

# Photodegradation of bisphenol A in Fe(III)-oxalate complexes solution

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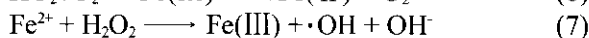
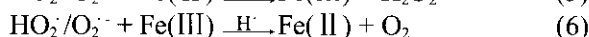
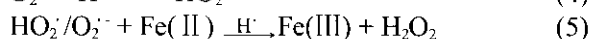
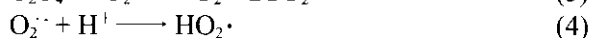
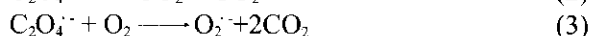
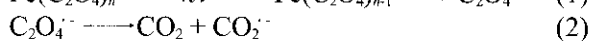
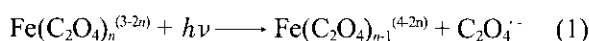
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**Abstract:** The aqueous photodegradation of bisphenol A (BPA) in the presence of Fe(III)-oxalate complexes (Fe(III)-Ox), which are common compositions of natural water, was investigated in this study. BPA underwent rapid indirect photolysis in Fe(III)-Ox solution under simulated solar irradiation, proceeding pseudo-first-order kinetics. The photolysis rate increased with decreasing pH or initial BPA level and increasing Fe(III)/oxalate concentration ratio. Hydroxyl radicals ( $\cdot\text{OH}$ ), which were generated from the photochemical processes of Fe(III)-Ox complexes and contributed to the photooxidation of BPA, were determined by molecular probe and electron spin resonance (ESR) methods with the steady-state concentration of  $2.56 \times 10^{-14}$  mol/L. Superoxide anion radical ( $\text{O}_2^{\cdot-}$ ) was considered as the precursor of  $\cdot\text{OH}$  and qualitatively determined by adding nitro blue tetrazolium as well as ESR experiments. Based on the structural analysis of the intermediate photoproducts of BPA in Fe(III)-Ox complexes solution, the possible degradation pathways of BPA were proposed, involving  $\cdot\text{OH}$  addition, alkyl scission and alky oxidation. The results indicate that the photochemical reactivity of Fe(III) may affect the environmental fate of BPA in natural water significantly.

**Keywords:** bisphenol A; Fe(III)-oxalate complexes; photooxidation; reactive oxygen species

## Introduction

Bisphenol A (2, 2-bis (4-dihydroxydiphenyl) propane) (BPA) is widely used as a raw material for polycarbonate and epoxy resins. In previous studies, the residue level of BPA was detected to be at a rather high level in natural water environment, ranging from  $4.4 \times 10^{-4}$  to  $5.3 \times 10^{-2}$   $\mu\text{mol/L}$  in surface water (Kolpin *et al.*, 2002) and  $5.7 \times 10^{-3}$  to  $57$   $\mu\text{mol/L}$  in hazardous waste landfill leachates (Yamamoto *et al.*, 2001). Furthermore, environmental fate of BPA is of great concern in recent years due to its endocrine-disrupting effect. Photochemical transformation is one of the main abiotic degradation pathways of BPA in natural environment (Staple *et al.*, 1998). Dissolved iron in natural water often exist as complexes with organic ligands, e.g. oxalate. Previous studies showed that Fe(III)-oxalate complexes (Fe(III)-Ox) could strongly absorb solar radiation (290–570 nm) and therefore undergo rapid photochemical reactions, producing Fe(II) and reactive oxygen species (ROS) including  $\text{O}_2^{\cdot-}$ ,  $\text{H}_2\text{O}_2$  and  $\cdot\text{OH}$  (Zuo and Hoigné, 1992). The mechanism could be simply expressed as follows (Cooper and DeGraff, 1972; Zuo and Hoigné, 1992; Faust and Zepp, 1993):



The objectives of this study were to (1) study the

photooxidative degradation of BPA induced by Fe(III)-Ox under simulated solar irradiation with various environmental conditions (pH value, concentration ratio of Fe(III)/Ox and initial BPA concentration); (2) characterize ROS generated from photolysis of Fe(III)-Ox complexes; and (3) identify the main photoproducts of BPA in Fe(III)-Ox solution and analyze the possibility of the BPA toxicity reduction mechanism in natural water.

## 1 Materials and methods

### 1.1 Materials

Bisphenol A, chemical grade, was obtained from Shanghai Chemical Reagent Co. Ltd. (China).  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{C}_2\text{O}_4$ , analytical grade, were purchased from Nanjing Chemical Reagent Factory (China). 2-Propanol, nitrobenzene, dichloromethane, anhydrous sodium sulfate were of analytical grade and used as received. HPLC grade acetonitrile was obtained from Tedia Ltd. Nitro blue tetrazolium (NBT) was obtained from Fluka. Superoxidedismutase (SOD) was obtained from Sigma. 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Aldrich (>97%). Bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) was obtained from Supelco.

### 1.2 Photochemical experiments

Photochemical experiments were performed in a merry-go-round photochemical reactor equipped with a 500-W medium-pressure mercury vapor lamp (Beijing Electric Light Source Institute, China) as the irradiation source. The lamp was immersed inside a borosilicate glass well (total thickness of 4 mm), which is fixed in the central axis of a disc plate with 12 small holes around it. Each 50 ml quartz tube was

placed in the hole at a fixed distance of 8.0 cm to the lamp. The tubes were rotated at 10 r/min. Cold tap water flowed through the glass well to keep the lamp cool. The borosilicate glass well filtered out light at wavelengths below 290 nm. The light intensity of 365 nm was measured as 250  $\mu\text{W}/\text{cm}^2$  by UV photometer (Photoelectric Instrument Factory of Beijing Normal University, China). 1 ml sample solution was removed from reaction solutions at selected intervals and was analyzed by HPLC.

### 1.3 Analytical methods

The concentrations of BPA and nitrobenzene in the photochemical reaction process were measured by HPLC (Agilent 1100, U.S.) fitted with a Discovery C<sub>18</sub> reversed-phase column (150 mm  $\times$  4.6 mm, 5  $\mu\text{m}$ ) at 30°C. Acetonitrile-water (60 : 40, v/v) was at a flow rate of 1.0 ml/min. A 5- $\mu\text{l}$  injection of each sample was done in duplicate using an autosampler. Detections were performed at the wavelength of 228 nm for BPA and 267 nm for nitrobenzene with a photodiode array detector.

For identifying the intermediates and photoproducts of BPA, 100 ml reaction mixtures (pH=3.0) containing 44  $\mu\text{mol}/\text{L}$  BPA, 10  $\mu\text{mol}/\text{L}$  Fe(III) and 100  $\mu\text{mol}/\text{L}$  Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> were photolyzed for 2 h and then extracted using dichloromethane (40 ml  $\times$  3) and dried by anhydrous sodium sulfate. The extracts were reduced to 2 ml under rotatory evaporator (Yarong, Shanghai) and were purged solvent by ultra pure N<sub>2</sub>, and then treated with 0.1 ml BSTFA. The silylated mixtures were analyzed by GC/MS (HP 5890-5971 MSD, U. S.) by injecting 0.8  $\mu\text{l}$  with split ratio 20:1 at an injection temperature 270°C into a HP-5 column (30 m  $\times$  0.25 mm) with helium as carrier gas at a flow rate of 1 ml/min. The MS was operated at the standard EI of 70 eV. The temperature program was: initial temperature 40°C for 5 min holding; 6°C/min to 280°C. Wiley 7 mass spectral database was used for the structural determination of BPA photoproducts.

The absorbance of diformazan formed by NBT reduction by O<sub>2</sub><sup>•-</sup> was detected by UV-Vis spectrophotometer (Shimadzu UV-2201, Japan) at wavelength 560 nm with 1 cm quartz cuvette.

Electron spin resonance (ESR) detection were performed at room temperature using an ESR spectrometer (Bruker EMX 10/12, Germany) equipped with a 180-W high pressure mercury lamp. Glass capillary containing the prepared solution was vertically placed into a cylindrical quartz ESR tube and irradiated in the cavity of ESR spectrometer. ESR measurements were conducted at X band under the following condition: magnetic field, (347.5  $\pm$  2.5) mT; modulation amplitude, 0.1 mT. Pseudo-first-order kinetic constants  $k$  of BPA photolysis were calculated by plotting  $\ln(C/C_0)$  versus irradiation time  $t$ , where  $C/C_0$  were the initial concentration of BPA at

irradiation time  $t$  and irradiation time  $t=0$ , respectively.

## 2 Results and discussion

### 2.1 Photodegradation kinetics

#### 2.1.1 Effect of BPA initial concentration

In recent years, BPA was detected at various levels in natural water and wastewater. BPA absorbed little light above 300 nm in acidic and neutral water (UV absorption spectrum not shown here). The photodegradation of BPA at various concentrations in Fe(III)-Ox solution under simulated solar irradiation is shown in Table 1, following the pseudo-first-order reaction kinetics. The photolysis rates of BPA decreased with the initial concentration increasing, which was coincident with the previous studies (Zhou *et al.*, 2004). The photolysis of BPA at 43.9  $\mu\text{mol}/\text{L}$  was insignificant in pure water at pH=3.0 (less than 6% degraded after 360 min irradiation), but showed rapid in Fe(III)-Ox complexes solution. It was suggested that the Fe (III)-Ox complexes-induced photochemical reaction could enhance BPA photodegradation of BPA in natural water and wastewater.

**Table 1** BPA photolysis kinetics in Fe(III)-Ox complexes

BPA, $\mu\text{mol}/\text{L}$	$K$ , $\text{min}^{-1}$	$t_{1/2}$ , min	$n$	$r$
8.77	0.0430	16.1	7	0.984
21.9	0.0164	42.2	7	0.927
43.9	0.0129	53.9	7	0.984
65.8	0.00474	146	7	0.936

Notes: [Fe(III)]<sub>0</sub> = 10  $\mu\text{mol}/\text{L}$ ; [Ox]<sub>0</sub> = 100  $\mu\text{mol}/\text{L}$ ; pH=3.0

#### 2.1.2 Effect of solution pH

The typical pH value of atmospheric water and surface water with high dissolved organic carbon (DOC) level ranged 3 to 6. The effects of pH value of Fe(III)-Ox solution ranging from 3 to 6 on the photodegradation of BPA are shown in Fig.1, indicating that BPA photolysis decreased with pH increased. Firstly, which is predominant species in Fe(III)-Ox complexes-O<sub>2</sub> system was primarily depend on pH value, i.e., Fe(III)-OH complexes or Fe(III)-Ox complexes. Visual MINTEQ software was used to calculate the distribution of speciations of Fe(III) at pH = 3—6 and at concentration ratio of Fe(III)/oxalate 1:3, 1:10, 1:15 when Fe(III) was fixed at 10  $\mu\text{mol}/\text{L}$ . Theoretical calculation results showed that, as a whole, the three species of Fe(III)-Ox complexes, Fe(Ox)<sup>+</sup>, Fe(Ox)<sub>2</sub><sup>-</sup>, Fe(Ox)<sub>3</sub><sup>3-</sup>, accounted for the predominant dissolved Fe (III) species and their total amounts decreased from 99.9% to 95.6%, whereas the total amounts of Fe(III)-OH complexes increased from less than 0.1% to 4.4% at pH ranging from 3 to 6. Fe(III)-Ox complexes showed more photoreactive than Fe(III)-OH complexes (Zuo and Hoigné, 1992) and therefore could efficiently absorb solar irradiation to produce ROS

(Equations 1–7) to induce the photooxidative degradation of BPA. Secondly, the competing reaction between Equation 5 and 6 depended on pH value, affecting the formation rate of ROS. That is to say,  $\text{HO}_2^-/\text{O}_2^{\cdot-}$  ( $\text{p}K_a=4.8$ ), the transient intermediate from the photolysis of Fe(III)-Ox complexes could undergo disproportionation to form  $\text{H}_2\text{O}_2$  or  $\text{O}_2$  depending on pH value of solution (Zuo and Hoigné, 1992). Under lower pH condition,  $\text{HO}_2^-$  reacted with Fe(II) to form  $\text{H}_2\text{O}_2$  with the reaction rate ( $k$ )  $1.2 \times 10^6 \text{ L}/(\text{mol} \cdot \text{s})$ , whereas it reacted with Fe(III) to form  $\text{O}_2$  with  $k$  below  $10^4 \text{ L}/(\text{mol} \cdot \text{s})$  (Faust and Zepp, 1993). Subsequently,  $\text{H}_2\text{O}_2$  photolyzed via photo-Fenton reaction to produce  $\cdot\text{OH}$  (Equation 7), which was one of the strongest ROS and could oxidize most organic compounds such as BPA. Under relatively higher pH condition,  $\text{O}_2^{\cdot-}$  became the dominant species and reacted with Fe(III) more rapidly to form  $\text{O}_2$  than with Fe(II) to produce  $\text{H}_2\text{O}_2$  (Wu *et al.*, 1999). Therefore, in lower pH condition such as  $\text{pH}=3$  here, ROS generated from the photolysis of Fe(III)-Ox complexes, including  $\text{HO}_2^-/\text{O}_2^{\cdot-}$ ,  $\text{H}_2\text{O}_2$  and subsequent  $\cdot\text{OH}$ , became more efficient and were possibly involved in the photooxidation of BPA.

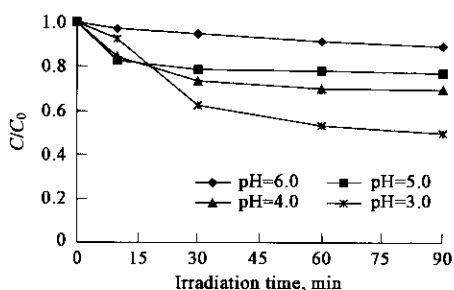


Fig.1 Effect of pH value on the BPA degradation in Fe(III)-Ox system  
 $[\text{BPA}]_0=44 \mu\text{mol/L}$ ,  $[\text{Fe(III)}]_0=10 \mu\text{mol/L}$ ,  $[\text{Ox}]_0=100 \mu\text{mol/L}$

### 2.1.3 Effect of concentration ratio of Fe(III) and oxalate

Oxalate is the common constituent of atmospheric, surface and soil solution with level reaching several tens of micromoles. pH and Fe(III)/Ox ratio were two important and integrated factors on the species composition of Fe(III). To examine the influences of Fe(III)/Ox ratio on BPA photodegradation, Fe(III) was held at  $10 \mu\text{mol/L}$  and the total oxalate was 30, 100 and  $150 \mu\text{mol/L}$ . Fig.2 indicates the increasing BPA photodegradation with the increasing Fe(III)/Ox ratio. It was coincident with the previous study that the accumulation of  $\text{H}_2\text{O}_2$  increased with the increases of oxalate concentration in Fe(III)-Ox complexes (Zuo and Hoigné, 1992), which subsequently photolyzed via photo-Fenton reaction to  $\cdot\text{OH}$  potentially involved in the photooxidation of BPA.

## 2.2 ROS determination

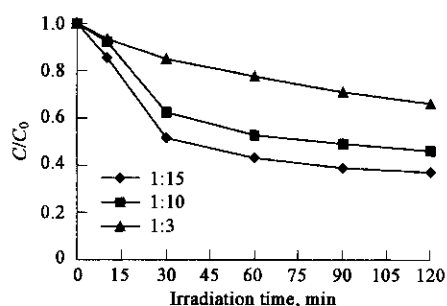


Fig.2 Effect of  $[\text{Fe(III)}]/[\text{Ox}]$  on the BPA photodegradation  
 $[\text{BPA}]_0=44 \mu\text{mol/L}$ ,  $[\text{Fe(III)}]_0=10 \mu\text{mol/L}$ ,  $\text{pH}=3.0$

### 2.2.1 Determination of $\cdot\text{OH}$

The results of BPA photodegradation kinetics showed that the Fe(III)-Ox complexes-induced photochemical reaction was a potential way to effectively eliminate BPA contamination from natural water and wastewater. To qualitatively determine if  $\cdot\text{OH}$  was involved in the photodegradation of BPA in Fe(III)-Ox complexes, 2-propanol was added in excess as scavenger to quench  $\cdot\text{OH}$  (Aguer and Richard, 1996). Fig.3 shows that the BPA degradation was greatly inhibited by adding 2-propanol in Fe(III)-Ox solution and showed very close to BPA direct photolysis in pure water, which suggested that BPA degradation was predominantly attributable to the photooxidation of  $\cdot\text{OH}$  generated from the photochemical reaction of Fe(III)-Ox complexes.

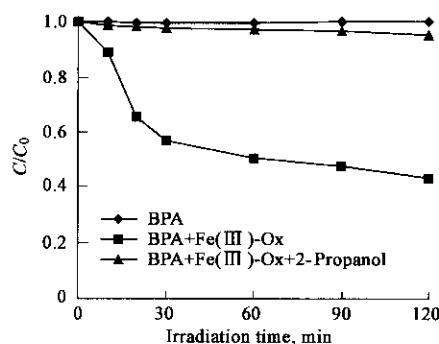


Fig.3 Comparison of BPA photodegradation  
 $[\text{BPA}]_0=44 \mu\text{mol/L}$ ,  $[\text{Fe(III)}]_0=10 \mu\text{mol/L}$ ,  $[\text{Ox}]_0=100 \mu\text{mol/L}$ ,  
 $[\text{2-propanol}]_0=0.25 \text{ mol/L}$ ,  $\text{pH}=3.0$

In order to quantify the steady-state concentration of  $\cdot\text{OH}$  ( $[\cdot\text{OH}]_{\text{ss}}$ ) in the photolysis of Fe(III)-Ox complexes, the competing kinetic experiment with nitrobenzene as molecular probe (P) (Brezonik and Brekken, 1998) was carried out. In this test, the  $\cdot\text{OH}$  decayed following two pathways:



Since the concentration of  $\cdot\text{OH}$  reached a steady-state under the constant irradiation, the loss of probe (P) could be expressed as:

$$-d[\text{P}]/dt = k_{\text{P,OH}}[\cdot\text{OH}]_{\text{ss}}[\text{P}] = k_{\text{exp}}[\text{P}] \quad (\text{III})$$

$$\ln([P]/[P]_0) = -k_{\text{exp}} t \quad (\text{IV})$$

where  $k_{\text{p,OH}}$  is the second-order rate constant for nitrobenzene with  $\cdot\text{OH}$  ( $3.0 \times 10^9 \text{ L}/(\text{mol} \cdot \text{s})$ ) (Zepp, 1992);  $k_{\text{exp}}$  is a measured pseudo-first-order rate constant ( $\text{s}^{-1}$ ),  $k_{\text{exp}} = k_{\text{p,OH}}[\cdot\text{OH}]_{\text{ss}}$ ;  $[P]$  is nitrobenzene probe concentration ( $\text{mol}/\text{L}$ );  $t$  is the irradiation time (s). The reaction solution containing  $44 \mu\text{mol}/\text{L}$  BPA and  $10 \mu\text{mol}/\text{L}$  Fe (III),  $100 \mu\text{mol}/\text{L}$  oxalate was irradiated with the addition of  $6.6 \mu\text{mol}/\text{L}$  nitrobenzene (P) to maintain a steady-state. A plot of  $\ln([P]/[P]_0)$  vs irradiation time  $t$  yielded a straight line ( $r = 0.930$ ) with the slope  $k_{\text{exp}} = 7.67 \times 10^{-5} \text{ s}^{-1}$ , and then  $[\cdot\text{OH}]_{\text{ss}}$  was calculated from the ratio:

$$[\cdot\text{OH}]_{\text{ss}} = k_{\text{exp}}/k_{\text{p,OH}} = 2.56 \times 10^{-14} \text{ mol}/\text{L}.$$

For the further confirmation of the  $\cdot\text{OH}$  produced upon the photolysis of Fe (III)-Ox complexes, the ESR experiments were conducted using 5,5-dimethylpyrroline-N-oxide (DMPO) as the spin trapper. In Fig.4, spectra a, b, c presented the time-dependent formation of ESR signals. And spectrum c showed 1:2:2:1 quartet with hyperfine splitting of  $a_{\text{N}} = a_{\text{H}} = 1.500 \text{ mT}$  and  $g$  value 2.0067, which was typical structure of DMPO-OH adduct (Brezova *et al.*, 2004). Spectrum d shows that ESR signal of DMPO-OH was greatly suppressed when 2-propanol was added as  $\cdot\text{OH}$  quencher into the system. In the light of above analyses,  $\cdot\text{OH}$  generated from the photolysis of Fe(III)-Ox complexes was determined accordingly.

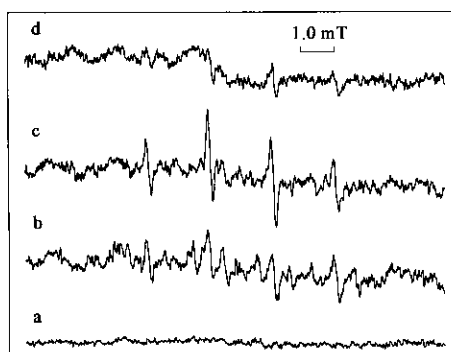


Fig.4 ESR spectra of DMPO-OH adduct in Fe(III)-Ox complexes  $[\text{Fe}(\text{III})]_0 = 10 \mu\text{mol}/\text{L}$ ,  $[\text{Ox}]_0 = 150 \mu\text{mol}/\text{L}$ ,  $[\text{DMPO}] = 0.5 \text{ mol}/\text{L}$ ,  $\text{pH} = 4.0$ ; spectra a, b, c: irradiation for 0, 10, 40 min; spectrum d: after 40 min irradiation with addition of 2-propanol ( $0.02 \text{ mol}/\text{L}$ )

### 2.2.2 Determination of $\text{O}_2^{\cdot-}$

The formation of  $\text{O}_2^{\cdot-}$ , the first-formed ROS in Fe (III)-Ox complexes, was detected by nitro blue tetrazolium (NBT) method (Yamakoshi *et al.*, 2003). The reduction of NBT by  $\text{O}_2^{\cdot-}$  produced diformazan, which was quantitated in terms of the maximum absorbance at 560 nm. In addition, in order to examine whether the formation of diformazan was due to  $\text{O}_2^{\cdot-}$ , the effective  $\text{O}_2^{\cdot-}$  scavenger superoxidodismutase (SOD) was added to inhibit the reduction of NBT by

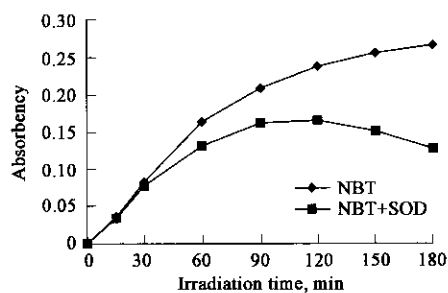


Fig.5 Photoinduced generation of  $\text{O}_2^{\cdot-}$  in Fe(III)-Ox complexes  $[\text{Fe}(\text{III})]_0 = 10 \mu\text{mol}/\text{L}$ ,  $[\text{Ox}]_0 = 150 \mu\text{mol}/\text{L}$ ,  $[\text{NBT}]_0 = 0.056 \mu\text{mol}/\text{L}$ ,  $[\text{SOD}]_0 = 50 \mu\text{mol}/\text{L}$ ,  $\text{pH} = 5.0$ ; NBT, nitroblue tetrazolium

$\text{O}_2^{\cdot-}$ . Fig.5 shows that the amounts of diformazan increased with increasing irradiation time, but was greatly depressed with the addition of SOD, suggesting that the formation of diformazan was due to  $\text{O}_2^{\cdot-}$ .

Equations (1)–(7) indicate that  $\text{O}_2^{\cdot-}$  was the transient precursor of  $\text{H}_2\text{O}_2$  and subsequent  $\cdot\text{OH}$ . As shown in Fig.4, spectrum b displayed multiple ESR signals involving DMPO-OH/DMPO-OOH adduct, but the clear DMPO-OOH signal could not be extracted. Firstly,  $\cdot\text{OH}$  could react rapidly with DMPO to give DMPO-OH adduct ( $k = 4.3 \times 10^9 \text{ L}/(\text{mol} \cdot \text{s})$ ), thus disturbing the formation of DMPO-OOH ( $k = 10 \text{ L}/(\text{mol} \cdot \text{s})$ ) with quite short lifetime (Fang and Zhen, 2002). Furthermore, in order to elucidate the role of  $\text{O}_2^{\cdot-}$  existing in the evolution of ROS, additional ESR experiment was carried out with SOD as effective  $\text{O}_2^{\cdot-}$  scavenger. Fig.6 shows that, during 40 min irradiation, the ESR signal of DMPO-OOH as well as DMPO-OH adduct was not observed. From this point of view, it was inferred that  $\text{O}_2^{\cdot-}$  was the precursor of  $\cdot\text{OH}$  which could induce the photodegradation of BPA in Fe(III)-Ox complexes solution.

### 2.3 Identification of intermediate photoproducts of BPA

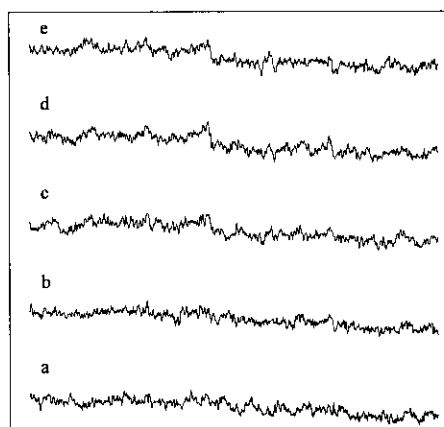


Fig.6 ESR spectra for DMPO adducts in Fe(III)-Ox complexes after the addition of SOD  $[\text{Fe}(\text{III})]_0 = 10 \mu\text{mol}/\text{L}$ ,  $[\text{Ox}]_0 = 150 \mu\text{mol}/\text{L}$ ,  $\text{pH} = 4.0$ ,  $[\text{DMPO}] = 0.5 \text{ mol}/\text{L}$ ,  $\text{SOD} = 0.84 \mu\text{mol}/\text{L}$ ; spectra a, b, c, d, e: irradiation for 0, 10, 20, 30, 40 min

The main ion fragments of photoproducts of BPA analyzed by GC-MS after the silylation treatment of BSTFA are listed in Table 2. Phenol, 2-hydroxy-propanoic acid, glycerol, *p*-hydroquinone (product 1,

2, 3, 5) and BPA were confirmed by comparison with mass spectra of standard chemicals with MS library data of Wiley 7 and retention time on GC-MS.

## 2.4 Photodegradation pathway of BPA in Fe(III)

**Table 2** GC-MS information about main fragment ions of intermediate products of BPA

No.	Retention time, min	Mass spectral data, $m/z$ (relative abundance)	Compound
1	11.35	166( $M^+$ , 24), 151(100), 121(4), 93(8), 77(14)	Phenol
2	11.62	219( $[M^+-CH_3]$ , 8), 190(12), 147(78), 117(66), 73(100)	2-Hydroxy-propanoic acid
3	17.18	293( $[M^+-CH_3]$ , 4), 205(30), 147(46), 117(24), 73(100)	Glycerol
4	19.20	206( $M^+$ , 100), 191(100), 151(16), 115(20), 73(40)	4-Isopropenylphenol
5	20.02	254( $M^+$ , 72), 239(100), 223(4), 112(16), 73(84)	<i>p</i> -Hydroquinone
6	35.10	372( $M^+$ , 16), 357(100), 285(4), 207(12), 191(8), 73(76)	BPA
7	36.85	460( $M^+$ , 16), 445(44), 357(4), 207(16), 191(8), 73(100)	mono-Hydroxylated BPA

## -Ox complexes solution

Based on the structural analyses of intermediate photoproducts by GC-MS and the determination of ROS generated in the photochemical reaction of Fe(III)-Ox complexes system, the proposed photodegradation pathway of BPA in Fe(III)-Ox complexes solution is shown in Fig.7.  $\cdot OH$  attacked BPA molecules in two different ways,  $\cdot OH$  addition and  $\cdot OH$  oxidation. Due to the steric hindrance of isopropyl group, the hydroxyl addition possibly took place on ortho position to phenolic hydroxyl moiety, resulting in mono-hydroxylated BPA (product 7). Under the  $\cdot OH$  oxidation, BPA molecule decomposed via the scission of isopropyl from one phenol moiety, resulting in isopropylphenol radical ( $\cdot C(CH_3)_2C_6H_4OH$ ) and phenol radical ( $\cdot C_6H_4OH$ ). The former was then converted to 4-isopropenylphenol (product 4) via radical reaction. The latter could form phenol (product 1) and also followed by the attack of  $\cdot OH$  to form *p*-hydroquinone (product 5). And further removal of isopropyl might occur by the  $\cdot OH$  attack. Then the cleaved isopropyl was subsequently oxidized by  $\cdot OH$  to 2-hydroxy-propanoic acid (product 2) and glycerol (product 3). Among the main intermediate products detected, product 7 (2-(3,4-dihydroxyphenyl)-2-(4-hydroxyphenyl) propane) transiently accumulated at relatively high level. It has been reported that

its estrogen activity was approximately 10 times less than that of BPA, moreover it showed lower acute toxicity compared with BPA (Suzuki *et al.*, 2004; Ike *et al.*, 2002; Nakagawa and Suzuki, 2001). As for the other decomposed intermediate products, the estrogen activity and the toxicity have not been evaluated and therefore would be brought to further study.

## 3 Conclusions

This study indicated that the Fe(III)-Ox complexes-induced photochemical process was effective for eliminating BPA contamination from natural water and wastewater. BPA underwent a slightly direct photolysis in pure water, but a rapid indirect photolysis in Fe(III)-Ox complex solution, following a pseudo-first-order kinetic reaction. The photodegradation rate of BPA increased with decreasing pH value and BPA initial concentration and with increasing oxalate concentration. The photolysis of Fe(III)-Ox complexes generated  $\cdot OH$  to oxidize BPA, which was definitely confirmed by molecular probe and ESR detection as well with steady-state concentration  $2.56 \times 10^{-14}$  mol/L. Another transient  $O_2^{\cdot -}$  was detected by NBT reduction method along with ESR detection and deduced as the precursor of  $\cdot OH$ . The  $\cdot OH$ -mediated photodegradation pathways of BPA included  $\cdot OH$  addition to BPA and  $\cdot OH$  oxidation resulting in alkyl scission and alkyl oxidation. This study gave better understanding for the environmental behaviors and photofate for endocrine disruptor BPA in natural water and further implication in advanced oxidation process for BPA in wastewater.

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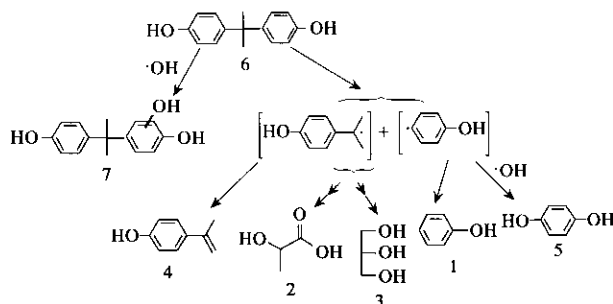


Fig.7 Proposed photodegradation pathway of BPA in Fe(III)-Ox complexes solution under simulated solar irradiation

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