Rapid degradation of bisphenol A using air as the oxidant catalyzed by polynuclear phthalocyanine complexes under visible light irradiation

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Abstract

The photocatalytic dechlorination and destruction of bisphenol A (BPA) using air as the oxidant catalyzed by polynuclear phthalocyanine complexes under visible light irradiation have been studied. Among the four complexes studied (FePPc, CuPPc, ZnPPc, AlPPc), ZnPPc and AlPPc show high catalytic activities. Under ambient conditions of temperature and pressure, an initial BPA concentration of 1 mM in water was completely converted to CO_2 and carboxylic acid in 20 min with a catalyst/substrate molar ratio of 2:100 using a 100 W tungsten lamp as the light source. Six HPLC peaks indicating intermediate products appeared in chromatograms monitored at 254 nm. Oxalic acid and maleic acid were detected as their methyl esters in the resulting solution by GC–MS after treated with trimethylsulfonium hydroxide. TOC measurements indicated that 21.3% of the carbon was mineralized after an hour of reaction. When sunlight was used as the light source, BPA could also be degraded efficiently. Full conversion of BPA and its intermediate products were observed in 40 min without stirring and blowing air. The results of ESR measurements suggested that the reaction possibly proceeded via the pathway with singlet oxygen. A possible reaction sequence of the degradation of BPA was proposed. The influences of catalyst/substrate molar ratio, flow rate of the air, and pH were investigated.
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Keywords: Bisphenol A; Photocatalysis; Degradation; Visible light; Singlet oxygen; Sunlight

1. Introduction

Recently, several types of environmental pollutants referred to as endocrine disruptors (EDs) have been suggested to be associated with abnormal sexual development and abnormal feminizing responses of animals in a number of reports [1]. Bisphenol A [2,2-bis(4-hydroxyphenyl) propane or BPA], which is a compound widely used as the monomer for the production of polycarbonate plastics and as a major component of epoxy resin, is widely suspected to act as an ED [2,3]. The BPA originating from the plastic products and various wastewaters has been found in rivers, lakes and ocean [4–6]. The adverse influence of BPA on aquatic animal has been of great concern [7,8].

Various methods have been suggested to remove BPA from water, such as biological method [9–12], chemical oxidation [13–14], electrochemical oxidation [15] and photocatalytic method [16,17]. Among them, photocatalysis has been the focus of numerous investigations in recent years for the potential use sunlight as the energy source to degrade pollutions [18,19]. As the most widely studied material in the field of photocatalysis, TiO_2 has been used to degrade BPA successfully [16,17]. However, TiO_2 can only be excited by high energy UV radiation with a wavelength of no longer than 387.5 nm for its high band gap ($E_g \approx 3.2$ eV). This practically rules out the use of sunlight as the energy source [20].

Since metallophthalocyanine complexes have intense absorption bands in the longer wavelength region of the vis-

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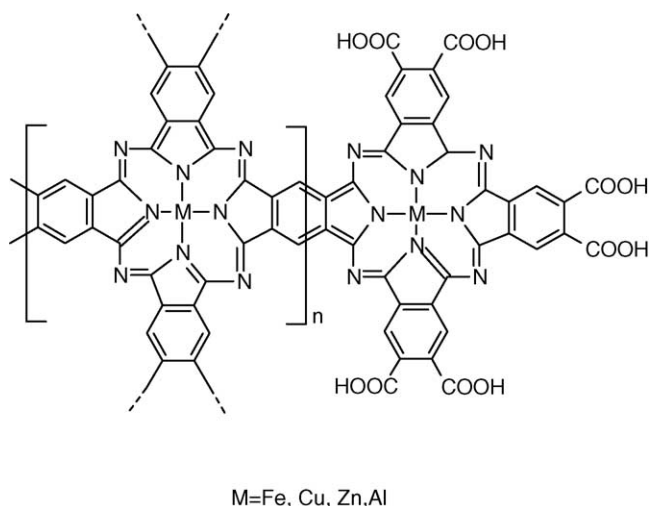*E-mail address:* gbjiang@mail.rcees.ac.cn (G. Jiang).

M=Fe, Cu, Zn,Al

Fig. 1. Structure of the polynuclear zinc polyphthalocyanine.

ible light in a solar spectrum and high quantum yield for photoexcited triplet state ($\Phi > 0.40$) with a long lifetime, they are attractive sensitizers for photoreduction of water and carbon dioxide, as well as a photodynamic therapy [21]. The photooxidation of substrates by oxygen in the presence of visible light activation of photosensitizers is of increasing interest. Various photosensitizers, such as dyes, porphyrines and phthalocyanines, have been used to be photosensitizers to oxidize thiols, sulfide, thioethers, phenol and monochlorophenols [22–26] Recently, polynuclear metal phthalocyanine complexes have attracted attentions because of their increased catalytic properties compared to mononuclear one [27,28]. Some polynuclear cobalt phthalocyanine complexes exhibit a much higher specific activity to activate the oxygen than the mononuclear compound in the oxidation of sulfide [29]. As the photocatalyst in the photooxidation of sulfide, thiosulfate, and phenol, the catalytic activity per mole of the polynuclear zinc and aluminium complexes is two to five times higher than that of the respective mononuclear phthalocyanine complexes [30,31].

Here we report rapid destruction of BPA and its intermediate products using air as the oxidant catalyzed by polynuclear phthalocyanine complexes under visible light irradiation. The major goals of this study were to examine the catalytic activity of different complexes of PPc (Fig. 1) under visible light irradiation for the degradation of BPA; and to optimize the operating conditions by investigating the effect of catalyst/substrate molar ratio, flow rate of the air and pH.

2. Materials and methods

2.1. Materials

BPA (99%) was purchased from Acros and used without further purification. Triethylsulfonium hydroxide was obtained from Tokyo Kasi. Polynuclear phthalocyanine complexes were synthesized according to the published method [32,33]. The water used in all experiments was purified with a Milli-Q water ion-exchange system.

2.2. Preparation and characterization of the catalysts

9.17 mmol 1,2,4,5-benzeneeracarboxylic dianhydride, 5 mmol metal chloride, 24.5 mmol urea, 0.73 mmol ammonium molybdate were mixed and heated for 3 h at 250 °C in a flask. The powdered reaction mixture was extracted for 20 h with dimethylsulfoxide in a Soxhlet apparatus and washed with acetone. Then the product was stirred with 300 ml of 3 mol l^{-1} hydrochloric acid for 16 h at room temperature and washed with water and acetone. The end imide groups in the polynuclear complexes were transformed into carboxylic groups upon heating the mixture for 5 h using 15 ml solution contain 1.2 g sodium hydroxide and 6 g sodium chloride. After filtration, the product was acidified with 2 mol l^{-1} hydrochloric acid and isolated and dried. Dark green products were prepared with a yield of 30–40%. FT-IR spectra were recorded on a PE2000 spectrophotometer, using KBr pellets. Elemental analyses were carried on Flash EA1112 elemental analyzer. The metal content was determined by flame atomic adsorption spectrophotometric method after treatment by conc. sulfuric and conc. nitric acid [32]. The UV–vis absorption spectra of polynuclear phthalocyanine complexes were shown in Fig. 2. Their UV–vis spectras show a maximum adsorption at 680–690 nm and a shoulder at 615–630 nm. The complexes synthesized different times gave the same results, suggesting the synthetic reproduction is very good. From the results of UV–vis spectra of the complexes, it can be seen that the aggregation of polynuclear phthalocyanine complexes in solution is a smaller extent than that of mononuclear complexes to receive a higher catalytic activity than mononuclear ones [34].
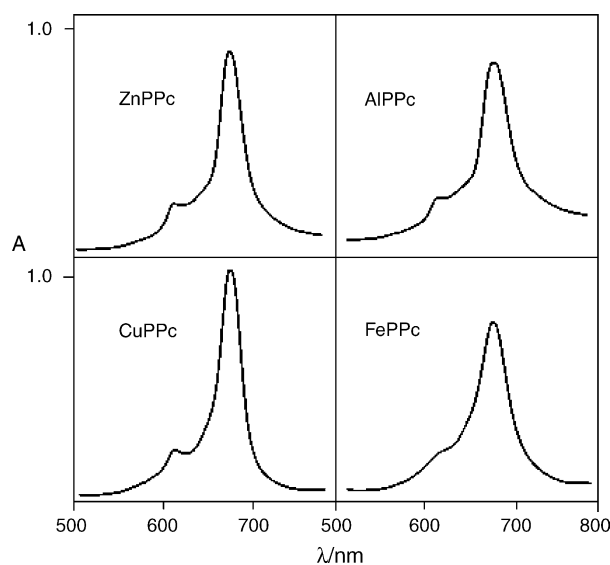

Fig. 2. The UV–vis spectra of ZnPPc, AlPPc, CuPPc and FePPc in water at 0.015 mmol l^{-1}, pH = 11.
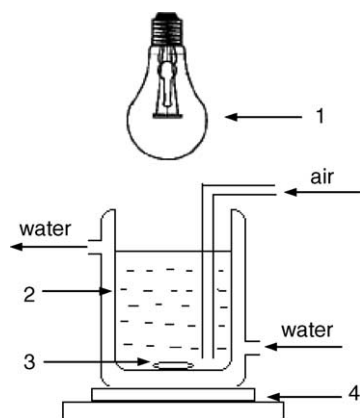
Fig. 3. Schematic illustration of the photoreactor: (1) tungsten lamp; (2) cylindrical Pyrex flask surrounded by a circulating water jacket; (3) stirrer; (4) magnetic stirrer.

2.3. Method

The irradiation source was a 100 W tungsten lamp positioned above a cylindrical vessel (diameter 4 cm, high 6 cm) surrounded by a circulating water jacket to cool the reaction solution (Fig. 3). 1.5 ml of $0.35 \, mmol \, l^{-1}$ ZnPPc and 2.5 ml of $10 \, mmol \, l^{-1}$ BPA (in $0.1 \, mol \, l^{-1}$ NaOH) were added then diluted to 25 ml. The photocatalytic reaction proceeded with the air blowing in at 200 ml/min under magnetic stirring. The degradation of BPA under sunlight irradiation was carried out in a culture dish (diameter 8 cm) without stirring and blowing air, the irradiation intensity of the sunlight was $608.3 \, \mu \, mol \, s^{-1} \, m^{-2}$. One milliliter of illuminated samples were removed from the photoreactor periodically and diluted to 5 ml and analyzed by HPLC.

2.3.1. Analytical methods

The HPLC equipment used was an Agilent 1100LC including a BinPump and a UV–vis detector. The UV–vis detector was set 254 nm wavelength. An Agilent Zorbax Eclipse XDB-C_{18} column (150 mm × 4.6 mm, particle size 5 μm) was used as analytical column. LC separation of BPA and its degradative products was conducted by using a mixture of acetonitrile and water (the pH was adjusted to 4 with trifluoroacetic acid) as mobile phase at a flow rate of 1.0 ml/min. The gradient profile was: increase from 10% to 50% acetonitrile in 0–15 min and then keep 50% for 5 min. A personal

computer equipped with an Agilent ChemStation program for LC systems was used to process chromatographic data.

The final products of the degradation of BPA are identified as follows: the reaction mixture was evaporated under vacuum. The residue was dissolved in $3 \, mol \, l^{-1}$ HCl to produce a pH < 2. The resulting solution was saturated with NaCl and extracted with diethyl ether (3 × 10 ml). The combined ether extracts were dried with anhydrous sodium sulfate and the ether was evaporated under vacuum. The residue was dissolved in methanol and treated with trimethylsulfonium hydroxide and analyzed by GC–MS with an Agilent 6890 gas chromatography coupled with 5973 mass spectrometry detection. The separation was performed with a 60 m length, 0.25 mm i.d. fused silica column HP-5MS with 0.25 mm film thickness, utilizing with helium as carrier gas at a flow rate of 1.0 ml/min in a constant flow mode. The oven temperature program used was as follow: held at 80 °C for 6 min, and ramped to 300 °C at 10 °C/min. Electron impact ionization at 70 eV was used. The injection was operated in splitless mode at a temperature of 300 °C, and purge flow was 50 ml/min until 0.75 min. A 1 μl aliquot of sample was injected. TOC measurements were carried out on an Apollo 9000 TOC Analyzer (Tekmar-Dohrmann Co., USA). ESR measurements were carried out on a Bruker ESP 300E Electron Spin Resonance Spectrometer.

3. Results and discussion

3.1. Characterization of the catalysts

FT-IR bands of the catalysts are listed in Table 1. The catalysts show absorption bands at 1620–1630, 1306–1310, 1067–1095, 900–910, and 745–750, which are the typical absorptions of phthalocyanine skeleton [32]. The presence of absorption bands near 1770 (v-C=O) and 3300 (v-OH) indicate the presence of carboxylic end groups, which is also proved by higher dissolvability of the catalysts in alkaline solution than in acidic and neutral solution. Results of elemental analyses are listed in Table 2. The C/N ratios of the elemental analysis of the complexes, which are sensitive to changes in the number of phthalocyanine units in polynuclear complexes [32], are in the range of 2.54–2.88. The results indicate the average number of phthalocyanine units in the complexes lies

Table 1
FT-IR data of PPcs (in KBr)

FePPc (732s, 745s, 799m)	CuPPc (738m, 752s, 779w)	ZnPPc (726s, 740sh, 773w)	AlPPc (732s, 750s, 796w)
900w	903w	907w	910w
1089s, 1133w	1095m, 1120sh	1093s, 1126sh	1067s, 1136m
1310s	1306m	1308m	1310m
1620m	1625sh	1627m	1624m
1713s	1723s	1710s	1717s
1767m	1775m	1763m	1765m
3152–3418w	3028–3425w	3191–3439w	3139–3418w

Frequencies in cm^{-1}; intensities: s = strong, m = medium, w = weak, sh = shoulder.

Table 2
Elemental analyses results of PPcs

Samples	C%	N%	H%	Metal%	C/N ratio	Content of Pc units (mmol g^{-1})
FePPc	47.97	18.85	2.67	4.4	2.54	0.78
CuPPc	42.82	14.85	2.59	7.0	2.88	1.09
ZnPPc	43.83	16.84	2.15	4.6	2.60	0.71
AlPPc	47.76	18.72	2.57	3.1	2.55	1.14

between 9 and 16. Since it is difficult to determine the definite molecular weight of the complexes, the concentration of the catalyst are defined as the concentration of phthalocyanine units, which can be calculated by the content of the metals (Table 2).

3.2. Degradative behavior

Among the four complexes studied (FePPc, CuPPc, ZnPPc, AlPPc), ZnPPc and AlPPc show high catalytic activities. Fig. 4 shows the photodegradation of BPA catalyzed by ZnPPc and AlPPc. It can be seen that ZnPPc has higher catalytic activity than AlPPc. The HPLC chromatograms (Fig. 5) of the samples, taken from the reactor during the photocatalytic process, show the disappearance of BPA (peak 7) and formation of its degradation products peaks (peaks 1–6). Fig. 6 shows the time dependences of the amounts of the intermediate products formed during the photocatalytic reaction. The vertical axis in Fig. 6 corresponds to the heights of the absorption peaks normalized to the height of the initial BPA peak. Peaks 2–6 reached a maximum concentration in 5 min, then decreased and disappeared in no longer than 20 min. Peak 1 reached its maximum height in 30 min and then decreased a little. Control experiments with ZnPPc in the dark or under visible light irradiation without ZnPPc indicated no degradation of BPA. It was found that the adsorption of
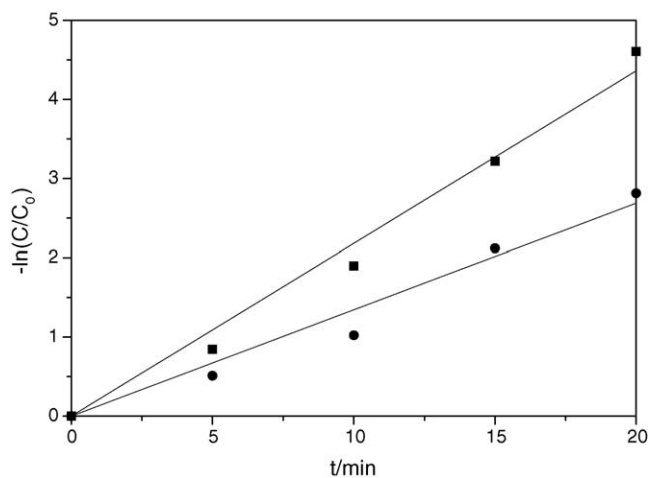

Fig. 4. The photodegradation of BPA catalyzed by ZnPPc and AlPPc, catalyst/substrate = 2%, [BPA]$_0$ = 1 mM, pH 12, the flow rate of the air was 200 ml/min, the 100 W tungsten lamp was used as the visible light source. (■) ZnPPc; (●) AlPPc.
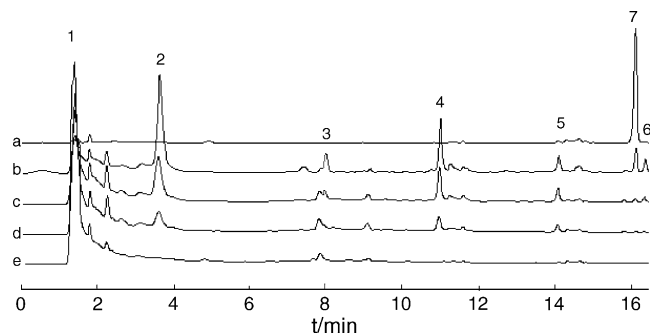

Fig. 5. Evolution of HPLC chromatograms during the photocatalytic treatment of a BPA solution. Catalyst/substrate = 2%, [BPA]$_0$ = 1 mM, pH 12, the flow rate of the air was 200 ml/min, the 100 W tungsten lamp was used as the visible light source. (a) 0 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min.
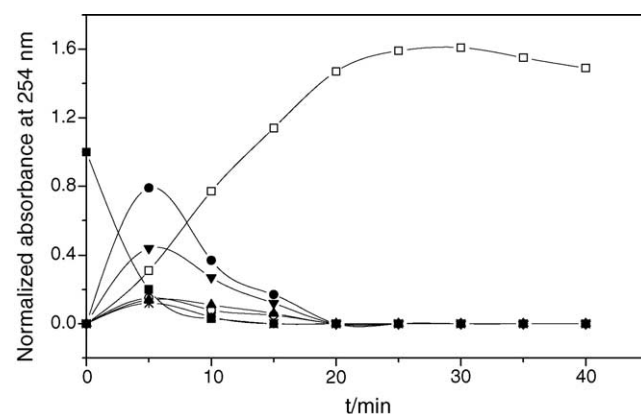

Fig. 6. Time course of degradation of BPA and the further destruction of the intermediate products. Catalyst/substrate = 2%, [BPA]$_0$ = 1 mM, pH 12, the flow rate of the air was 200 ml/min, the 100 W tungsten lamp was used as the visible light source. (■) Peak 1; (●) peak 2; (○) peak 3; (▼) peak 4; (▲) peak 5; (*) peak 6; (□) peak 7.

ZnPPc and AlPPc at 680 nm decreased during the catalytic reaction, which indicated that the complexes also degraded. About 46% of ZnPPc and 57% of AlPPc were degraded in the first 5 min. After a reaction of 30 min, about 87% of ZnPPc and 96% AlPPc were found to disappeared.

3.3. Analyses of degradation products

Peaks 1–5 had retention times shorter than BPA, which indicates that they are more polar than BPA. Because peak 1 could not disappeared completely in our prescriptive time, it was necessary to identify what kind of compound it was. Peak 1 could be even eluted from the column with water (pH = 4) in 2 min, which indicated that it was possibly carboxylic acids. GC–MS was used to identify the intermediate products after treat with trimethylsulfonium hydroxide [35,36]. Two organic acids were detected as their methyl esters: oxalic acid 1 and maleic acid 2. Hydroquinone 3 and 4-isopropenyl-phenol 4 were also detected. GC–MS data of the products of degradation of BPA was show in Table 3. TOC measurements indicated that 21.3% of the carbon was

Table 3
GC–MS data of the products of degradation of BPA

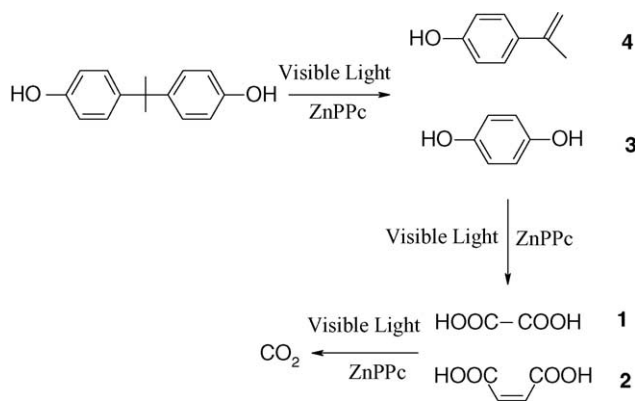| Compounds	Retention time (min)	Derivatized product	Mass spectrum m/z (relative intensity)
Oxalic acid **1**	6.88	Oxalic acid, dimethyl ester	59 (100), 45 (36.1), 29 (25.6), 31 (4.9), 118 (3.6), 30 (2.2)
Maleic acid **2**	11.44	Maleic acid, dimethyl ester	113 (100), 85 (98.6), 59 (49.1), 53 (37), 114 (14.6),
Hydroquinone **3**	16.36	–	110 (100), 81 (39.7), 53 (32.5), 55 (23.5), 39 (19.1)
4-Isopropenyl-phenol **4**	16.80	–	134 (100), 119 (86.1), 91 (40.4), 65 (24.6), 133 (22.0)

Fig. 7. Schematic representation of possible reaction sequence of the degradation of BPA.

mineralized after an hour of reaction. From the results above, a possible reaction sequence of the degradation of BPA was proposed (Fig. 7).

3.4. Degradation mechanism

The degradation of BPA was extensively inhibited by the addition of aqueous sodium azide, a singlet oxygen scavenger, to the solution, such depression was not observed by the addition of 3,5-di-*tert*-butyl-4-hydroxytoluene, a superoxide scavenger [22]. The ESR technique was also used to gain insight into the nature of radicals formed during the photodegradation with 2,2,6,6-tetramethylpiperidine (TEMP) as probe for the singlet oxygen. Fig. 8 illustrates the ESR spectra in different conditions. No signals of significant intensity were observed when the experiments were run in the dark or in the absence of ZnPPc. However, when the system was irradiated with visible light in the presence of ZnPPc, the ESR signal displayed a 1:1:1 triplet signal characteristic of TEMPO obtained by reaction with singlet oxygen [37]. The results suggested that the reaction possibly proceeded via the pathway with singlet oxygen.

3.5. Determination of rate constants

Singlet oxygen is very short-lived species. Its concentration may be considered in a quasistationary state. In our experiments, the solution was continuously saturated with air, the concentration of ZnPPc and the irradiation intense were constant. In these

$$BPA + {}^1O_2 \rightarrow products \tag{1}$$

conditions, the degradation of BPA was a pseudo-order reaction. So the rate constant of the BPA degradation (1) might be comparatively determined taking the 2,4,6-trichlorophenol (TCP) as standard. In fact, TCP was chosen because its rate constant of the reaction with singlet oxygen (2) was well established [38] $(1.67 \pm 0.07 \times 10^8 \, (mol\, l^{-1})^{-1}\, s^{-1}, 25\,^\circ C)$.

$$TCP + {}^1O_2 \rightarrow products \tag{2}$$

Assuming that there were no side reaction of BPA and the standard compound TCP, other than the reaction with singlet oxygen, the rates of the two reactions were given by

$$\frac{-d[BPA]}{dt} = k_{BPA}[{}^1O_2][BPA]$$

$$\frac{-d[TCP]}{dt} = k_{TCP}[{}^1O_2][TCP]$$

Which can be integrated and combined to give the following equation:

$$\ln\left(\frac{[BPA]_0}{[BPA]_t}\right) = \left(\frac{k_{BPA}}{k_{TCP}}\right) \times \ln\left(\frac{[TCP]_0}{[TCP]_t}\right) \tag{3}$$

where the subscripts 0 and t indicate concentration at the beginning of the experiment and at time t, respectively. A plot of $\ln([BPA]_0/[BPA]_t)$ versus $\ln([TCP]_0/[TCP]_t)$ thus yields
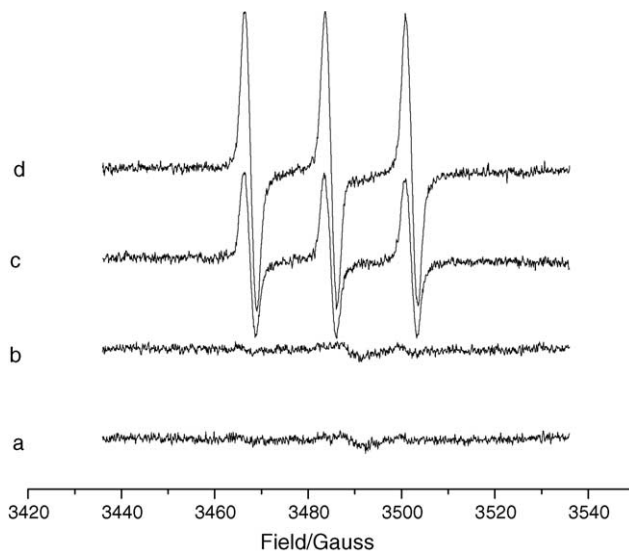

Fig. 8. ESR spectra of solutions under different conditions in the presence of 10 mM TEMP. (a) In the absence of ZnPPc under visible light irradiation; (b) in the presence of ZnPPc in the dark; (c) in the presence of ZnPPc under visible light irradiation for 5 min; (d) in the presence of ZnPPc under visible light irradiation for 10 min.
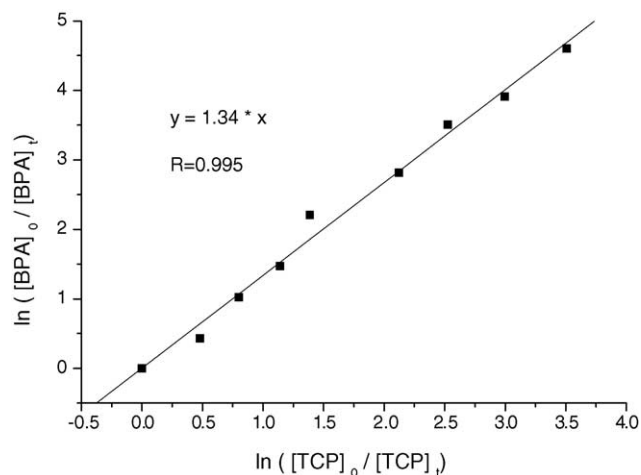
Fig. 9. Determination of rate constants with TCP as the standard.

the rate constant ratio $k_{BPA,25\,°C}$ $2.23 \times 10^8\,(mol\,l^{-1})^{-1}\,s^{-1}$ (Fig. 9).

3.6. Effect of experimental conditions

The reaction parameters that were optimized were the catalyst/substrate molar ratio, flow rate of the air, light source and the pH. The disappearance and the concentration change of the intermediate product 2, were used to depict the catalytic behavior of ZnPPc under different conditions.

3.6.1. Catalyst/substrate molar ratio

fluence of the catalyst/substrate molar ratio was studied at the pH 12 with a BPA concentration of $1\,mmol\,l^{-1}$. Fig. 10a shows the influence of catalyst/substrate molar ratio on the disappearance of BPA under a 100 W tungsten lamp. Fig. 10b shows the concentration change of the intermediate product 2 during the photocatalytic reaction with different catalyst/substrate molar ratio. It can be seen from Fig. 10a that BPA disappears with a catalyst/substrate molar ratio of 0.7% after 20 min irradiation. However, with this catalyst/substrate molar ratio, intermediate product 2 cannot be completely further degraded within 20 min (Fig. 10b). A catalyst/substrate molar ratio of more than 2% was needed to destruct both BPA and the intermediate products.

3.6.2. Flow rate of the air

The concentration of dissolved oxygen in water is about $0.31\,mmol\,l^{-1}$, which is not enough for the degradation of BPA with a concentration of $1\,mmol\,l^{-1}$. It can be seen from Fig. 11 that only 50% BPA is degraded in 20 min without air or oxygen blowing in. Air was chosen in our experiments as the oxidant because of its low cost. Fig. 11 shows influence of flow rate of the air on the degradation of BPA and the further destruction of intermediate product 2. BPA was degraded completely in 20 min with a flow rate of 100 ml/min (Fig. 11a). Therefore, a flow rate of 200 ml/min was needed to destruct the intermediate product 2 in 20 min (Fig. 11b).
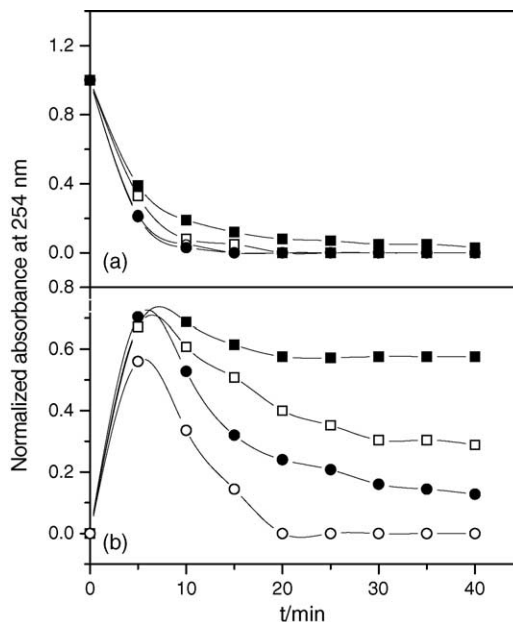

Fig. 10. Effect of the catalyst/substrate molar ratio on the degradation of BPA (a) and the further destruction of the intermediate product 2 (b). $[BPA]_0 = 1\,mM$, pH 12, the flow rate of the air was 200 ml/min, the 100 W tungsten lamp was used as the visible light source. (■) Catalyst/substrate = 2%; (□) catalyst/substrate = 1.5%; (●) catalyst/substrate = 0.7%; (○) catalyst/substrate = 0.4%.

3.6.3. Light source

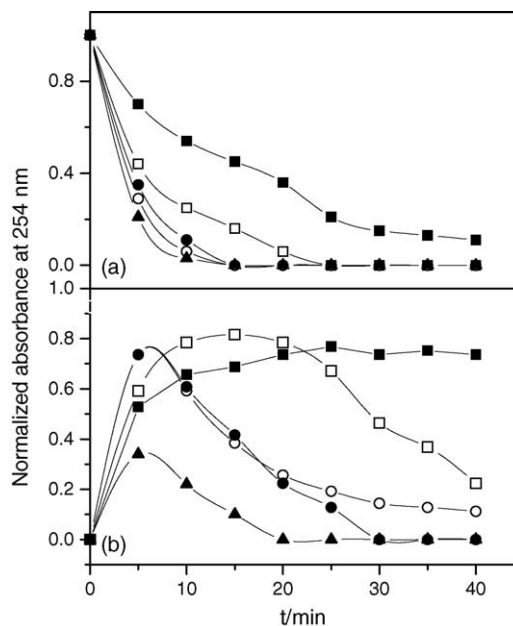The influences of the light source on the degradation of BPA were studied. Tungsten lamps of different power were

Fig. 11. Effect of flow rate of the air on the degradation of BPA (a) and the further destruction of the intermediate product 2 (b). $[BPA]_0 = 1\,mM$, pH 12, catalyst/substrate = 2%, the 100 W tungsten lamp was used as the visible light source. (■) 0 ml/min; (□) 25 m/min; (●) 50 ml/min; (○) 100 ml/min; (▲) 200 ml/min.
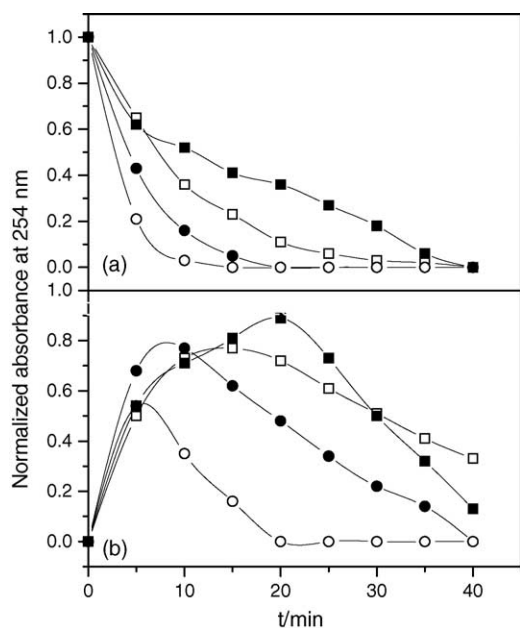
Fig. 12. Effect of the light source on the degradation of BPA (a) and the further destruction of the intermediate product 2 (b). [BPA]$_0$ = 1 mM, catalyst/substrate = 2%, the flow rate of the air was 200 ml/min. (■) Sun light with the irradiation intensity of 608.3 μmol s^{-1} m^{-2}; (□) 40 W tungsten lamp with the irradiation intensity of 79.6 μmol s^{-1} m^{-2}; (●) 60 W tungsten lamp with the irradiation intensity of 123.8 μmol s^{-1} m^{-2}; (○) 100 W tungsten lamp with the irradiation intensity of 297.3 μmol s^{-1} m^{-2}.
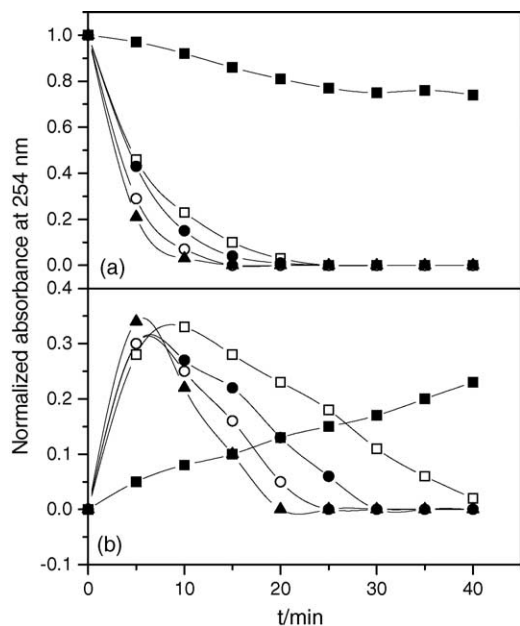

Fig. 13. Effect of the pH the degradation of BPA (a) and the further destruction of the intermediate product 2 (b). Catalyst/substrate = 2%, [BPA]$_0$ = 1 mM, the flow rate of the air was 200 ml/min, the 100 W tungsten lamp was used as the visible light source. (■) pH = 8; (□) pH = 9; (●) pH = 10; (○) pH = 11; (▲) pH = 12.

used as the light source. The results are shown in Fig. 12. The rate of BPA degradation increased remarkably with the increase of the lamp power. With a 100 W tungsten lamp as the light source, BPA and the intermediate products degraded completely in 20 min. More importantly, when sunlight was used as the light source, without stirring and blowing air, BPA (Fig. 12a) and the intermediate products (Fig. 12b) could also be destructed in 40 min. This result made it possible to utilize solar energy in large scale to address environmental needs.

3.6.4. pH

Since the pH of industrial aqueous effluents may vary, the pH dependences of the degradation of BPA and the further destruction of the intermediate products were studied. Phosphonic acid and sodium hydroxide were chosen to adjust the pH in the range of 8–12. Fig. 13 shows the effect of pH on the degradation of BPA (Fig. 13a) and the intermediate products (Fig. 13b). No degradation of BPA was detected with the pH less than 7. The degradation efficiency increased with the increase of pH. Good degradation efficiency could be obtained at the pH ranging from 9 to 13. It is perhaps because the first step of the BPA degradation is the oxidation of the phenolate anion, which presents in the acidic solution in a small amount, leading to the poor conversions [38].

4. Conclusions

In conclusion, the ZnPPc is a promising photocatalyst for the degradation of BPA with the air as the low-cost and environmentally safe oxidant. Under ambient conditions of temperature and pressure, BPA was completely converted to CO$_2$ and carboxylic acid in 20 min using a 100 W tungsten lamp as the light source. When sunlight was used as the light source, BPA could also be degraded efficiently. Full conversion of BPA and its intermediate products were observed in 40 min without stirring and blowing air. The results of ESR measurements suggested that the reaction possibly proceeded via the pathway with singlet oxygen. ZnPPc can be synthesized by a clean solid phase synthesis method in high yield in one-step reaction, in which 1,2,4,5-benzeneeracarboxylic dianhydride and urea, two cheap commercial compounds, are used as the precursors. This makes it possible to utilize solar energy in large scale to address environmental needs.

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