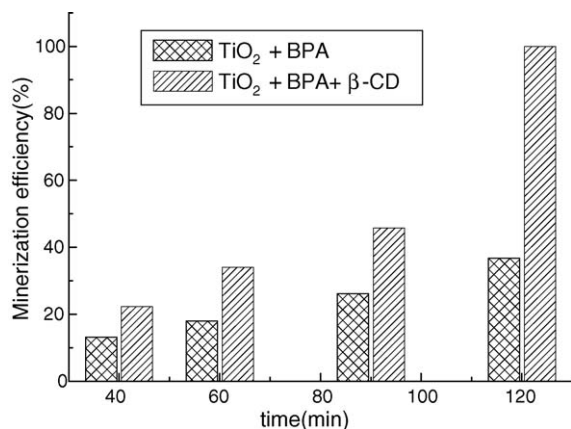


Fig. 9. Comparison of mineralization efficiency of BPA with β-CD and without β-CD where [BPA] = 10 mg l⁻¹, [β-CD] = 4.4 × 10⁻⁵ mol l⁻¹, [TiO₂] = 2.5 g l⁻¹, pH 6.0.

3.7. Effect of β-CD on mineralization of BPA

To investigate the effect of β-CD on the mineralization degree of BPA, the amount of CO₂ produced by the photocatalytic degradation reaction was measured. The results are shown in Fig. 9. It is well shown that the mineralization efficiency increases with increasing of irradiation time and the mineralization efficiency of BPA in the system containing β-CD and TiO₂ is obviously higher than that in the system containing only TiO₂, after 120 min of irradiation, the mineralization efficiency of BPA reached 100% in the presence of β-CD, whereas the mineralization efficiency was only 36.7% in the absence of β-CD, which indicates the β-CD has obvious enhancement on the mineralization of BPA.

3.8. Result of HPLC chromatogram analysis

HPLC chromatograms of BPA with β-CD and without β-CD during photodegradation are shown in Fig. 10. It can be seen that the peak area of BPA decreases with increasing reaction time and some obvious products with lower molecular weight and higher polarity formed at shorter retention time [30]. No other product peaks obviously occurred in HPLC chromatogram, this is because that some products have lower absorption at wavelength 280 nm. Comparing groups (a and b), we find that peak area of BPA 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

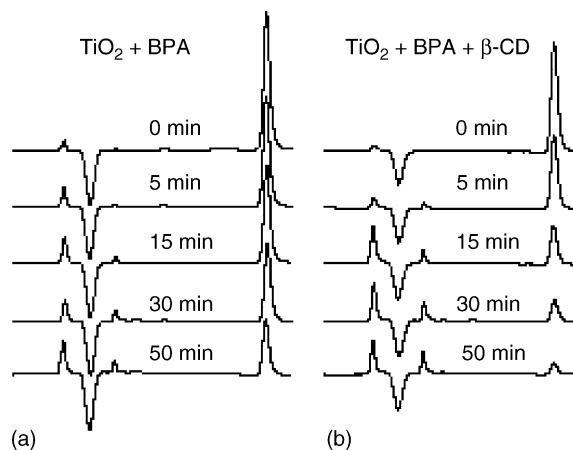


Fig. 10. HPLC chromatograms of BPA with β-CD and without β-CD during photodegradation (UV detector wavelength 280 nm) where [BPA] = 10 mg l⁻¹, [β-CD] = 4.4 × 10⁻⁵ mol l⁻¹, [TiO₂] = 1.0 g l⁻¹, pH 6.0.

of BPA in the system containing β-CD and TiO₂ is obviously lower than that in the system containing only TiO₂, which indicates that more BPA molecules were adsorbed on the TiO₂ surface in the presence of β-CD, which results in enhancement effect of BPA photodegradation because of the inclusion of BPA 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 [21,26], we have known that β-CD can be bonded or adsorbed on TiO₂. To preliminary inspect the mechanism of the enhancement of BPA photodegradation, we first investigated the adsorption of BPA on TiO₂ surface in the presence or in the absence of β-CD in order to confirm that β-CD can enhance adsorption of BPA on TiO₂ surface. The adsorption of BPA on TiO₂ surface is followed Langmuir-type isotherm, which is described as follows [19]:

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

where θ is the maximum adsorption amount of BPA on TiO₂ (μmol g⁻¹), K_{ad} the adsorption binding constant (l μmol⁻¹), M the equilibrium adsorption amount of BPA on TiO₂ (μmol g⁻¹) and C is the equilibrium concentration of BPA in solutions (μmol l⁻¹). The results are listed in Table 3. From Table 3, it is well shown that the maximum adsorption amount and the adsorption constant of BPA in the system containing β-CD and TiO₂ are obviously higher than those in the sys-

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

	Adsorption equation	Maximum adsorption amount θ (μmol g ⁻¹)	Adsorption constant K_{ad} (l μmol ⁻¹)
Without β-CD	$\frac{1}{M} = 0.2443 + \frac{22.38}{C}$ ($r_2 = 0.9955$)	4.09	1.09×10^{-2}
With β-CD	$\frac{1}{M} = 0.0485 + \frac{3.210}{C}$ ($r_2 = 0.9992$)	20.62	1.51×10^{-2}

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

Table 4
Bond length between atoms in BPA molecule before and after inclusion

Bond length (Å)	Before inclusion	After inclusion
R(7.3)	1.563	1.572
R(7.8)	1.563	1.572
R(7.14)	1.557	1.564
R(7.15)	1.557	1.564
R(4.3)	1.423	1.424
R(8.13)	1.423	1.425
R(3.2)	1.422	1.424
R(8.9)	1.422	1.424
R(2.1)	1.418	1.418
R(10.9)	1.418	1.417
R(6.1)	1.417	1.415
R(11.10)	1.417	1.415
R(6.5)	1.417	1.415
R(12.11)	1.417	1.415
R(16.6)	1.411	1.412
R(17.11)	1.411	1.411

tem containing only TiO₂. Therefore, more BPA molecules can be adsorbed on TiO₂ surface because of inclusion with β-CD, which results in enhanced photochemical degradation of BPA.

On the other hand, β-CD can form inclusion complex with BPA which possibly results in varieties of structure parameters (such as bond length) of BPA molecule because of interactions between non-bonded atoms. The bond lengths of BPA calculated following the B3LYP-optimized model before and after inclusion are listed in Table 4. From Table 4, we can find that the bond length of C₇–C₃, C₇–C₈, C₇–C₁₄ and C₁₄–C₁₅ are obviously lengthened, respectively, so the bond energy is weakened correspondingly, which results in easier degradation of BPA in the system containing TiO₂ and β-CD.

Based on the above results, we can draw a preliminary conclusion that the enhancement of photodegradation of BPA mainly results from the enhanced adsorption of BPA on the TiO₂ surface and the weakening of bond energy between some atoms in BPA molecule because of inclusion interactions with β-CD. So we propose a trinity interaction model of BPA–CD–TiO₂, which is described in Fig. 11. Since β-CD can include BPA in its cave and be adsorbed onto the surface of TiO₂, it could play a role as “bridge” or “channel” for

BPA to get onto the TiO₂ surface and accumulate to higher concentration which makes BPA degrade more easily in the presence of hydroxyl radicals photoproducted by TiO₂.

4. Conclusion

β-CD can enhance the photodegradation of BPA under the irradiation of a near UV light. The photodegradation rate of BPA depends on β-CD concentration, pH and BPA initial concentration. The photodegradation rate of BPA 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 0.831 mg l⁻¹ min⁻¹, 1.51 × 10⁻² l μmol⁻¹, respectively, in the system containing TiO₂ and β-CD, whereas they are 0.350 mg l⁻¹ min⁻¹, 1.09 × 10⁻² l μmol⁻¹, respectively, in the system containing only TiO₂. The photodegradation efficiency of BPA decreased with increasing initial BPA concentration and the photodegradation efficiency of BPA in aqueous solution containing β-CD and TiO₂ was obviously higher than that in aqueous solution containing only TiO₂. After 60 min of irradiation, β-CD could increase the photodegradation efficiency by about 23% for 10 mg l⁻¹ BPA in the UV–vis/TiO₂ system at pH 6.0. After 120 min of irradiation, the mineralization efficiency of BPA reached 100% in the presence of β-CD, whereas mineralization efficiency was only 36.7% in the absence of β-CD. The enhancement of photodegradation of BPA mainly results from the enhancement of adsorption of BPA on TiO₂ and the weakening of bond energy between some atoms in BPA molecule because of inclusion interactions with β-CD.

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References

- [1] T. Colborn, C. Clement, *Chemically Induced Alterations in Sexual Development: The Wildlife/Human Connection*, Princeton Scientific Publishing Company Inc., Princeton, 1992.
- [2] C.A. Staples, P.B. Dom, G.M. Klecka, et al., *Chemosphere* 36 (10) (1998) 2149–2174.
- [3] G. Lyons, *World Wide Fund for Nature, Substances in the Marine Environment (SIME)*, February 1997.
- [4] T. Kamiura, Y. Tajiima, T. Nakahara, *J. Environ. Chem.* 7 (2) (1997) 275–279.

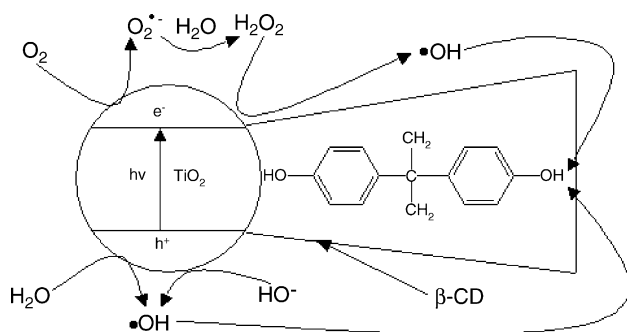


Fig. 11. Mechanism of the enhancement of BPA photodegradation.

- [5] A.V. Krishnan, P. Starhis, S.F. Permeth, et al., *Endocrinology* 132 (1993) 2279–2286.
- [6] J.A. Brotons, M.F. Olea-serrano, M. Villalobos, et al., *Environ. Health Persp.* 103 (1995) 608–612.
- [7] J. Ashby, R.W. Tennant, *Mutat. Res.* 204 (1) (1988) 17–115.
- [8] S. Suarez, R.A. Sueiro, J. Garrido, *Mutat. Res.* 470 (2) (2000) 221–228.
- [9] H.C. Alexander, D.C. Dill, L.A. Simth, et al., *Environ. Toxicol. Chem.* 7 (1998) 119–126.
- [10] Y. Tsutsumi, T. Haneda, T. Nishida, *Chemosphere* 42 (2001) 271–276.
- [11] A. Atkinson, D. Roy, *Biochem. Biophys. Res. Commun.* 210 (1995) 424–433.
- [12] J. Sajiki, *Environ. Int.* 27 (2001) 315–320.
- [13] J. Sajiki, J. Yonekubo, *Chemosphere* 46 (2002) 345–354.
- [14] J. Sajiki, J. Yonekubo, *Chemosphere* 51 (2003) 55–62.
- [15] H. Kuramitz, Y. Nakata, M. Kawasaki, et al., *Chemosphere* 45 (2001) 37–43.
- [16] H. Katsumata, S. Kawabe, S. Kaneco, et al., *J. Photochem. Photobiol. A: Chem.* 162 (2003) 297–305.
- [17] D.N. Zhou, F. Wu, N.S. Deng, et al., *Water Res.* 34 (2004) 2408–2411.
- [18] A. Mills, S. Le Hunte, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 1–35.
- [19] Y. Ohko, I. Ando, C. Niwa, et al., *Environ. Sci. Technol.* 35 (2001) 2365–2368.
- [20] M. Kamiya, K. Nakamura, C. Sasaki, *Chemosphere* 28 (1994) 1961–1966.
- [21] P. Lu, F. Wu, N.S. Deng, *Appl. Catal. B—Environ.* 53 (2004) 87–93.
- [22] A.J. Frank, I. Willner, Z. Goren, et al., *J. Am. Chem. Soc.* 109 (1987) 3568.
- [23] G. Dagan, S. Sampath, O. Lev, *Chem. Mater.* 7 (1995) 446.
- [24] I. Willner, Y. Eichen, A.J. Frank, et al., *J. Phys. Chem.* 97 (1993) 7264.
- [25] T. Nakahira, M. Graetzel, *J. Phys. Chem.* 88 (1984) 4006.
- [26] I. Willner, Y. Eichen, B. Willner, *Res. Chem. Intermediat.* 20 (7) (1994) 681–700.
- [27] O. Bajt, G. Mailhot, M. Bolte, *Appl. Catal. B—Environ.* 33 (2001) 239–248.
- [28] M.D. Olmo, A. Zafra, A.G. Casado, et al., *Int. J. Environ. Anal. Chem.* 69 (1998) 99–110.
- [29] M.R. Hoffmann, S.T. Martin, W. Choi, et al., *Chem. Rev.* 95 (1995) 69–96.
- [30] J. Ma, J.D. Nigel Graham, *Water Res.* 34 (2000) 3822–3828.