

β -Cyclodextrin-enhanced photodegradation of bis(4-hydroxyphenyl)ethane under UV irradiation

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Abstract

β -Cyclodextrin (β -CD) reacts with bis(4-hydroxyphenyl)ethane (BPE) forming a 1:1 inclusion complex, the formation constant of which is $7.81 \times 10^3 \text{ l mol}^{-1}$. In the present study, the enhanced photodegradation behavior of BPE in the presence of β -CD was investigated under a 30 W UV lamp ($\lambda_{\text{max}} = 254 \text{ nm}$). As a result, the photodegradation rate constant of BPE in aqueous solution with β -CD showed a 5.37-fold increase. After 60 min UV irradiation, addition of β -CD increased the photodegradation efficiency of 10.0 mg l^{-1} BPE by about 54.4%, simultaneously enhancing the mineralization of BPE. The effect of β -CD concentration, the presence/absence of organic solvent and pH on the photodegradation of BPE were also studied. The predominant photodegradation products were *p*-hydroxybenzoic acid, *m*-hydroxylated BPE and *o*-hydroxylated BPE. The enhancement of photodegradation of BPE was mainly shown to be the result of an increase in the frontier electron density of BPE after inclusion of β -CD and the moderate inclusion depth of BPE molecules in the β -CD cavity.

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Keywords: Bis(4-hydroxyphenyl)ethane; β -CD; Photodegradation; Enhancement; UV irradiation

1. Introduction

Recently, research into endocrine disruptors (EDs) in the environment has received increasing attention among the scientific community and general public because of their potential adverse effects [1,2]. Bis(4-hydroxyphenyl)ethane (BPE) is believed to be a kind of suspected ED, but is also an important industrial chemical, being used as the monomer for production of polycarbonate plastics and epoxy resins. Release into the natural environment as well as surface water can occur during manufacturing and through leaching from storage devices. BPE was reported to have an EC_{50} of 18 mg l^{-1} against *Daphnia magna*, and its acute toxicity and estrogenic activity are comparable to those of bisphenol A [3–5]. Thus, the development of methods to remove BPE is urgently needed. Recently, photochemical methods have been successfully used for the treatment of ED [6–8].

Cyclodextrins (CDs) are cyclic oligosaccharides made up of six to eight α -D-glucose units connected through glyco-

sidic α -1,4 bonds. CDs with six to eight α -D-glucose units are denoted α -, β -, and γ -CDs, respectively. They have the ability to form an inclusion complex with various guest molecules of suitable polarity and dimension because of their unique molecular structure (they possess a hydrophobic internal cavity) and hydrophilic external surface [9,10]. Kitano et al. reported that CD and its derivatives are able to form an inclusion complex with bisphenols such as bisphenol A, B, F and S [11], and their potential as media for controlling chemical and photochemical reactions has been extensively proven [12]. In the field of environmental research, because of their non-toxicity and biodegradability, CDs have been used to promote degradation of hazardous pollutants discharged into aqueous environments. Kamiya et al. investigated the inclusion effect of CDs on the photodegradation rate of paraoxon and found that β -CD had a large promoting effect [13,14]. Lindsey et al. also reported that β -CD and carboxymethyl- β -CD can selectively enhance the degradation of hydrophobic organic compounds through the Fenton system [15]. In addition, Hanna et al. reported that hydroxypropyl- β -CD has a beneficial effect on the degradation rates of pentachlorophenol through the Electro-Fenton system [16].

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In this work, the formation of an inclusion complex between BPE and β -CD was studied and the enhanced photodegradation behavior of BPE in the presence of β -CD was investigated under UV light. The effects of β -CD concentration, pH, and organic solvent on BPE photodegradation were also evaluated, and kinetics analysis was carried out. Mineralization of BPE was observed during the photodegradation process, possibly suggesting a new method for the treatment of EDs in wastewater.

2. Experimental

2.1. Materials

BPE was purchased from Sigma–Aldrich Chemical Co. (Beijing, PRC) (GC grade > 99%); its chemical structure is presented in Fig. 1. α -CD and γ -CD were purchased from Seebio Biotechnology Inc. (Shanghai, PRC), and β -CD from Shuanxuan Microbe Medium Products Factory (Beijing, PRC). Acetonitrile was of HPLC grade (Lingfeng Chemical Reagent Co., Shanghai, PRC). HCl and NaOH were used to adjust the pH values of the solutions. All other reagents were of analytic reagent grade. Double distilled water was used in all experiments.

2.2. Photodegradation

Reaction solutions containing BPE or BPE plus β -CD were adjusted to the desired pH with HCl and NaOH. The reaction solution was used to fill eight quartz glass tubes (about 8.0 cm long, 1.5 cm in diameter and 2 mm thick), which were then irradiated with a 30 W UV lamp ($\lambda_{\max} = 254$ nm, Shanghai Lamp Co. Ltd., PRC). The concentration of BPE was determined by HPLC–UV at different time intervals.

2.3. Analysis and calculations

All fluorescence measurements were performed with a Hitachi F-4500FL fluorescence spectrophotometer (Tokyo, Japan). Excitation and emission wavelengths were set at 276 and 325 nm, respectively. BPE in aqueous solution was determined by HPLC [Shimadzu LC-10ATVP pump, Shim-pack VP-DDS-C18 column (4.6 mm \times 150 mm, 5 μ m)] at a flow rate of 1.0 ml min⁻¹ and a UV detector (Shimadzu UV–vis detector) at 280 nm. The mobile phase was acetonitrile/water mixture (50/50, v/v) and the injection volume was 20 μ l. The retention time of BPE was about 5.0 min. Analysis of the photodegradation products was performed with LC–MS for BPE plus β -CD after 60 min UV irradiation. LC–MS analysis conditions were as reported by Zhou et al. [17].

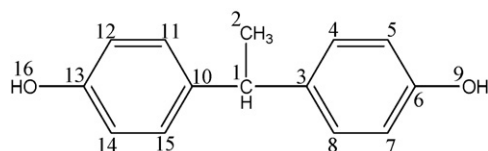


Fig. 1. The chemical structure of BPE.

The formation of CO₂ as a result of BPE mineralization was observed during the photodegradation process. Carbon dioxide produced upon irradiation was determined as BaCO₃ to determine the mineralization efficiency of BPE [18,19].

The initial geometry of BPE and β -CD were constructed with the help of a Chemoffice model (2004) (Cambridge Soft Co., USA). The structure of BPE, β -CD and BPE/ β -CD were first optimized using molecular mechanics methods and then parameter method 3 (PM3), a semi-empirical method with an improved performance compared to Austin model 1 because of its improved description of the interactions between non-bonded atoms, such as Van der Waals, hydrogen bonding and hydrophobic forces [20,21]. BPE attack by hydroxyl radicals was estimated by calculating the frontier electron density [7]. All calculations were carried out using a P4 personal computer.

3. Results and discussion

3.1. Determination of the formation constant

The formation constant (K) was obtained from a modified Benesi-Hildebrand equation [22]:

$$\frac{1}{\Delta F} = \frac{1}{KkQ[G]_0[CD]_0} + \frac{1}{kQ[G]_0}$$

where $[G]_0$ and $[CD]_0$ refer to the total concentration of BPE and β -CD, respectively, ΔF the change in fluorescence intensity of BPE with step-wise addition of β -CD, k the instrument constant, and Q represents the fluorescence quantum yield of the inclusion complex. $1/(F - F_0)$ versus $1/[H]_0$ was plotted, and K was calculated from the ratio of the intercept to the slope. Fig. 2 shows double reciprocal plots for BPE with β -CD. Good linearity implies that the stoichiometry of complexation is 1:1. The calculated formation constant of the complex was 7.81×10^3 l mol⁻¹.

3.2. Photodegradation of BPE under UV irradiation

BPE solution with or without CD was irradiated under UV light; the results are shown in Fig. 3. The concentration of BPE in aqueous solution decreased with time because of BPE pho-

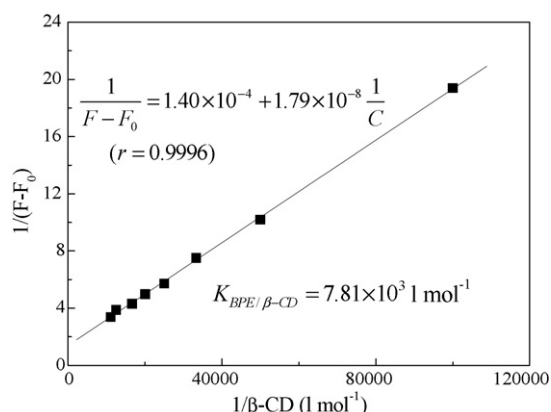


Fig. 2. Double reciprocal plots of the β -CD/BPE inclusion complex.

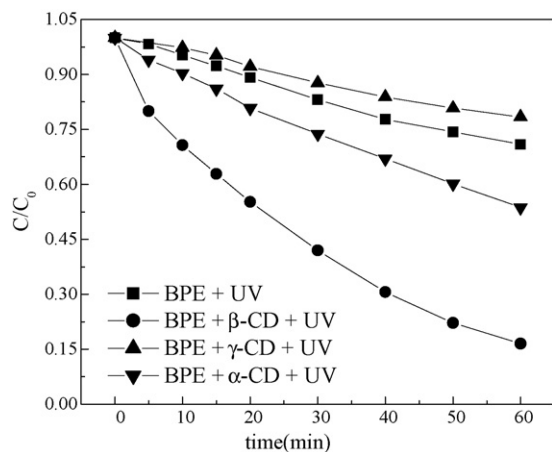


Fig. 3. Changes in BPE concentration with time in the control experiments. $[BPE] = 10.0 \text{ mg l}^{-1}$, $[\alpha\text{-CD}] = [\beta\text{-CD}] = [\gamma\text{-CD}] = 9.2 \times 10^{-5} \text{ M}$, pH 7.0.

todegradation under UV irradiation, and the photodegradation rate of BPE plus β -CD was also notably faster than that without β -CD. After 60 min UV irradiation, BPE in the absence of β -CD was degraded by only about 29.1%; however, in the presence of β -CD, BPE was degraded by about 83.5% at the same time point. This finding suggests that α -CD induces slight enhancement of BPE photodegradation, unlike γ -CD, which induces a small inhibition effect. These differences could arise from the size of the CD cavity. The inner diameter of the hydrophobic cavities of α -, β - and γ -CDs are approximately 0.47–0.53, 0.60–0.65, and 0.75–0.83 nm, respectively [23]. That is, the γ -CD cavity is the largest, suggesting that BPE molecules can enter easily, preventing interaction with the CD secondary hydroxyl groups and oxygen molecules in the aqueous solution. However, despite their moderate size, BPE can also partly enter the cavities of α -CD and β -CD, resulting in sufficient proximity to catalytically active secondary hydroxyl groups surrounding the CD top torus, which could enhance oxidation of BPE [13].

The effect of different CDs on the fluorescence intensity of BPE was also examined; the results are shown in Fig. 4. As indicated the fluorescence intensity of the inclusion complex between BPE and β -CD was higher than that of the inclu-

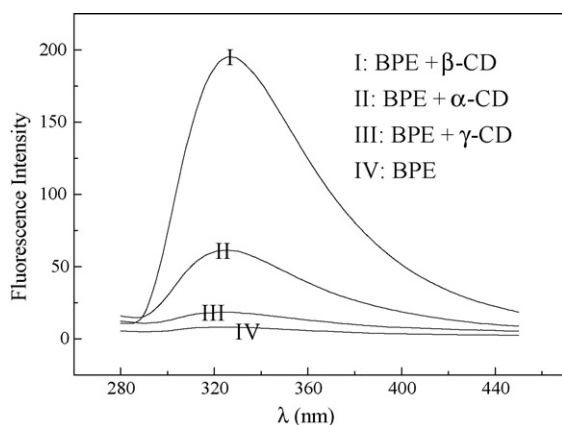


Fig. 4. Effect of different CDs on the fluorescence intensity of BPE. $[BPE] = 10.0 \text{ mg l}^{-1}$, $[\alpha\text{-CD}] = [\beta\text{-CD}] = [\gamma\text{-CD}] = 9.2 \times 10^{-5} \text{ M}$, pH 7.0.

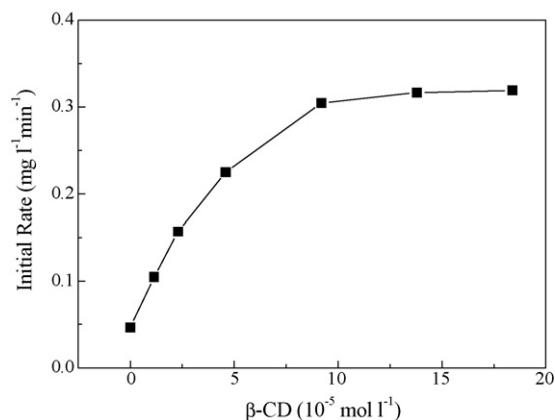


Fig. 5. Effect of β -CD concentration on the photodegradation of BPE. $[BPE] = 10 \text{ mg l}^{-1}$, pH 7.0.

sion complex between BPE and α -CD or γ -CD. Goodness-of-fit between BPE and β -CD was therefore observed, indicating that among the various CDs, β -CD forms the most stable inclusion complex with BPE, resulting in a high photodegradation efficiency.

3.3. Effect of β -CD concentration

The effect of β -CD concentration on the photodegradation of BPE was also investigated under UV light; the results are shown in Fig. 5. The photodegradation rate of BPE in the presence of β -CD was clearly shown to be faster than that in the absence of β -CD, increasing with increasing β -CD concentration in a range of 0– $9.2 \times 10^{-5} \text{ M}$. There was no further increase in the photodegradation rate when the concentration of β -CD exceeded $9.2 \times 10^{-5} \text{ M}$.

3.4. Effect of the initial pH

The effect of the initial pH value on the photodegradation of BPE was also investigated under UV irradiation; the results are also shown in Fig. 6. As shown, the photodegradation rate of BPE in aqueous solution with β -CD was notably faster than

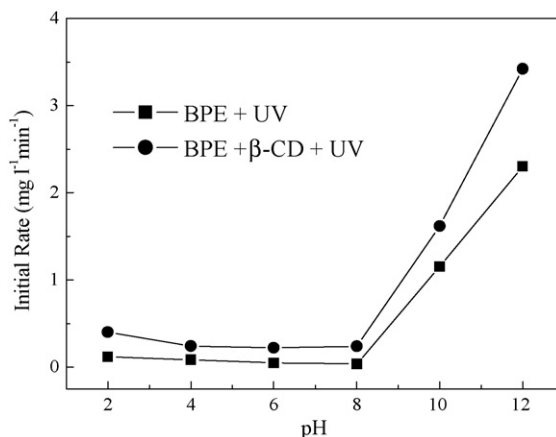


Fig. 6. Effect of pH on the photodegradation rates of BPE. $[BPE] = 10 \text{ mg l}^{-1}$, $[\beta\text{-CD}] = 9.2 \times 10^{-5} \text{ M}$.

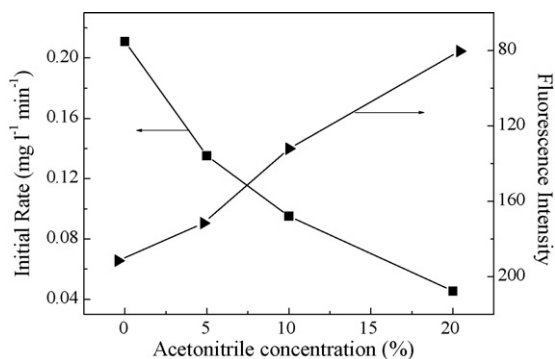


Fig. 7. Effect of organic solvent on the photodegradation of BPE and fluorescence intensity of the BPE/ β -CD inclusion complex. [BPE] = 10 mg l^{-1} , [β -CD] = $9.2 \times 10^{-5} \text{ mol l}^{-1}$, $\lambda_{\text{ex}} = 276 \text{ nm}$, $\lambda_{\text{em}} = 325 \text{ nm}$, pH 7.0.

that without β -CD in a pH range of 2–10. There were no obvious variations in the photodegradation rate in a pH range of 2–8; however, there was an obvious increase above pH 8 for BPE solution both with and without β -CD. This is thought to be related to the fact that BPE can form bisphenolate anions in alkaline solution (pH > 8), since UV irradiation can be easily absorbed by bisphenolate anions through the deprotonated form of bisphenol E. Alkaline conditions are therefore beneficial for photodegradation of BPE.

3.5. Effect of organic solvent on photodegradation of BPE

To investigate the effect of organic solvent on photodegradation of BPE in the presence of β -CD under UV light, acetonitrile was added to the reaction solution at a concentration of 5%, 10%, and 20%, respectively. The results are shown in Fig. 7. Organic solvent had an inhibitory effect on the photodegradation of BPE and this effect increased with increasing concentration of acetonitrile. This result could be dependent on the effect of the organic solvent on inclusion interaction between BPE and β -CD, which can be characterized by variation in the fluorescence intensity of the inclusion complex. As shown in Fig. 7, the fluorescence intensity of the inclusion complex decreased with increasing concentration of acetonitrile, indicating that the ability of β -CD to include BPE seems to be weakened in the presence of organic solvent, thus also weakening the photodegradation effect.

3.6. Effect of β -CD on mineralization of BPE

During the photochemical process, the photodegradation of organic substrates results in their mineralization because of the formation of carboxylic acids [7]. In this experiment, the pH and electrical conductivity of the solution were measured in order to evaluate the effect of β -CD on the mineralization of BPE; the results are shown in Fig. 8a. As shown, pH dropped from 6.50 to 6.04 and electrical conductivity varied from 2.58 to $5.12 \mu\text{S cm}^{-1}$ for solution without β -CD after 60 min UV irradiation. However, pH dropped from 6.50 to 5.40 and electrical conductivity varied from 2.53 to $10.20 \mu\text{S cm}^{-1}$ for solution with β -CD after 60 min UV irradiation, indicating that β -CD

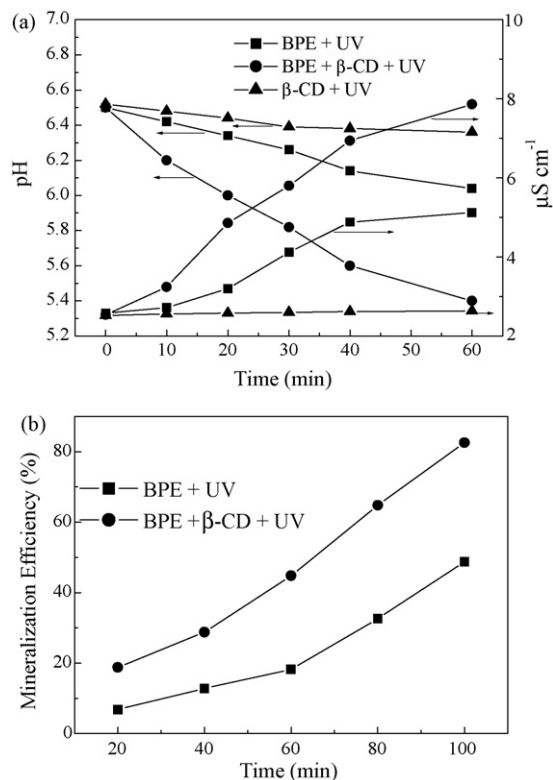


Fig. 8. Effect of β -CD on the mineralization of BPE. (a) Variation in the pH and electrical conductivity of the solution. (b) The mineralization efficiency of BPE. [BPE] = 10 mg l^{-1} , [β -CD] = $9.2 \times 10^{-5} \text{ M}$.

enhances the mineralization of BPE through increased electrical conductivity and decreased pH under UV irradiation. Despite these findings, there were only slight variations in the electrical conductivity and pH of β -CD itself under UV irradiation. This is because UV irradiation is only weakly absorbed by β -CD. As shown in Fig. 8b, the mineralization efficiency of BPE with β -CD was notably higher than that of BPE without β -CD. After 100 min UV irradiation, the mineralization efficiencies of BPE with/without β -CD reached 82.6% and 48.8%, respectively, further suggesting that β -CD enhances the mineralization of BPE.

3.7. Analysis of photodegradation kinetics

In this experiment, a linear semi-log plot of the initial concentration of BPE versus irradiation time was observed, indicating overall pseudo-first-order kinetics. The experiment was repeated with a range of initial BPE concentrations varying from 5.0 to 30.0 mg l^{-1} . The initial rate of each concentration was calculated by multiplying the pseudo-first-order rate constant by the initial concentration. The data were then fitted according to the equation $R = -dC/dt = aC^b$ [24] and photodegradation kinetics equations were obtained; the results are shown in Table 1. As shown, the initial rate of BPE photodegradation increased with increasing initial concentration of BPE and the reaction rate constant of BPE with β -CD was clearly higher than that without. In addition, the reaction rate constant of BPE in the presence of β -CD showed a 5.37-fold increase, again suggest-

Table 1
Kinetic analysis of the photodegradation of BPE

System	Initial concentration of BPE (mg l^{-1})	Initial rate, R ($\text{mg l}^{-1} \text{min}^{-1}$)	Kinetics equation ^a	Reaction rate constant, k (min^{-1})
BPE/UV	2.5	0.0122	$R = 0.00469C$ ($r = 0.9998$)	0.00469
	5.0	0.0240		
	7.5	0.0348		
	10.0	0.0466		
	15.0	0.0704		
BPE/ β -CD/UV	2.5	0.076	$R = 0.0299C$ ($r = 0.9997$)	0.0299
	5.0	0.145		
	7.5	0.229		
	10.0	0.302		
	15.0	0.448		

^a r represents the correlation coefficient between R and C .

ing that the photodegradation reaction of BPE is enhanced by β -CD.

3.8. Results of HPLC chromatogram analysis

HPLC chromatograms of BPE photodegradation in the presence and absence of β -CD are shown in Fig. 9. Peak 2 occurred after 5 min UV irradiation, and was attributed to a strong polar component with a low molecular weight [25]. During 60 min photodegradation, the area of peak 2 increased with increasing irradiation time. Comparing groups (a) and (b), we find that the area of peak 1 (BPE) in the presence of β -CD decreases much faster than that in the absence of β -CD during the photodegradation process. After 10 min UV irradiation, other product peaks such as peaks 3 and 4 were observed in the presence of β -CD, the areas of which increased with increasing irradiation time. In addition, the area of peak 2 in the presence of β -CD increased much faster than in the absence of β -CD, indicating that β -CD enhances the photodegradation and mineralization of BPE.

3.9. LC–MS analysis of the photodegradation products

The HPLC chromatograms (Fig. 9) of BPE during photodegradation show that the photodegradation products of BPE

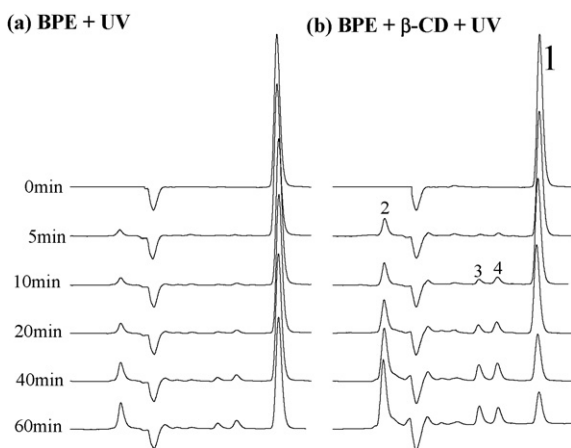


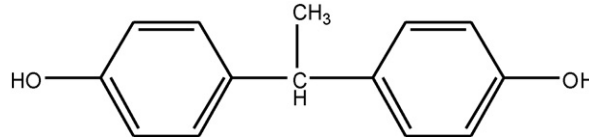
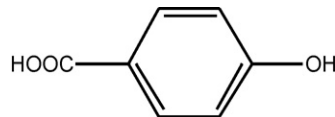
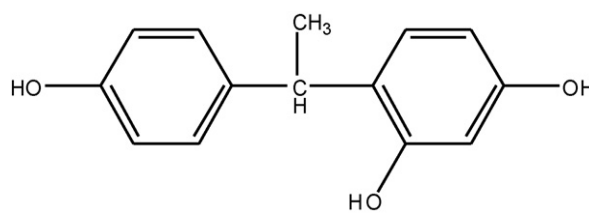
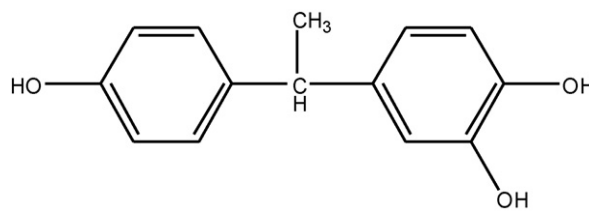
Fig. 9. HPLC chromatograms of BPE with and without β -CD during photodegradation (UV detector wavelength: 280 nm). $[\text{BPE}] = 10 \text{ mg l}^{-1}$, $[\beta\text{-CD}] = 9.2 \times 10^{-5} \text{ M}$, pH 7.0.

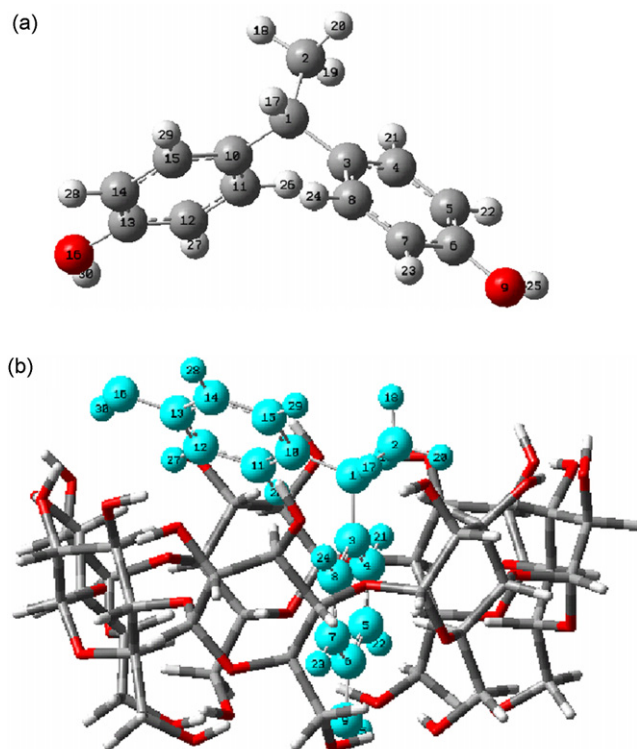
with β -CD are identical to those without β -CD because of the identical retention time. In order to investigate the photodegradation products, LC–MS was carried out. Table 2 summarizes the main fragments (m/z) of the intermediate products of BPE in aqueous solution with β -CD after 60 min UV irradiation. Four main peaks were observed with retention times of 1.0, 2.4, 3.5, and 6.6 min, respectively. As shown, the compound observed at 6.6 min was BPE with a m/z of 213 ($[\text{BPE}-\text{H}^+]$). Those observed at 1.0, 2.4 and 3.5 min had an m/z of 138, 229 and 229, respectively, and were believed to be hydroxylation products of BPE; namely, *p*-hydroxybenzoic acid ($K_{\text{ow}} = 1.45$, peak 2), *m*-hydroxylated BPE ($K_{\text{ow}} = 2.41$, peak 3), and *o*-hydroxylated BPE ($K_{\text{ow}} = 2.67$, peak 4), respectively. These hydroxylation products have a greater hydrophilicity than BPE, and therefore, shorter retention times under the HPLC condition in our experiment. This result is similar to that reported by Gozmen et al. in their study on the indirect electrochemical oxidation of bisphenol A [26].

3.10. Mechanism behind the enhanced photodegradation of BPE

In the supramolecular photodegradation system based on β -CD, the photooxidation of BPE was proven through the formation of hydroxylation products as indicated by LC–MS. From the area of peaks 3 and 4 in the HPLC chromatograms (Fig. 9), we can determine that the hydroxylation products of BPE in the presence of β -CD were more than those in its absence, indicating enhanced photodegradation of BPE in the presence of β -CD under UV irradiation. To further explain the mechanism behind this enhancement, the PM3 optimized structure of BPE and the BPE/ β -CD inclusion complex were obtained using a molecular modeling technique (Fig. 10). It is well known that the PM3 optimized structure of BPE has a non-planar configuration, with the two benzene rings in the BPE molecular structure being on a different plane, thus the BPE molecules can partly enter the β -CD cavity. The remarkable enhancement effect of β -CD on the photooxidation of BPE could also be dependent on the moderate inclusion depth [13,14], which allows BPE to gain sufficient proximity to secondary hydroxyl groups of the β -CD cavity, which can then be activated and converted to hydroxyl radicals under UV irradiation, enhancing photooxidation.

Table 2
Main fragment ions (m/z) obtained for peaks 1–4 by LC–MS

Peak no.	Retention time (min)	Detected ions (m/z)	Molecular weight	Molecular structure
1	6.6	213	214	
2	1.0	138	139	
3	2.4	229	230	
4	3.5	229	230	



In addition, the frontier electron densities of BPE before and after inclusion are listed in Table 3 according to the results of the PM3 simulation. It is well known that the frontier electron densities of BPE with β -CD inclusion are higher than those without; therefore, BPE in aqueous solution with β -CD can be more easily attacked by hydroxyl radicals. In addition, the frontier electron densities of C5, C8, C12 and C15 in the BPE molecules were higher than those at other positions. Thus, m -

Table 3
Calculation of the frontier electron density of BPE with and without β -CD

Atom	Frontier electron density	
	Before inclusion	After inclusion
C ₁	0.0055	0.00747
C ₂	0.01084	0.0136
C ₃	0.21484	0.26603
C ₄	0.07596	0.10831
C ₅	0.3426	0.3660
C ₆	0.15617	0.36651
C ₇	0.05904	0.09858
C ₈	0.3662	0.3774
O ₉	0.05864	0.11962
C ₁₀	0.20169	0.30845
C ₁₁	0.07724	0.08075
C ₁₂	0.3625	0.40721
C ₁₃	0.1116	0.25837
C ₁₄	0.08656	0.0905
C ₁₅	0.39675	0.4294
O ₁₆	0.01035	0.01256

Fig. 10. PM3 optimized structure of (a) BPE and (b) the BPE/ β -CD inclusion complex.

hydroxylated BPE and *o*-hydroxylated BPE are obtained due to attack by hydroxyl radicals during the photochemical reaction. Based on the above results, we can draw a preliminary conclusion that the enhancement of BPE photodegradation mainly results from an increase in the frontier electron density of BPE after inclusion with β -CD and the moderate inclusion depth of BPE molecules in the β -CD cavity.

4. Conclusions

The photodegradation of BPE in the presence of β -CD was shown to be enhanced under UV irradiation. Further, the photodegradation rate was shown to be dependent on the concentration of β -CD, pH, and the presence/absence of an organic solvent. The photodegradation rate of BPE in aqueous solution with β -CD showed a 5.37-fold increase under UV irradiation. After 60 min UV irradiation, addition of β -CD increased the photodegradation efficiency of 10.0 mg l^{-1} BPE by about 54.4%. The enhancement of BPE photodegradation under UV irradiation was deemed to be the result of an increase in the frontier electron density after inclusion with β -CD and the moderate inclusion depth of BPE in the β -CD cavity. These factors allowed the BPE to gain sufficient proximity to secondary hydroxyl groups in the β -CD cavity, which were then activated and converted into hydroxyl radicals under UV irradiation, enhancing photooxidation.

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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] S.M. Choies, S.D. Yoo, B.M. Lee, *J. Toxicol. Environ. Health B* 7 (2004) 1.
- [3] C.A. Staples, P.B. Dom, G.M. Klecka, S.T. O'Block, L.R. Harris, *Chemosphere* 36 (1998) 2149.
- [4] M.Y. Chen, M. Ike, M. Fujita, *Environ. Toxicol.* 17 (2002) 80.
- [5] S. Kitamura, T. Suzuki, S. Sanoh, R. Kohta, N. Jinno, K. Sugihara, S. Yoshihara, N. Fujimoto, H. Watanabe, S. Ohta, *Toxicol. Sci.* 84 (2005) 249.
- [6] Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, A. Fujishima, *Environ. Sci. Technol.* 35 (2001) 2365.
- [7] N. Watanabe, S. Horikoshi, H. Kawabe, Y. Sugie, J.C. Zhao, H. Hidaka, *Chemosphere* 52 (2003) 851.
- [8] E.J. Rosenfeldt, K.G. Linden, *Environ. Sci. Technol.* 38 (2004) 5476.
- [9] K.A. Connors, *Chem. Rev.* 97 (1997) 1325.
- [10] J. Szejtli, *Chem. Rev.* 98 (1998) 1743.
- [11] H. Kitano, H. Endo, M. Gemmeide, M. Kyogoku, J. Inclusion Phenom. *Macromol. Chem.* 47 (2003) 83.
- [12] G.D. Reddy, V. Ramamurthy, *J. Org. Chem.* 52 (1987) 3952.
- [13] M. Kamiya, K. Nakamura, *Environ. Int.* 21 (1995) 299.
- [14] M. Kamiya, K. Nakamura, C. Sasaki, *Chemosphere* 28 (1994) 1961.
- [15] M.E. Lindsey, G. Xu, J. Lu, M.A. Tarr, *Sci. Total Environ.* 307 (2003) 215.
- [16] K. Hanna, S. Chiron, M.A. Oturan, *Water Res.* 39 (2005) 2763.
- [17] D.N. Zhou, F. Wu, N.S. Deng, W. Xiang, *Water Res.* 38 (2004) 4107.
- [18] O. Bajt, G. Mailhot, M. Bolte, *Appl. Catal. B: Environ.* 33 (2001) 239.
- [19] G.H. Wang, P.R. Qi, X.F. Xue, F. Wu, N.S. Deng, *Chemosphere* 67 (2007) 762.
- [20] J.N. Murrell, *J. Mol. Struct. (Theochem)*. 424 (1998) 93.
- [21] Y.J. Zheng, K.M. Merz, *J. Comput. Chem.* 13 (1992) 1151.
- [22] G.C. Catena, F.V. Bright, *Anal. Chem.* 61 (1989) 905.
- [23] T. Loftsson, M.E. Brewster, *J. Pharm. Sci.* 85 (1996) 1017.
- [24] X.H. Feng, S.M. Ding, J.F. Tu, F. Wu, N.S. Deng, *Sci. Total Environ.* 345 (2005) 229.
- [25] J. Ma, J.D. Graham, *Water Res.* 34 (2000) 3822.
- [26] B. Gozmen, M.A. Oturan, N. Oturan, O. Erbatur, *Environ. Sci. Technol.* 37 (2003) 3716.