

# Efficient photodegradation of 2,4-dichlorophenol in aqueous solution catalyzed by polydivinylbenzene-supported zinc phthalocyanine

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## Abstract

In this study, photodegradation of 2,4-dichlorophenol (2,4-DCP) in aerated aqueous solution at pH 13 in the presence of hydrogen peroxide catalyzed by polydivinylbenzene-supported zinc phthalocyanine (PDVB-ZnPc) prepared from chloromethylated polydivinylbenzene and zinc phthalocyanine via a Friedel–Crafts reaction has been investigated. The reaction intermediates were identified by gas chromatography–mass spectrometry (GC–MS). The reactive oxygen species involved in the reaction were determined by electron paramagnetic resonance (EPR) technique. Based on the experimental results obtained, PDVB-ZnPc was found to be effective for removing and mineralizing the toxic 2,4-DCP in aqueous solution. The removal yield amounted to 98% after 4 h of irradiation. The reaction followed pseudo-first-order kinetics, and was well fitted into the Langmuir–Hinshelwood-type equation. The optimal concentration of PDVB-ZnPc was 1.0 g/l. The reaction intermediates were some biodegradable organic acids which were subsequently mineralized to  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$  in alkaline solution. Hydroxyl radical and superoxide anion radical other than singlet oxygen were probably generated during the photodegradation of 2,4-DCP in our reaction system.

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**Keywords:** Photodegradation; 2,4-Dichlorophenol; Polydivinylbenzene; Zinc phthalocyanine

## 1. Introduction

Chlorinated phenols used largely as fungicide, herbicide and pesticide intermediate are a kind of typical organic pollutants and listed among top priority control pollutants because of their toxicity and possible accumulation [1–3]. A large number of them exist in industrial wastewater and trace of them in drinking water. Increasing research activities have been devoted to the development of various treatment methods for removing or destroying chlorinated phenols including biodegradable processes [4–9], photocatalytic oxidation [10–12], electrochemical oxidation [13,14] and adsorption [15–17], etc. Among them, photocatalytic oxidation of chlorinated phenols using semiconductors such as  $\text{TiO}_2$  [3,12,18–22] or by photo-assisted Fenton reaction [2,23] has been received much attention for the potential use of sunlight. However, these two methods need high energy

UV light with a wavelength of no longer than 387.5 nm which contains only about 4–5% of the sunlight and the catalyst is difficult to be separated. As a result, removal of recalcitrant and toxic chlorinated phenols in water by green chemical method has been extensively studied in recent years [24–27]. Green chemistry means the quest for environmentally friendly processes (e.g. the use of hydrogen peroxide or molecular oxygen as the oxidant and water as the solvent and the easy separation of the catalyst) [28–30]. Activation of  $\text{H}_2\text{O}_2$  and oxygen by supported-metallophthalocyanine under visible light irradiation is an active research topic in dealing with organic pollutants in recent years [31–37], in which aluminum and zinc phthalocyanine have been more attractive because they have intense absorption in the blue-green bands and exhibit long triplet life time and give high quantum yields for singlet oxygen formation [38–41]. Immobilization of metal complex onto solid support could exhibit unique advantage over corresponding homogeneous systems for their long life time, facile recovery and easy separation of the catalyst due to the stabilization and isolation of metal complex [24,42,43].

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In the present work, a novel heterogeneous polymer-supported photosensitizer PDVB-ZnPc was synthesized and used for photocatalytic degradation of 2,4-dichlorophenol in aerated aqueous solution at pH 13 in the presence of hydrogen peroxide. The influence of substrate concentration, and the amount of catalyst on the degradation rate has been investigated. The reaction intermediates as well as reactive oxygen species involved in the reaction were determined.

## 2. Experimental

### 2.1. Materials and reagents

Zinc phthalocyanine (ZnPc) was synthesized in solid state by condensation of phthalic anhydride and urea according to the literature [44,45]. Benzoquinone, 4-chlorophenol (99.5%) and 2,4-dichlorophenol were purchased from Shanghai Chemicals Inc., and 2,4,6-trichlorophenol (98%) from Acros Organics. Divinylbenzene (55.6%) was supplied by Shandong Shengli Chemical Plant and was further treated with 5% NaOH, followed by drying with anhydrous  $\text{MgSO}_4$ . The reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), used as spin-trapping reagent in EPR studies, was purchased from Sigma Chemical Co. Other chemicals were of reagent grade and used without further purification. Doubly distilled water was utilized throughout the study.

### 2.2. Preparation and characterization of PDVB-ZnPc

Chloromethylated polydivinylbenzene (PDVB) was self-prepared by free-radical suspension polymerization of divinylbenzene with benzoyl peroxide as initiator in bulk, followed by chloromethylation reaction. The spherical PDVB-ZnPc was synthesized via a Friedel–Crafts reaction between chloromethylated polydivinylbenzene (Cl: 10.2% in weight) and ZnPc, and then was extracted for 24 h with dry acetone in Soxhlet apparatus and washed with ethanol before use.

Diffuse reflectance spectrum (190–900 nm) of the PDVB-ZnPc was recorded on a spectrophotometer Perkin-Elmer Lambda 35 equipped with an integrating sphere attachment, for which  $\text{BaSO}_4$  was used as the reference. FT-IR spectra were recorded on a Nicolet Nexus 870 spectrometer (KBr pellets). BET specific surface area was obtained from nitrogen adsorption/desorption at 77 K on a Thermo Electron Co. Sorptomatic 1990. The inner shape of the catalyst was seen by scanning electron microscopy (JEOL, JSM-6380LV), and the element content was determined by the attached energy dispersive spectrometer (EDAX).

### 2.3. Photodecomposition experiment

All irradiation experiments were carried out in a 500 ml cylindrical Pyrex vessel with magnetic stirring, fixed inside a quartz circulating water jacket. A 500 W tungsten halogen lamp (Institute of Electric Light Source, Beijing) was used as the irradiation source. In a typical run, the suspension containing 0.5 g catalyst and 500 ml aqueous solution of 2,4-DCP (0.10–0.40 mM, pH 13) was stirred first in the dark overnight to access the adsorp-

tion/desorption equilibrium and then irradiated. Before light irradiation, the suspension was bubbled with air. When necessary, 1 ml hydrogen peroxide (30%) was also added. At certain intervals, small aliquots (2 ml) were withdrawn by syringe and filtered through a membrane (0.45  $\mu\text{m}$ ). The filtrate was then analyzed by high performance liquid chromatography (Waters 600 HPLC, C 18 reverse column, 5  $\mu\text{m}$ , 250 mm  $\times$  4.6 mm) using methanol–water (60%:40%) as an eluent at a flow rate of 1.0 ml  $\text{min}^{-1}$ . The reaction intermediates were identified by GC–MS on an Agilent 689/5973I instrument equipped with a DB-5MS capillary column (30 m  $\times$  0.25 mm). The column temperature was programmed at 50 °C for 2 min, and from 50 to 250 °C as a rate of 10 °C  $\text{min}^{-1}$ . The samples used for GC–MS analysis were prepared according to the following procedure. The reaction suspension was first filtered to remove the catalyst particles. Then the filtrate was acidified to pH 1, subsequently extracted with dichloromethane. After dichloromethane was evaporated to dryness under vacuum, 10 ml methanol was added to dissolve the residue, and then 1 ml concentrated sulfuric acid was added, and the combined solution was refluxed for about 3 h. The solution was further extracted with dichloromethane, followed by concentrating to about 1 ml under reduced pressure. The reaction products of chlorine ion and  $\text{CO}_2$  were detected by  $\text{AgNO}_3$  and  $\text{Ba}(\text{OH})_2$  method, respectively. EPR experiments were conducted on a Bruker model EPR EMX-10/12 spectrometer.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

Fig. 1 gives the FT-IR spectra (500–1800  $\text{cm}^{-1}$ ) of ZnPc, PDVB and PDVB-ZnPc. The spectrum of ZnPc shows the absorption peaks at 725, 752, 889, 1058, 1087, 1166, 1286 and 1330  $\text{cm}^{-1}$  (Fig. 1a), which are the typical absorptions of phthalocyanine skeleton, while the characteristic absorption bands of PDVB appear at 674, 706, 792, 828, 892, 964, 1044, 1117, 1262, 1447 and 1485  $\text{cm}^{-1}$  (Fig. 1b). The presence of absorption peaks at 674 and 1262  $\text{cm}^{-1}$  indicates the presence of  $-\text{CH}_2\text{Cl}-$ , which is important functional group for the next Friedel–Crafts reaction. When the ZnPc was immobilized onto PDVB via a Friedel–Crafts reaction, the peak of 1044  $\text{cm}^{-1}$  of PDVB disappeared, while the three new peaks of 1061, 1018 and 1168  $\text{cm}^{-1}$  emerged, at the same time, absorption intensity of the chloromethyl functional group decreased (Fig. 1c). In addition, energy dispersive spectrum of PDVB-ZnPc giving the data of C: 82.13%, N: 6.25%, Cl: 2.08% and Zn: 0.78% further confirmed that ZnPc was really bound onto PDVB.

UV–vis diffuse reflectance spectrum of the PDVB-ZnPc (Fig. 2) shows absorption at 670–680 nm and two shoulder peaks at 600–640 nm corresponding to the monomer and aggregate form of ZnPc, respectively, indicating that the PDVB-ZnPc can absorb visible light.

The BET specific surface area of the catalyst was evaluated to be 282  $\text{m}^2/\text{g}$ , and the pore size lies mainly in the region of micropore (<2 nm) (Fig. 3), such porous behavior would facilitate organic adsorption of 2,4-DCP from aqueous medium,

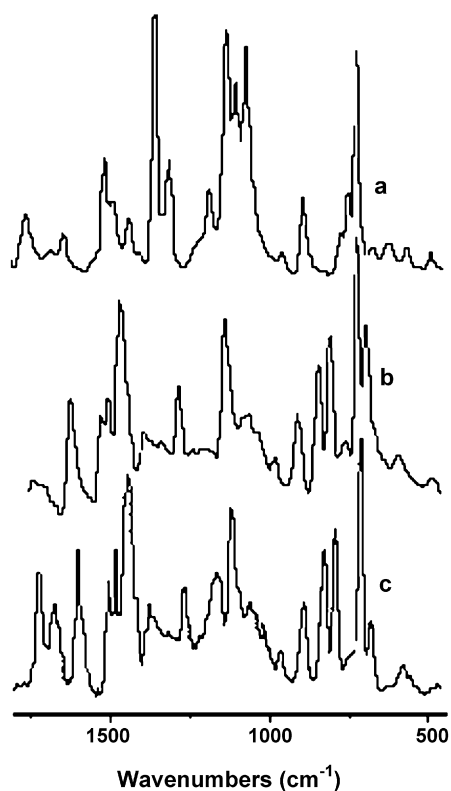


Fig. 1. Comparison of FT-IR spectra of ZnPc (a), PDVB (b) and (c) PDVB-ZnPc.

consequently accelerating the substrate photodegradation over the catalyst [46,47].

### 3.2. Effect of the 2,4-DCP concentration

Based on the reaction kinetics shown in Fig. 4a and Table 1, which was fitted well into the first-order kinetic equation  $\ln(C_0/C) = k_{\text{obs}} t$ , the apparent rate constant,  $k_{\text{obs}}$ , of 2,4-DCP photodegradation decreased from 0.0189 to 0.0081  $\text{min}^{-1}$  as the initial concentration of 2,4-DCP increased from 16.3 to 65.2 mg/l. It was found that the more dilute the initial solution, the faster is the photodegradation. For example, 82% removal of

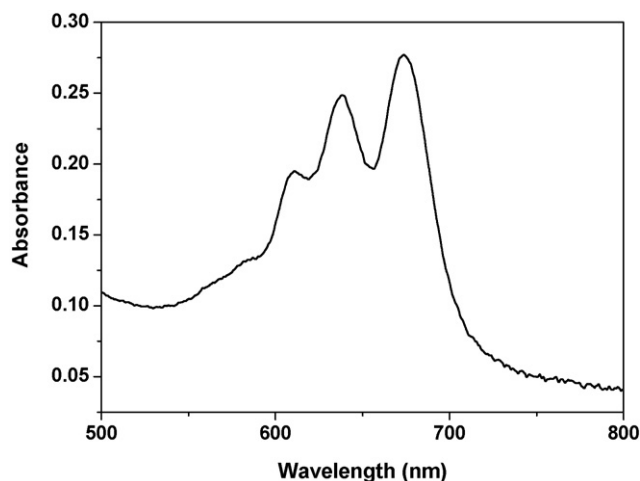


Fig. 2. UV-vis diffuse reflectance spectrum of the PDVB-ZnPc.

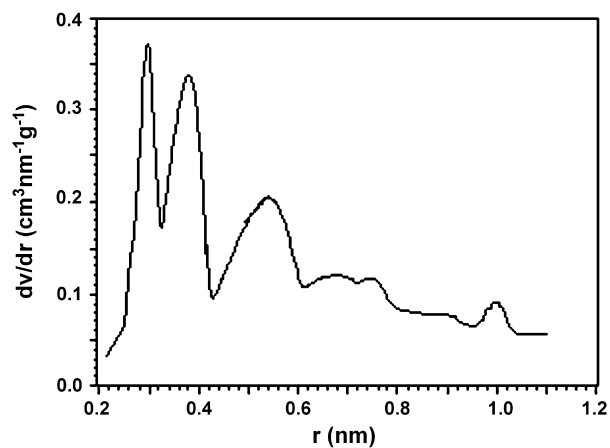


Fig. 3. Horvath Kawazoe poresizes of PDVB-ZnPc.

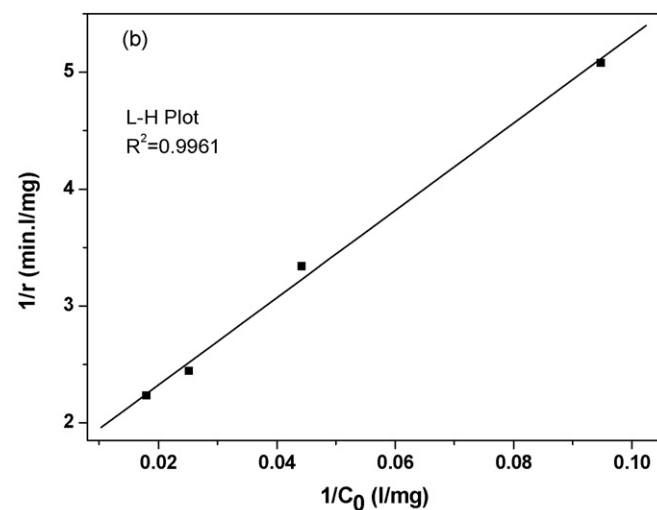
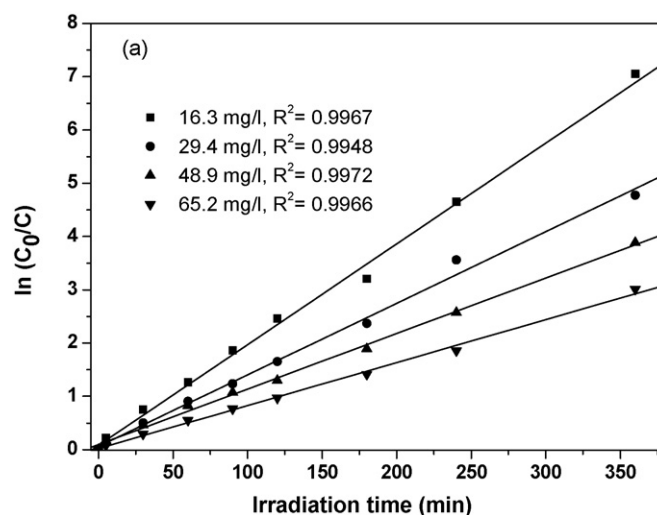


Fig. 4. Effect of initial concentration on the initial photodegradation rate of 2,4-DCP. All the reactions were performed at pH 13; PDVB-ZnPc: 1.0 g/l;  $\text{H}_2\text{O}_2$  (30%): 1 ml.

Table 1

$k_{\text{obs}}$  kinetic constant, half-life ( $t_{1/2}$ ) and maximum amount of adsorption  $Q_s$  for various concentration

| Concentration (mg/l) | $R^2$  | $Q_s$ | $k_{\text{obs}}$ ( $\text{min}^{-1}$ ) | $t_{1/2}$ (min) |
|----------------------|--------|-------|--|-----------------|
| 16.3                 | 0.9967 | 5.74  | 0.0190                                 | 36.7            |
| 29.4                 | 0.9948 | 6.76  | 0.0134                                 | 51.7            |
| 48.9                 | 0.9972 | 9.14  | 0.0104                                 | 66.6            |
| 65.2                 | 0.9966 | 13.89 | 0.0081                                 | 85.6            |

2,4-DCP has been achieved at 60 min when the initial concentration was 16.3 mg/l, but only 51% of 2,4-DCP was removed at 60 min when the initial concentration was 65.2 mg/l. Although the initial amount of 2,4-DCP dark adsorption  $Q_s$  over the catalyst increased with the initial concentration, the apparent first-order rate constants  $k_{\text{obs}}$  decreased correspondingly.

Langmuir–Hinshelwood rate Eqs. (1) and (2) have been successfully used for heterogenous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial equilibrium concentration of organic substrate [22,31–33]:

$$r = -\frac{dc}{dt} = k_{L-H} \frac{k_a C}{1 + k_a C} \quad \text{or} \quad \frac{1}{r} = \frac{1}{k_{L-H} k_a C} + \frac{1}{k_{L-H}} \quad (1)$$

when the concentration of organic substrate is low enough, thus  $k_a C \ll 1$ :

$$r = -\frac{dc}{dt} = k_{L-H} k_a C = k_{\text{obs}} C \quad (\text{if } k_a C \ll 1) \quad (2)$$

where  $k_{L-H}$  is the L–H rate constant, obtained by a linear plot of  $1/r$  versus  $1/C_0$ ,  $C_0$  the initial equilibrium concentration of organic substrate (mg/l) (adsorption equilibrium concentration in the dark in this paper),  $C$  the concentration at time  $t$  and  $k_a$  is the L–H adsorption equilibrium constant. As shown in Fig. 4b, the initial degradation rate of 2,4-DCP,  $r$ , calculated from the decreased concentration at 2 min of irradiation according to reported method [32], increased with the initial equilibrium concentration of 2,4-DCP,  $C_0$ . This can be explained by the following pathway. Because of a limited lifetime, the reactive oxygen species once formed on the immobilized photosensitizer surface would not go far away, and would react preferably with the adsorbed 2,4-DCP. Thus, the more 2,4-DCP adsorbed, the faster was the initial degradation rate. The results above demonstrate that the kinetics of photodegradation of 2,4-DCP under our experimental conditions follows well the Langmuir–Hinshelwood rate equation.

### 3.3. Effect of the PDVB-ZnPc amount

According to the mechanism of photosensitization reaction, the oxidative species ( $^1\text{O}_2$ , or superoxide radicals) were generated via energy transfer or electron transfer from an electronically excited photosensitizer to the ground-state molecular oxygen [48]. Hence, the amount of PDVB-ZnPc added into the reaction bulk would affect the photodegradation rate. In this regard, the effect of PDVB-ZnPc concentration in suspension was investigated for an optimal condition (Fig. 5). The degradation rate increased with the increasing amount of catalyst added from

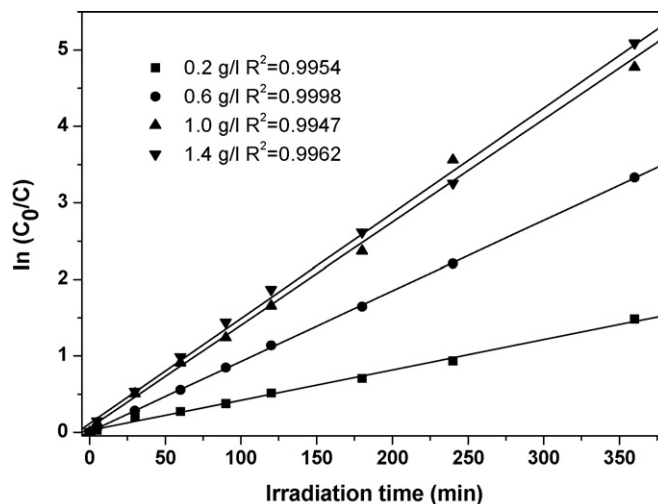


Fig. 5. Effect of catalyst concentration on the 2,4-DCP photodegradation rate.  $[2,4\text{-DCP}]_0 = 0.18 \text{ mM}$ ; pH 13;  $\text{H}_2\text{O}_2$  (30%): 1 ml.

0.2 to 1.0 g/l. The relevant value of  $k_{\text{obs}}$  increased from 0.0040 to  $0.0134 \text{ min}^{-1}$  during the time for experiments carried out with a 2,4-DCP concentration of 0.18 mM. The excess catalyst could not be obviously enhanced the degradation rate, approaching the maximum value  $0.0136 \text{ min}^{-1}$  at 1.4 g/l. This could be explained by the fact that increasing amount of catalyst probably lead to the increasing rate of active oxygen species generation under light irradiation in a fixed reactor. On the other hand, the catalyst concentration higher than a certain value may result in light scattering, consequently decreasing the reactor rate.

### 3.4. Photodecomposition of other chlorinated phenols

Photodecomposition of different chlorinated phenols has been studied. It was noted that photodegradation rate of phenolic compound was greatly dependent on the effect of the substituents on the aromatic ring. The rate was accelerated by electron-donating, but retarded by electron-withdrawing substituents [22]. On the other hand, the reactive oxygen species generated by metallophthalocyanine under light irradiation can react rapidly with unsaturated and/or electron-rich molecules [31]. In this regard, the more the chlorine substituents, the slower is the photodegradation for chlorinated phenols (Fig. 6). That is, after 60 min of irradiation of 0.2 mM chlorinated phenol aqueous solutions, the removal yields of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol were 48%, 46%, and 36%, respectively.

### 3.5. Determination of degradation products

During the 2,4-DCP photodegradation in the aerated aqueous solution without hydrogen peroxide, some reddish brown intermediates were formed, but they could not be examined by HPLC with UV detector. In order to obtain the more information about highly polar and small molecular weight intermediates, GC–MS technique was employed. Fig. 7 and Table 2 give the methyl

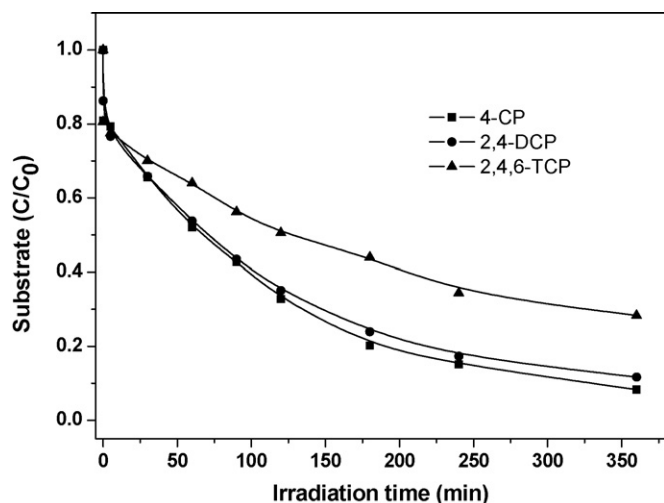


Fig. 6. Photodegradation of different chlorinated phenols. [Chlorinated phenol]<sub>0</sub> = 0.20 mM; pH 13; PDVB-ZnPc: 1.0 g/l; H<sub>2</sub>O<sub>2</sub> (30%): 1 ml.

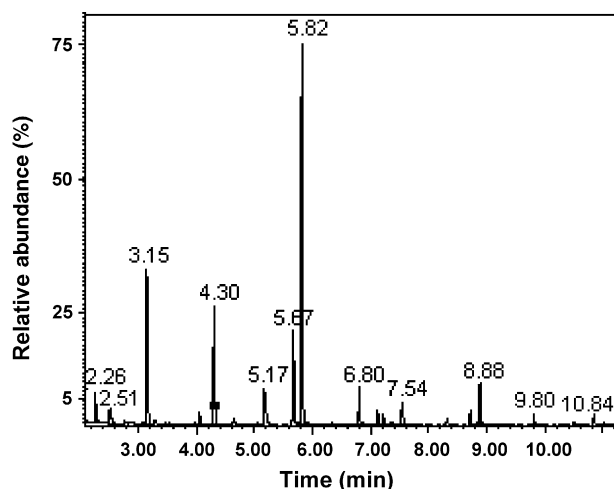


Fig. 7. GC chromatogram of photodegradation of 0.20 mM 2,4-DCP after 6 h of irradiation.

ester derivatives of major reaction intermediates containing carboxylic acid functions. Besides those organic intermediates, chlorine ion and carbon dioxide were also detected as the final products by AgNO<sub>3</sub> and Ba(OH)<sub>2</sub> method, respectively.

Table 2

Intermediates of the 2,4-DCP photodegradation determined by GC/MS<sup>a</sup>

| Retention time (min) | Product                                    | Molecular structure  |
|----------------------|--|--|
| 2.26                 | Propanoic acid, 2-oxo-, methyl ester       | H <sub>3</sub> CCOOCOCH <sub>3</sub>                                       |
| 2.51                 | Acetic acid, methoxyl-, methyl ester       | H <sub>3</sub> C OCH <sub>2</sub> COOCH <sub>3</sub>                       |
| 3.15                 | Ethanedioic acid, dimethyl ester           | H <sub>3</sub> COOCCOOCH <sub>3</sub>                                      |
| 4.30                 | Propanedioic acid, dimethyl ester          | H <sub>3</sub> COOCCH <sub>2</sub> COOCH <sub>3</sub>                      |
| 5.17                 | Pentanoic acid, 4-oxo-, methyl ester       | CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>       |
| 5.67                 | 2-Butenedioic acid (z)-, dimethyl ester    | CH <sub>3</sub> OOCCH=CHCOOCH <sub>3</sub> (z)                             |
| 5.82                 | Butanedioic acid, dimethyl ester           | H <sub>3</sub> COOCCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>      |
| 6.80                 | Benzoic acid, methyl ester                 | C <sub>6</sub> H <sub>5</sub> COOCH <sub>3</sub>                           |
| 7.54                 | Butanedioic acid, methoxy-, dimethyl ester | H <sub>3</sub> COOCCH(OCH <sub>3</sub> )CH <sub>2</sub> COOCH <sub>3</sub> |

<sup>a</sup> All the acids were detected in the form of methanolic esters because the samples were prepared by esterification of acids using concentrated sulfuric acid as catalyst.

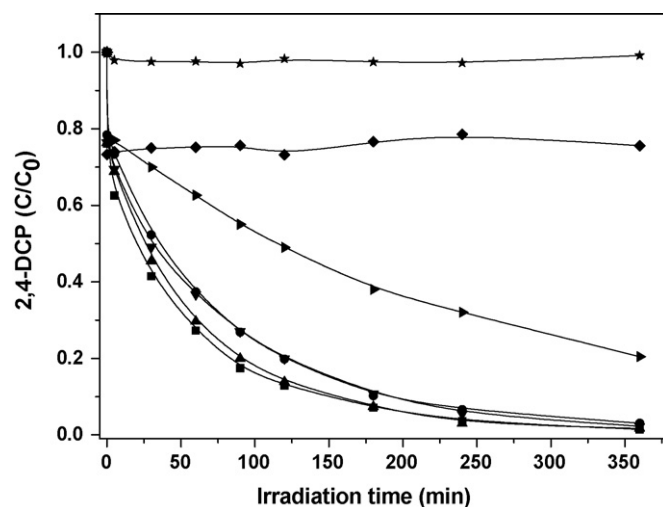


Fig. 8. Concentration change of 2,4-DCP under various conditions: (a, ■) air + H<sub>2</sub>O<sub>2</sub>; (b, ●) air + NaN<sub>3</sub>; (c, ▲) N<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>; (d, ▼) N<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> + isopropanol; (e, ►) same as (a), except that benzoquinone and sodium azide were added; (f, ◆) in the dark; (g, ★) same as (a), except that PDVB was added instead of PDVB-ZnPc. [2,4-DCP]<sub>0</sub> = 0.20 mM; pH 13; PDVB-ZnPc: 1.0 g/l.

### 3.6. Analyses of active oxygen species

Fig. 8 shows the concentration change of 2,4-DCP under various conditions. Control experiments indicate that light and PDVB-ZnPc are essential for the efficient degradation of 2,4-DCP in the aerated aqueous solution, which was hardly degraded in the dark even in the presence of hydrogen peroxide and PDVB-ZnPc (Fig. 8f) or using PDVB instead of PDVB-ZnPc as the catalyst under the same conditions of irradiation (Fig. 8g). The concentration difference of 2,4-DCP (curve f versus curve g) could result from the adsorption of 2,4-DCP on the PDVB-ZnPc. It can be seen that in the presence of both PDVB-ZnPc and light irradiation, the concentration of 2,4-DCP decreased remarkably with the irradiation time (Fig. 8a). It was further noted that with nitrogen-bubbling, the photodegradation of 2,4-DCP could also proceed efficiently in the presence of PDVB and H<sub>2</sub>O<sub>2</sub> added (Fig. 8c), indicating that the presence of H<sub>2</sub>O<sub>2</sub> was sufficient enough to oxidize 2,4-DCP in the presence of catalyst and under light irradiation. In addition, the presence of H<sub>2</sub>O<sub>2</sub> was found to eliminate the reddish brown intermediates, which was in good

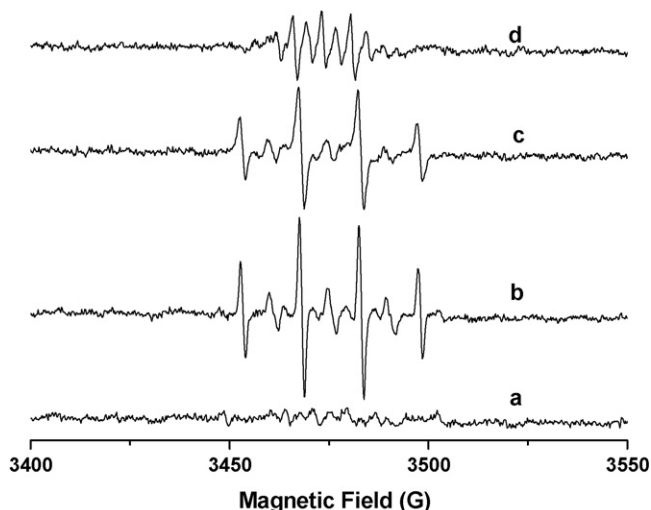


Fig. 9. EPR signals of DMPO adducts in phosphate buffer (pH 7.0) produced from: (a) DMPO/PDVB-ZnPc in the dark; (b) DMPO/PDVB-ZnPc after 10 min of irradiation; (c) DMPO/PDVB-ZnPc/2,4-DCP after 10 min of irradiation; (d) DMPO/PDVB-ZnPc/2,4-DCP/H<sub>2</sub>O<sub>2</sub> after 10 min of irradiation (instrumental settings: microwave power, 19.92 mW; microwave frequency, 9.77 GHz; modulation amplitude, 1.00 G; sweep width, 200 G; receiver gain,  $6.32 \times 10^4$ ).

agreement with the result reported by Xu and co-workers [31]. However, when the isopropanol as a hydroxyl radical scavenger (Fig. 8d), or the sodium azide as a <sup>1</sup>O<sub>2</sub> quencher (Fig. 8b) was added, the reaction rate became a little slower as compared to (Fig. 8c and a), respectively. It suggests that both singlet oxygen and hydroxyl radical probably take part in the photodegradation. Interestingly, once benzoquinone as a superoxide anion radical (O<sub>2</sub><sup>•-</sup>) scavenger and sodium azide were added into the reaction mixture simultaneously, the photodegradation was obviously suppressed (Fig. 8e), this demonstrates that superoxide anion radical is also possibly involved in the photodegradation under our experimental conditions.

It has been generally accepted that singlet oxygen participates undoubtedly in the photooxidation of 4-CP sensitized by metallosulphophthalocyanines process [38], and the production of the free radicals O<sub>2</sub><sup>•-</sup> and •OH by irradiation of photosensitizer ZnPc has been reported elsewhere [49]. To further investigate whether hydroxyl radical and/or superoxide radical take part in the photodegradation of 2,4-DCP, electron paramagnetic trapping technique was employed. The experiments were carried out in phosphate buffer using DMPO as spin-trapping reagent. The EPR signals are shown in Fig. 9. In the dark, almost no EPR signals were detected in the system of DMPO/PDVB-ZnPc (Fig. 9a), the background probably arose because the DMPO was not purified before use and the samples were manipulated in scattered daylight, and could be eliminated by purification and preparing the samples in the dark [50]. Under light irradiation for 10 min, however, the characteristic peak of DMPO-•OH adducts with an intensity ratio of 1:2:2:1 (Fig. 9b) appeared. The addition of 2,4-DCP did not change the signal of the DMPO-•OH adducts (Fig. 9c) as compared to (Fig. 9b). When the H<sub>2</sub>O<sub>2</sub> was added, after 10 min of irradiation, interestingly, the EPR spectrum exhibits seven lines (Fig. 9d), corresponding to an oxidized derivative of DMPO by singlet

oxygen, 5,5-dimethyl-2-pyrrolidone-1-oxyl (DMPOX) [51]. All the above observations (Figs. 8 and 9) suggest that hydroxyl radical and superoxide radical other than singlet oxygen participated in the photodegradation of 2,4-DCP in our reaction system.

#### 4. Conclusions

ZnPc can be firmly anchored to PDVB polymer by Friedel–Crafts reaction. The resulting catalyst displays an efficient photoactivity for the degradation and partial mineralization of 2,4-DCP in the presence of air or H<sub>2</sub>O<sub>2</sub> under halogen lamp illumination, with the formation of more biodegradable low molecular weight compounds.

The reaction followed pseudo-first-order kinetics with respect to 2,4-DCP concentration (0.18–0.40 mM) or catalyst concentration (0.2–1.4 g/l). Hydroxyl radical and superoxide anion radical other than singlet oxygen were probably generated during the photodegradation of 2,4-DCP in our reaction system.

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