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Dependence of bisphenol A photodegradation on the initial concentration of oxalate in the lepidocrocite-oxalate complex system

DONG Jun^{1,3}, LI Fang-bai^{2,*}, LAN Chong-yu¹, LIU Cheng-shuai², LI Xiao-min², LUAN Tian-gang¹ (1. School of Life Science, Sun Yat-sen University, Guangzhou 510275, China; 2. Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environment and Soil Science, Guangzhou 510650, China. E-mail: cefbli@soil.gd.cn; 3. Zhongshan Institute, University of Electronic Science and Technology of China, Zhongshan 528402, China)

Abstract: To understand the degradation of endocrine disrupting chemicals (EDCs) in natural environment with existence of iron oxides and carboxylic acids, the dependence of bisphenol A (BPA) photodegradation on the initial concentration of oxalate (C_{ox}) in lepidocrocite (γ -FeOOH) aqueous suspension was investigated under both UV and visible lights in this study. Lepidocrocite powder was home-prepared by a hydrothermal process. It was found that BPA degradation was promoted greatly in the presence of oxalate owing to the formation of lepidocrocite-oxalate complex. And there was an optimal C_{ox} , which was 2.0 and 2.4 mmol/L, under UV and visible lights, respectively. The first-order kinetic constant, k value increased 38 times from 0.17×10^2 min⁻¹ in the absence of oxalate with an optimal C_{ox} (2.0 mmol/L) under UV irradiation, and almost 306 times from 0.02×10^2 min⁻¹ in the absence of oxalate to 6.11×10^2 min⁻¹ in the presence of oxalate with an optimal C_{ox} (2.4 mmol/L) under visible irradiation. The BPA degradation rate increased and the first-order kinetic constants decreased with the increase in BPA initial concentration. The dependence of the variation of pH value, total-Fe and Fe²⁺ during the photoreaction on C_{ox} was also investigated. The pH value increased obviously with the reaction time. Total-Fe increased dramatically at the first 5 min and then decreased quickly under UV irradiation and slowly under visible irradiation. The initial concentration of oxalate is a main factor to affect BPA photodegradation in aqueous suspension under both UV and visible lights.

Keywords: bisphenol A; lepidocrocite; oxalate; photodegradation

Introduction

Bisphenol A (BPA), 2,2-bis (4-hydroxyphenyl) propane (CAS 80-05-07), is a representative material among endocrine disrupting chemicals (EDCs) and has been extensively used as a raw material of epoxy and polycarbonate resins, and also as antioxidants in softeners, fungicides, and similar products at about 1700 t annually all over the world (Cousins et al., 2002). BPA can be released into the natural environment as well as surface water during manufacturing, processing and using of products. Concern has recently been raised over the exposure of humans and wildlife to environmental levels of BPA. because BPA is associated with abnormal sexual development and abnormal feminizing responses of animals, like some other EDCs. Since BPA was detected in aquatic environment, air and soil from μg/L to mg/L level (Cousins et al., 2002), great attention has been paid to its removal and degradation. Many literature reported the photocatalytic degradation of BPA by using TiO2, TiO2-zeolite, and TiO2 pillared montmorillonite (Ohko et al., 2001; Fukahori et al., 2003; Watanabe et al., 2003) for wastewater treatment. However, it is necessary to seek for some effective ways to enhance its degradation in natural environment.

It is noticeable that heterogeneous catalytic process at mineral surfaces or geocatalysts should be

very important for organic pollutant degradation in natural environment (Schoonen, et al., 1998). Iron oxides should be a kind of natural minerals and geocatalysts, existing in the earth's crust with great content (Cornell and Schwertmann, 2003). Major iron oxides include goethite (α-FeOOH), lepidocrocite (γ-FeOOH), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃). Among them, γ-FeOOH has a lower chemical stability and thermal stability, and was easily transferred under certain temperature and pressure. Most of iron oxides show semiconductor properties with a narrow band gap and should be photoactive under solar irradiation as photocatalysts (Leland and Bard, 1987). Photochemical transformations catalyzed by the iron oxides have also been investigated extensively (Faust et al., 1989; Pal and Sharon, 1998; Andreozzi et al., 2003; Fu et al., 2004). Unfortunately, the photochemical transformation rate for organic pollutants was very slow and might be negligible under visible light irradiation.

However, iron oxides and hydrogen peroxide (H_2O_2) can form a photo-Fenton-like system with much higher oxidative potential (He *et al.*, 2002). In fact, iron oxides and polycarboxylic acids can also set up a similar photo-Fenton-like system (Zuo and Holgné, 1992; Balmer and Sulzberger, 1999). The photochemistry of Fe(III)-carboxylate complexes in natural aquatic environment, fog, precipitation, tropospheric aerosols, and soil solution have received

considerable attention over the past three decades (Faust and Allen, 1993; Mazellier and Sulzberger, 2001).

On the other hand, a number of investigations focused on ferrioxalate/UV and ferrioxalate/H2O2/UV systems for wastewater treatment (Lee et al., 2003; Jeong and Yoon, 2004). During the photochemical reaction, hydrogen peroxide and hydroxyl radical ·(OH) are also formed (Zuo and Holgné, 1992; Mazellier and Sulzberger, 2001). Therefore, organic pollutants will be mineralized efficiently in the above photochemical systems. However, the mentioned reactions are not natural reactions. To our best knowledge, the heterogeneous photoreaction for the degradation of organic pollutants in the lepidocrocite-oxalate complex system has only had limited studies so far.

To better understand the heterogeneous photodegradation of endocrine disrupting chemicals (EDCs) in natural environment with existence of iron oxides and polycarboxylic acids, lepidocrocite powder was selected as an iron oxide owing to its lower stability and prepared at our laboratory (Hall *et al.*, 1995), and oxalic acid was applied as polycarboxylic acid. The objective of this study was to disclose the effect of oxalic acid initial concentration on BPA photodegradation with a purpose of seeking for an effective way in enhancing EDCs degradation.

1 Experimental

1.1 Preparation of lepidocrocite

In order to obtain pure lepidocrocite powder, ferrous chloride (FeCl₂·4H₂O), hexamethylenetetramine((CH₂)₆N₄), and sodium nitrite were used as precursor reagents. Firstly, 20 g of FeCl₂·4H₂O, 28 g of (CH₂)₆N₄, and 7.0 g of NaNO₂ were dissolved in 400, 80, and 80 ml of distilled water, respectively, to obtain three solutions. Then three solutions were well mixed to obtain a bluish green precipitate. The precipitate remained in the solution was aged at 65°C for 3 h. The product was centrifuged to separate the precipitate. The precipitate was washed once with 95% alcohol and three times with distilled water. After washing, the wet precipitate was dried at 65°C for 48 h. The dried gel was then ground to obtain the orange color product lepidocrocite powder γ-FeOOH eventually confirmed by X-ray diffraction (XRD). The specific surface area, micropore surface area, and total pore volume were 125.6 m²/g, 4.92 m²/g, and 0.298 m³/g, respectively measured by the Brunauer-Emmett-Teller (BET) method, in which N₂ adsorption at 77 K was applied and a Carlo Erba Sorptometer was used (Yu et al., 2003). All chemicals were purchased from Aldrich.

1.2 Experiment of BPA photodegradation

A Pyrex cylindrical photoreactor was used to

conduct photodegradation experiments, in which an 8-W LZC-UVA lamp (Luzchem Research Inc., Canada) with main emission at 365 nm was positioned at the centre of the cylindrical vessel as a UV light source, while a 70-W high-pressure sodium lamp with main emission in the range of 400-800 nm was used as a visible light source. This cylindrical photoreactor was surrounded by a Pyrex circulating water jacket to control the temperatures during reaction. The photoreactor is covered by aluminium foil to avoid any indoor light irradiation. The reaction suspension was prepared by adding 0.25 g of γ-FeOOH powder into 250 ml of aqueous BPA solution or the mixture solution of BPA and oxalic acid. photoreaction, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption/ desorption equilibrium. The aqueous suspension was irradiated by a UV/visible light with constant aeration. At the given time intervals, the analytical samples were taken from the suspension and stored in dark, then centrifuged for 20 min, and filtered through a 0.45-µm Millipore filter to remove the particles.

1.3 Analytical methods

BPA concentration was determined by liquid chromatography (Finnigan LCQ DUO), which consists of a gradient pump (Spectra System P4000), an autosampler (Spectra System Tem AS3000) with a 20- μ l injection loop, and a photodiode array UV detector (Spectra System UV6000LP). A Pinnacle II column (C18, 5 μ m, 250 \times 4.6 mm ID) was used for BPA analysis, in which the mobile phase (70% HCN + 30% HPLC water) was operated at a flow rate of 0.8 m/min and a maximum absorption wavelength of 278 nm was applied. The concentration of total Fe ions was determined by atomic absorption spectrometry, while ferrous ion (Fe²⁺) was tested by the ferrozine method.

2 Results and discussion

2.1 Photodegradation of BPA with lepidocrocite and oxalate together

It is believed that the initial concentration of oxalate (C_{ox}) should be a key factor to affect the photodegradation of BPA in aqueous suspension under both UV and visible lights. To study the effect of the C_{ox} on BPA photodegradation, the first set of experiments with initial BPA concentration of 0.078 mmol/L and lepidocrocite dosage of 1.0 g/L was carried out, followed by the experiments on different initial concentrations of oxalate in the range of 0—3.0 mmol/L under UV illumination without pH control. The results in Fig.1a show that the BPA degradation depended strongly on the C_{ox} . In the low range, the BPA degradation was increased significantly with the increase in C_{ox} , but was inhibited slightly with an excessive amount of oxalate. Obviously, there should

be an optimal amount of oxalate to achieve the best performance of BPA photodegradation under the conditions of this experiment. The experimental data were well fitted by the first-order kinetic model and the first-order kinetic constant (k) was determined to be 0.17×10^{-2} ($R^2 = 0.9823$), 1.39×10^{-2} ($R^2 = 0.9870$), 3.76×10^{-2} ($R^2 = 0.9945$), 5.08×10^{-2} ($R^2 = 0.9771$), 5.93×10^{-2} 10^{-2} ($R^2 = 0.9736$), 6.39×10^{-2} ($R^2 = 0.9726$), 5.81×10^{-2} 10^{-2} ($R^2 = 0.9834$), and 5.44×10^{-2} ($R^2 = 0.9928$) min⁻¹ at the C_{ox} of 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, and 3.0 mmol/L, respectively, as summarized in Fig.2. It was found that the optimal $C_{\rm ox}$ was 2.0 mmol/L. The second set of experiments under similar conditions was conducted under visible light irradiation and the results are shown in Fig.1b. Similar to the results under UV irradiation, the BPA degradation also depended strongly on the C_{ox} . The first-order kinetic constant (k) was determined to be 0.02×10^{-2} ($R^2 =$ 0.8283), 1.12×10^{-2} ($R^2 = 0.9726$), 3.57×10^{-2} ($R^2 = 0.9726$) 0.9825), 4.76×10^{-2} ($R^2 = 0.9905$), 5.49×10^{-2} ($R^2 = 0.9905$) 0.9850), 5.78×10^{-2} ($R^2 = 0.9849$), 6.11×10^{-2} ($R^2 =$ 0.9900), and 5.32×10^{-2} ($R^2 = 0.9820$) min⁻¹ at the C_{ox} of 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, and 3.0 mmol/L, respectively, as also summarized in Fig.2. The optimal C_{ox} was found to be 2.4 mmol/L.

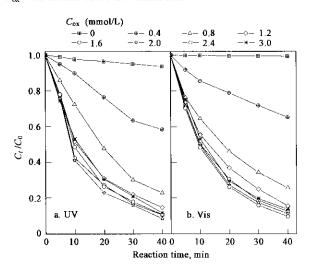


Fig.1 Dependence of BPA photodegradation with the initial concentration of 0.078 mmol/L on the initial concentration of oxalate (C_{ox}) under UV (a) and visible light (Vis) (b) irradiations

In the absence of oxalate, lepidocrocite acted as a photocatalyst and could be excited to generate electron-hole pairs, although BPA was degraded at a low k value under UV light and a negligible k value under visible light. In the presence of oxalate, lepidocrocite-oxalate complex formed photo-Fenton-like system was set up. It was confirmed that the presence of lepidocrocite and oxalate in greatly accelerate cooperation can the degradation reaction. While the first-order kinetic constant (k) was increased more than 38 times from 0.17×10⁻² to 6.39×10⁻² min⁻¹ under UV light irradiation,

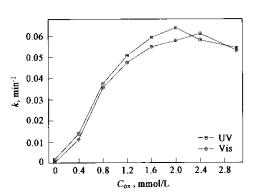


Fig.2 Dependence of the first-order kinetic constants of BPA degradation on the initial concentration of oxalic acid both under UV and visible lights

and it was increased almost 306 times from 0.02×10^{-2} to 6.11×10^{-2} min⁻¹ under visible light irradiation.

2.2 Photodegradation of BPA affected by initial concentration of BPA

In the presence of oxalate with an initial concentration of 1.6 mmol/L and lepidocrocite with the dosage of 1.0 g/L together, a set of experiments was carried out under UV irradiation to investigate the effect of the initial concentration of BPA (C_{BPA}) on BPA degradation. And C_{BPA} was ranged 0.023—0.301 mmol/L. The experimental results are shown in Fig.3. The reaction lasted for 60, 60, 60, 100, and 100 min, respectively in the presence of C_{BPA} at 0.023, 0.062, 0.116, 0.173, and 0.301 mmol/L, and the removal percentage of BPA was achieved by 98.6%, 98.0%, 89.2%, 87.9%, and 69.7%, respectively and the rate of BPA degradation was determined to be 5.75×10^{-7} , 1.46×10-6, 2.49×10-6, 2.99×10-6, and 3.92×10-6 mol/(L. min), respectively. It is clear that the rate of BPA degradation increased with the increase in C_{BPA} . However, it was found that the first-order kinetic constant (k) decreased from 1.20×10^{-1} to 9.40×10^{-3} min-1, while the initial concentration of BPA increased from 0.023 to 0.301 mmol/L. This significant variation of k value indicates that intermediates and products of BPA would affect the BPA degradation rate significantly.

2.3 Variation of pH value

The pH value is a very important factor affecting photo-Fenton reaction (He et al., 2002). BPA photodegradation was strongly dependent on the pH value in the solution. Our group (Lei et al., 2005) reported that the optimal pH value was at 3.94 for the photodegradation of organic pollutants in lepidocrocite-oxalate complex system and photodegradation of organic pollutants might be inhibited greatly when pH value was less than 3. In this investigation, the test of pH value during the reaction were also conducted to investigate the dependence of pH value on C_{ox} in the presence of BPA with the initial concentration of 0.078 mmol/L under

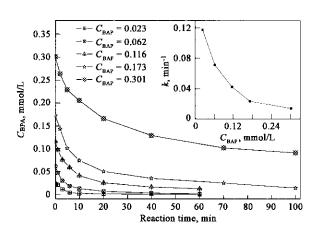


Fig.3 Photodegradation of BPA with different initial concentrations and the dependence of the first-order kinetic constants on the initial concentrations of BPA (C_{BPA}) in the presence of 1.6 mmol/L oxalic acid, C_{OI} =0.023; C_{IGS} =0.062; C_{IGS} =0.116; C_{OI} =0.173; C_{OS} =0.301 mmol/L

UV and visible light irradiation, respectively. The change of pH values with reaction time is plotted in Fig.4. The pH value increased significantly from 3.66, 3.38, 3.25, 3.08, 3.01, 2.91, and 2.75 at the beginning to 4.69, 4.74, 5.03, 5.26, 5.28, 5.30, and 5.30 after 40 min under UV light irradiation, and to 4.15, 4.56, 4.70, 4.68, 4.76, 4.73, and 3.64 under visible light irradiation in the solution when the $C_{\rm ox}$ was 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, and 3.0 mmol/L, respectively. The increase in pH value was attributed to the degradation of oxalate.

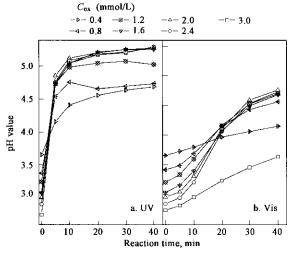


Fig.4 Dependence of the variation of pH value in the solution on reaction time and on the initial concentration of oxalate under UV (a) and visible light (Vis) (b) irradiations

2.4 Formation of dissolved iron

During the photoreaction, lepidocrocite would be photo-dissolved with the BPA degradation and dissolved iron was generated. The oxalate could greatly enhance the dissolution of lepidocrocite under both UV light and visible lights, as showed in Fig.5. Fig.5a shows that the concentration of total-Fe

increased dramatically at the first 5 min and then decreased quickly along with reaction time under UV light irradiation because the dissolved iron ions such as Fe³⁺ can precipitate as Fe(OH)₃ at a pH range of 5—9 and the quick degradation of oxalate may change the pH value of solution significantly. Fig.5b shows that total-Fe increased greatly at the first 5 min, and then increased slightly during 5—10 min at a higher C_{ox} (1.6—3.0 mmol/L), and then decreased gradually along with reaction time under visible light because oxalate was degraded at a low rate under visible light. Obviously, total-Fe depended strongly on the C_{ox} under both UV and visible lights. A higher initial concentration of oxalate has resulted in a higher concentration of total-Fe.

During the photo-dissolution of lepidocrocite, dissolved iron could be photo-reduced to generate Fe²⁺. The dissolved Fe²⁺ concentration was also monitored during the BPA degradation reaction under

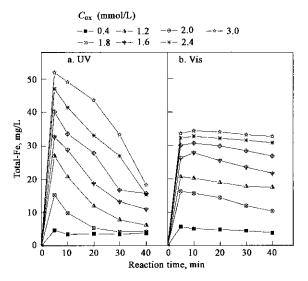


Fig.5 Dependence of the concentration of total dissolved Ferric ion (Total-Fe) on reaction time and on the initial concentration of oxalate under UV (a) and visible light (Vis) (b) irradiations

UV/visible light irradiation. In contrast, Fig.6a shows that the concentration of dissolved Fe²⁺ also increased dramatically at the first 5 min and then decreased gradually along with reaction time under UV light. Fig.6b shows that the concentration of dissolved Fe²⁺ kept increasing along with reaction time under visible irradiation. On the other hand, the concentrations dissolved Fe²⁺ was much less than those of total-Fe. It is therefore concluded that the amount of dissolved Fe²⁺ also depended strongly on the light sources and the initial concentration of oxalate.

3 Discussion

Actually in such a lepidocrocite-oxalate complex system, both types of reactions should be involved on the surface of lepidocrocite and also in the solution

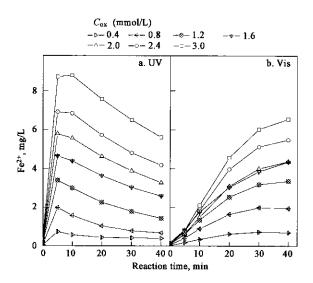


Fig.6 Dependence of the concentration of dissolved ferrous (Fe²⁺) on reaction time and on the initial concentration of oxalate under UV (a) and visible light (Vis) (b) irradiations

(Zuo and Holgné, 1992; Faust and Allen, 1993; Balmer and Sulzberger, 1999; Mazellier Sulzberger, 2001). These reactions can be summarized as: the oxalate in the bulk solution is easily adsorbed onto the surface of y-FeOOH particles to form lepidocrocite-oxalate complexes $[\equiv \text{Fe}^{11}(C_2O_4)_n]^{3-2n}$ on the surface and [Fe^{III} (C₂O₄)_n]_{3-2n} in solution (Reaction 1); then $[\equiv \text{Fe}^{111}(C_2O_4)_n]^{3\cdot 2n}$ and $[\text{Fe}^{111}(C_2O_4)_n]^{3\cdot 2n}$ can be excited to form $[\equiv \text{Fe}^{\parallel} (C_2O_4)_{(n-1)}]^{4\cdot 2n}$ $(C_2O_4)_{(n-1)}$ ⁴⁻²ⁿ) and oxalate radical (C_2O_4) . (Reaction 2); could be transferred into carbon-centered radical (CO₂) (Reaction 3); and the excited electron is transferred from (CO₂) into adsorbed oxygen (O₂) to form superoxide ion O_2 (Reaction 4); and O_2 reacts with H⁺ to form •OOH (Reaction 5). In acidic solution, O2. (or •OOH) reacts with Fe2+ to form H2O2 (Reaction 6). At the meantime, O_2 (or •OOH) reacts with Fe3+ to form Fe2+ (Reaction 7). Fe2+ reacts with H₂O₂ to form •OH (Reaction 8). BPA and oxalate were all attacked and degraded by ·OH (Reaction 9). In this study, the concentration of total-Fe could be used to estimate an equivalent amount of various dissolved iron oxides as $Fe^{III}(C_2O_4)_n^{3\cdot 2n}$ or $[Fe^{II}(C_2O_4)_{(n-1)}]^{4\cdot 2n}$ in solution. It is difficult to estimate the concentration of $[\equiv Fe^{|||} (C_2O_4)_n]^{3\cdot 2n}$ or $[\equiv Fe^{|||} (C_2O_4)_{(n-1)}]^{4\cdot 2n}$ on the surface.

The lepidocrocite-oxalate complex includes [\equiv Fe^{III}(C₂O₄)_n]³⁻²ⁿ or [\equiv Fe^{III}(C₂O₄)_(n-1)]⁴⁻²ⁿ on the surface, and Fe^{III} (C₂O₄)_n³⁻²ⁿ or [Fe^{III} (C₂O₄)_(n-1)]⁴⁻²ⁿ in solution, which are much more photoactive than other Fe³⁺ species. Therefore, BPA degradation could be efficiently enhanced with certain amounts of oxalate and be promoted greatly with the increase in oxalate concentration. However, the excessive oxalate would occupy the adsorption sites on the surface of iron oxide and react competitively with hydroxyl radical.

The adsorption of BPA on the surface was hindered and only a part of hydroxyl radical was utilized. On the other hand, when $C_{\rm ox}$ was up to 2.4 mmol/L, the initial pH value was less than 3. As above mentioned, a lower pH value is not favorable to BPA degradation. Therefore, BPA degradation is inhibited by excessive oxalate and an optimal concentration of oxalate used is thus taken into account.

On the other hand, the reaction quantum yields of lepidocrocite-oxalate complexes are nearly independent on wavelength in the range of 285—440 nm and their absorbance becomes weak at above 440 nm. The wavelength of sodium lamp emission was almost all over 420 nm. Therefore, BPA was degraded at a lower reaction rate under visible irradiation than under UV irradiation in the lepidocrocite-oxalate system.

$$\equiv \text{FeOOH} + n\text{H}_2\text{C}_2\text{O}_4 \longrightarrow \left[\equiv \text{Fe}(\text{C}_2\text{O}_4)_n \right]^{3\cdot 2n}$$

$$+ \left[\text{Fe}(\text{C}_2\text{O}_4)_n \right]^{3\cdot 2n}$$

$$\left[\equiv \text{Fe}(\text{C}_2\text{O}_4)_n \right]^{3\cdot 2n} + h\nu \longrightarrow$$

$$(1)$$

$$\equiv \operatorname{Fe}^{\mathrm{ll}}(C_2O_4)_2^{42n} \left(\left[\operatorname{Fe}^{\mathrm{ll}}(C_2O_4)_{(n-1)} \right]^{42n} \right) + \left(C_2O_4 \right)^{-1}$$
 (2)

$$(C_2O_4)^{-1} \longrightarrow CO_2 + CO_2^{-1}$$
 (3)

$$CO_2 + O_2 \longrightarrow CO_2 + O_2$$
 (4)

$$O_2^{-} + H^{\dagger} \longleftrightarrow OOH$$
 (5)

$$O_2$$
 (·OOH) + nH^+ + Fe^{2+} \longrightarrow Fe^{3+} + H_2O_2 (6)

$$O_{7} \cdot (OOH) + Fe^{3+} \rightarrow Fe^{2+} + O_{7}$$
 (7)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + OH$$
 (8)

$$\cdot OH + BPA (HC, O_4) \rightarrow \rightarrow \rightarrow \cdots \rightarrow CO_2 + H_2O \qquad (9)$$

4 Conclusions

The lepidocrocite-oxalate complex formed and a photo-Fenton-like system was set up in the presence of lepidocrocite and oxalate together, and then BPA photodegradation was promoted greatly. And there was an optimal C_{ox} , which was 2.0 and 2.4 mmol/L under UV and visible light, respectively. The BPA degradation rate increased and the first-order kinetic constants decreased with the increase in BPA initial concentration. The variation of pH value, total-Fe and Fe²⁺ during the photoreaction was also strongly dependent on C_{ox} . The pH value increased obviously with the reaction time. It is concluded that the C_{ox} should be a vital factor to affect BPA photodegradation in aqueous suspension under both UV and visible light irradiations.

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