Chemical Engineering Journal 262 (2015) 34–40

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Degradation of bisphenol A by ferrate(VI) oxidation: Kinetics, products and toxicity assessment

Qi Han [a], Hongjie Wang [a,b,*], Wenyi Dong [a,b], Tongzhou Liu [a,b], Yulei Yin [a], Hongkai Fan [a]

[a] School of Civil and Environment Engineering, Harbin Institute of Technology Shenzhen Graduate School, Shenzhen 518055, China
[b] Shenzhen Key Laboratory of Water Resource Utilization and Environmental Pollution Control, Shenzhen 518055, China

HIGHLIGHTS

- Ferrate oxidation was an effective method in removing BPA and related toxicity.
- The reaction between ferrate and BPA was fitted with pseudo-second order kinetics.
- Based on the twelve determined intermediates, two possible pathways were proposed.
- Removal of toxicity exhibited a hysteresis effect compared to BPA degradation.
- The increase of toxicity was due to the formation of more toxic intermediates.

ARTICLE INFO

Article history:
Received 24 June 2014
Received in revised form 17 September 2014
Accepted 21 September 2014
Available online 28 September 2014

Keywords:
Ferrate(VI)
BPA
Degradation
Intermediates
Toxicity

ABSTRACT

A series of batch experiments were carried out to investigate the factors influencing BPA degradation by ferrate(VI) and the reaction rate kinetics, including molar ratio of ferrate(VI) to BPA (0.1–8.0), initial solution pH (3.0–11.0) and temperature (283–323 K). Reaction pathways were proposed according to the determination of intermediate products and the toxicity variation during the BPA degradation process was evaluated by marine luminescent bacteria (*Vibrio fischeri*). BPA degradation by ferrate(VI) was effective and rapid, with a major BPA removal happening within 3 min. With an initial BPA concentration of 4.4 μmol/L, a ferrate(VI) to BPA molar ratio of 8.0, an initial solution pH of 7.0 and a temperature 298 K, ca. 97.5% BPA removal was achieved. Twelve reaction products were identified by gas chromatography/mass spectrometry–mass spectrometry (GC/MS–MS) and two possible pathways for BPA degradation by ferrate(VI) were proposed, featuring a series of steps including dehydroxylation, cleavage of C–C bond, OH group addition, and oxidation. Unlike the rapid degradation of BPA by ferrate(VI), the elimination of toxicity exhibited a hysteresis effect and there was a rise tendency within the first 5 min, which might be caused by formation of more toxic intermediates, such as benzoquinone, hydroquinone, styrene.

1. Introduction

Bisphenol A (BPA) is an important raw material widely used as a monomer for the production of polycarbonates, epoxy resins, plasticizers, flame retardants, paints and other chemical products. Because of its widespread use, numerous of daily use plastic products contain BPA, including drinking water bottles, polycarbonate baby bottles, food packaging and tableware [1]. Studies indicate that the global demand for BPA was ca. 5 million tons in 2010 and is expected to increase significantly yearly [2]. With the increasing use of BPA, environmental release is likely from plastic manufacturing processes, effluents from wastewater treatment plants (WWPTs) and landfill leachates, etc. [3]. As reported, BPA is ubiquitous presence in aquatic environments and detected concentrations are in the range of 0.01–21 μg/L in natural waters and 1.3–17,200 μg/L in landfills [3,4]. It has been confirmed by many studies that BPA has the potential to cause adverse effects on wildlife and human health with toxicities including liver damage, reproductive and developmental toxicity, diabetes risk, breast cancer, cardiovascular disease, estrogenic activity and thyroid hormone disruption, leading to its classification as an endocrine disrupting chemical (EDC) by the U.S. Environmental Protection Agency (EPA) [5–7]. In addition, it has been proved that some metabolites of BPA exhibit increased toxicity to aquatic organisms [1,8]. As a consequence of its wide usage and negative health

---

* Corresponding author at: School of Civil and Environment Engineering, Harbin Institute of Technology Shenzhen Graduate School, Shenzhen 518055, China. Tel./fax: +86 0755 26033482.

E-mail addresses: hanhanqiqi1986@163.com (Q. Han), whj1533qihan@163.com (H. Wang), dwy1967@qq.com (W. Dong), yulei_010@126.com (Y. Yin).

http://dx.doi.org/10.1016/j.cej.2014.09.071
1385-8947/© 2014 Elsevier B.V. All rights reserved.

impacts it is necessary to develop efficient methods to remove BPA from wastewater and freshwater systems.

Various technologies have been mooted to eliminate BPA from the aquatic environment in recent years, including biodegradation [9], adsorption [10,11], photocatalysis [12–14] and advanced oxidation processes [15–17]. Biodegradation is economical, long lasting with a wide utility, however, research has indicated that BPA is degraded very slowly, requiring more than 28 days for 90% elimination [18]. As biodegradation is widely used by conventional biological wastewater treatment plants, they cannot effectively remove BPA from contaminated water. Alternatively, due to the hydrophobicity of BPA, it can be easily removed by physical adsorption methods, including nanofiltration, reverse osmosis, and membrane filtration [19]. However, the intrinsic problems associated with these processes including inability to treat concentrated wastewater, membrane fouling and high operational and maintenance costs, make them less attractive compared to conventional treatment processes. The copious chemical oxidation methods which have been examined for the effective degradation of BPA include oxidation by manganese dioxide [20] and permanganate [21], ozonation [15], photodegradation (UV photolysis and photocatalysis) [14,22] and Fenton and Fenton-like processes [17], etc. However, heavy metal pollution may result from the manganese dioxide or permanganate oxidation processes. Additionally, the potent carcinogen bromate, which is difficult to remove from water, can be formed during ozonation of bromide-bearing water [23]. Fenton and Fenton-like processes perform optimally under very harsh condition with an extra drawback of sludge production. Finally, the application of photodegradation is being restricted by an inability to prepare an effective, economical and long-life catalyst. Additionally, photodegradation performed poorly compared to permanganate in an estrogenic activity test, however, ozonation can be significantly more estrogen reducing with the addition of an alumina catalyst [21,24]. A toxicity study utilizing *Daphnia magna* indicated that the toxicity of a photoreaction-induced BPA solution initially increased due to the formation of more toxic intermediates, such as hydroquinone, phenol, and 4-hydroxybenzoic acid [14].

Ferrate(VI) oxidation has become one of the most promising methods in water and wastewater treatment due to its strong oxidation, disinfection, coagulation, low toxigenicity and high-security [25]. Ferrate(VI) is a powerful oxidizing agent across the entire pH range with a redox potential varying from 2.2 to 0.7 V in acidic and basic solutions, respectively. Thus, it has be effectively applied in water treatment with low dosage for inactivation of bacterial community [26] and degradation of various refractory contaminants, such as endocrine disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs) [27–29]. The final products of ferrate(VI) oxidation reaction, Fe(III) species, have flocculation and precipitation functions, which hence enhances the removal of particulates, organic matter, nutrients and metals [30]. Moreover, the Fe(III) products are non-toxic, avoiding the metal pollution which might be caused by manganese dioxide or permanganate. Furthermore, ferrate(VI) could also avoid the formation of chlorinated DBPs and the potent carcinogenic bromate which were formed during chlorination and ozonation processes [31,32]. Thus, ferrate(VI) oxidation has received considerable attention as an environmental friendly and effective treatment method for the purification of waters containing refractory contaminants [33]. Li et al. found that BPA could be very readily degraded by ferrate(VI) oxidation and the reaction was very rapid, with a major BPA removal happening during the initial 60 s [34]. They also investigated the rate constants and confirmed that the reaction between BPA and ferrate(VI) was well fitted with the second-order kinetic model [35]. Series of reaction products have also been identified and the BPA degradation pathways were proposed [35,36]. However, very little information is available regarding the toxicity of BPA solution during ferrate(VI) oxidizing process. Since the intermediate products originating from BPA degradation might be more toxic and cause secondary pollution [22], it is necessary to determine the intermediates and their associated toxicity.

Thus, the main objectives of this study are (1) to investigate the factors influencing BPA removal by ferrate(VI) oxidation and the reaction rate constants, such as the molar ratio of ferrate(VI) to BPA, initial pH and temperature; (2) to identify the intermediate products by gas chromatography/mass spectrometry–mass spectrometry (GC/MS–MS) and propose the possible degradation pathways of BPA by ferrate(VI); (3) to further evaluate the variation of the BPA solution toxicity during the oxidation process.

2. Materials and methods

2.1. Materials

All solutions were prepared with deionized and ultra pure water (Milli-Q Direct 8, USA). Bisphenol A (99%) and potassium ferrate(VI) (97%) were purchased from Sigma–Aldrich and used without further purification. The ferrate(VI) stock solution was freshly prepared prior to the experiment at 2.52 mol/L with a pH of 9.0 and used within 10 min to minimize the self-decomposition reactions of ferrate(VI) [37]. BPA solutions at concentration of 4.4 μmol/L were prepared prior to experiments with deionized distilled water.

Methanol, acetonitrile and dichloromethane (Merck, Germany) used in the experiments were of chromatographic grade. Other chemicals and reagents used in the experiments were of analytical grade. The freeze-dried bacteria *Vibrio fischeri* used for toxicity assessment was obtained from the manufacturer (DeltaTox, SDIX, USA) and stored at −20 °C.

2.2. Experimental methods

To assess BPA degradation by ferrate(VI), 500 mL of prepared BPA solution was transferred into conical flasks. The degradation reactions were initiated by addition of certain volume of ferrate(VI) stock solution into the reactor according to the experimental conditions, which was vigorously magnetically stirred for 30 min. Samples were collected at given time intervals and 0.18 mol/L hydroxylamine hydrochloride was added immediately in order to quench the oxidation process. The samples were then centrifuged for 5 min prior to subsequent analysis. All experiments were carried out in duplicate.

In order to determine the degradation products of BPA, the molar ratio of ferrate(VI) to BPA was fixed at 5.7 with a BPA concentration of 4.4 μmol/L, initial pH 7.0 and temperature 298 K. The sample of 50 mL was withdrawn into a separatory funnel at determined intervals. The reaction was ceased by 0.18 mol/L hydroxylamine hydrochloride and the sample pH was adjusted to 2.0 by HCl. Subsequently, 0.5 g NaCl and 3 mL dichloromethane were added into the funnel before the sample was vigorously shaken. After the solution was extracted for 5 min, the organic phase was transferred into a colorimetric cylinder. The sample was extracted repeated twice more and the organic phases combined. Finally, the extract was concentrated and quantified to 1 mL by dichloromethane after drying with solid anhydrous sodium sulfate. Similar pretreatment method for analysis of intermediates of BPA degradation has also been reported by other researche [15].

2.3. Analytical methods

The residual concentration of BPA during the reaction was analyzed by a ultra performance liquid chromatography (Acquity

H-class UPLC, Waters, USA) with a 100 mm BEH C18 column (1.7 × 100 mm, 3.5 μm) at 30 °C and TUV detector set at 280 nm. The mobile phase was a methanol/water mixture (70/30, v/v) at a flow rate of 0.2 mL/min with an injection volume of 5 μL [21]. The method detection limit was 0.02 μmol/L.

The intermediates formed during degradation of BPA by ferrate(VI) were determined by GC/MS–MS (7890A-5975C, Agilent, USA) combined with a HP-5 (30 × 0.25 mm, 0.25 μm) quartz capillary column and an electron impact (EI) detector (70 eV). The carrier gas was helium at a flow rate of 1 mL/min and the injection volume was 1 μL with a spilt ratio of 1/10. The temperature program was as follows: the initial temperature was 40 °C and held for 3 min; then it increased at 15 °C/min to 280 °C where it was held for 8 min. The temperatures of the injection port, interface and the ion source were 260, 250 and 230 °C, respectively. The variation of ultraviolet (UV)-spectrum during BPA degradation was tested by an ultraviolet–visible (UV–VIS) spectrophotometer (UV2450, Shimadzu, Japan).

The toxicity of BPA and its degradation products was assessed by luminescent bacteria toxicity test according to the ISO standard [38]. Luminescent bacteria were exposed to the initial BPA solution and the treated samples for 15 min at 15 ± 0.5 °C and the relative inhibitory rate (*T*%) was calculated for each sample relative to the control. The luminescence was measured on a DeltaTox II luminometer (SDIX, USA).

The solution pH was measured using a portable digital pH-meter throughout experiment (pHS-3B, Shanghai, China).

3. Results and discussion

3.1. Factors influencing the degradation of BPA by ferrate(VI)

3.1.1. Effect of the ferrate(VI) to BPA molar ratio

The effect of ferrate(VI) to BPA molar ratio on BPA degradation was investigated with results shown in Fig. 1(a). The experiments were carried out at a range of molar ratios ([Fe(VI)]/[BPA]) 0.1–8.0 with a fixed BPA concentration of 4.4 μmol/L, initial pH 7.0 and temperature 298 K. It is evident that the degradation of BPA by ferrate(VI) was a rapid process, with a major removal of BPA obtained in the initial 3 min, and the molar ratio has a significant effect on BPA removal. As [Fe(VI)]/[BPA] increased from 0.1 to 5.7, the removal of BPA by ferrate(VI) increased appreciably from 15.1% to 92.5%. When the molar ratio further increased up to 8.0, there was only a slight increase of BPA removal by 5.9%. It has been confirmed that degradation of organic pollutants by ferrate(VI) oxidation are through two pathways, namely the direct oxidation by ferrate(VI) and the indirect oxidation by the new generated free radicals (as shown in Eqs. (1) and (2)) [36]. It is expected that the increase in the molar ratio of ferrate(VI) to BPA enhances both the direct and the indirect oxidation pathways, leading to the promotion of BPA degradation [39]. However, the simultaneous ferrate(VI) self-decomposition would be obviously observed when the molar ratio of ferrate(VI) to BPA was high, which is not favorable to BPA removal [40]. As shown in Fig. S1, the decomposition curves of ferrate(VI) at different values of [Fe(VI)]/[BPA] reflected that the decomposition rate of ferrate(VI) increased with increasing molar ratio, indicating that the proportion of ferrate(VI) taking part in BPA degradation would relatively decrease.

$$2FeO_4^{2-} + H_2O \rightarrow 2Fe(OH)_3 + 5[O] \quad k = 1.5 \times 10^3\ M^{-1}\ s^{-1} \tag{1}$$

$$[O] + H_2O \rightarrow 2HO^{\cdot} \tag{2}$$

Kinetics of BPA degradation by ferrate(VI) oxidation in this study is shown in Fig. 1(b) and it can been seen that the pseudo-second order reaction model fitted the experimental data closely ($R^2 = 0.993$), which is agreed with the results of Zhang et al. and shown as Eqs. (3) [36]. Where C_{BPA} was the concentration of BPA, t was the reaction time, k_{app} was the apparent second-order rate constant.

$$-\frac{dC_{BPA}}{dt} = k_{app}C_{BPA}^2 \tag{3}$$

It has also been confirmed by Li et al. [35] that reaction between BPA and ferrate(VI) was well fitted the second order rate law. The value of k_{app} in this study was determined to be 8356 mol^{-1} L s^{-1} with the molar ratio of ferrate(VI) to BPA of 5.7 and a fixed initial BPA concentration of 4.4 μmol/L, which is much lower than that in Ref. [35]. This might be caused by the relatively low initial BPA concentration in this study.

3.1.2. Effect of initial pH

Figs. 2 and 2S shows that initial pH had a similar effect on BPA removal and the reaction rate constant (k_{app}). When the initial pH increased from 3.0 to 5.0, the BPA removal increased obviously from 85.1% to 95.2% and the reaction rate constant increased significantly from 1.9 × 10^3 mol^{-1} L s^{-1} to 8.4 × 10^3 mol^{-1} L s^{-1}. Further initial pH increase to 11.0 resulted in slightly reduced BPA removal while k_{app} declined more sharply. This can be explained from the species of both ferrate(VI) and BPA present in the acidic to basic pH range [41]. As shown in Fig. S3, ferrate(VI) exists as four

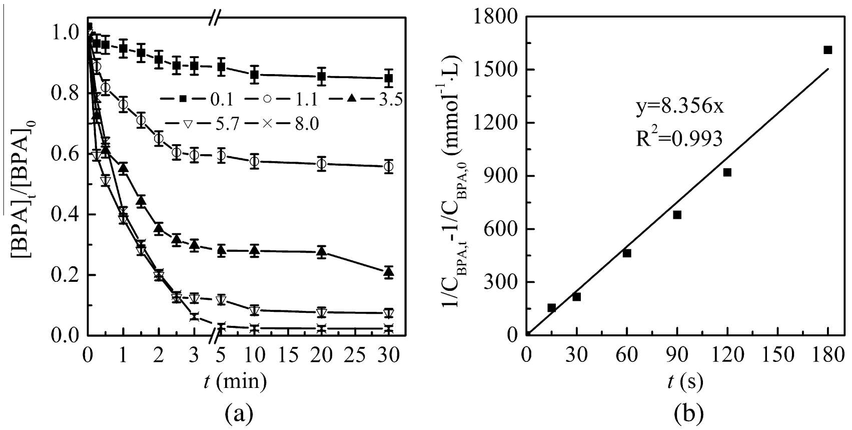

Fig. 1. (a) Effect of ferrate(VI) to BPA molar ratio on BPA removal (Experimental conditions: BPA concentration = 4.4 μmol/L; the molar ratio [Fe(VI)]/[BPA] = 0.1–8.0; initial pH = 7.0; temperature = 298 K.); (b) kinetics of BPA removal by ferrate(VI) oxidation (Experimental conditions: BPA concentration = 4.4 μmol/L; the molar ratio [Fe(VI)]/[BPA] = 5.7; initial pH = 7.0; temperature = 298 K.).

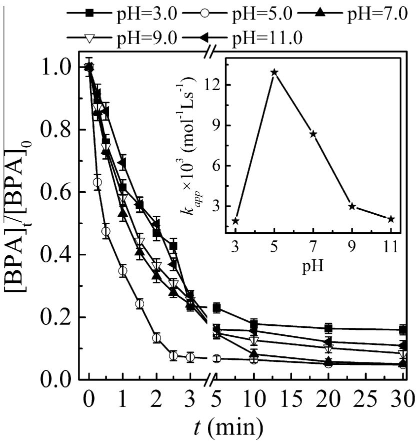

Fig. 2. Effect of initial pH on BPA removal and the reaction rate constant (k_{app}). (Experimental conditions: BPA concentration = 4.4 μmol/L; the molar ratio [Fe(VI)]/[BPA] = 5.7; temperature = 298 K.)

species across the pH range, $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-} [42]. The monoprotonated species ($HFeO_4^-$) is predominated at pH 3.5–7.23 and has a larger spin density on the oxo-ligands and stronger oxidizing capacity than FeO_4^{2-} [43,44]. Thus, the rapid increase in $HFeO_4^-$ from an initial pH of 3 to 5 explains the increased degradation of BPA. The subsequent decrease in $HFeO_4^-$ results in the significant decrease of the reaction rate constant. However, the total BPA removal didn't change obviously during pH 5.0–7.0 due to the predomination of $HFeO_4^-$. In basic conditions, FeO_4^{2-} becomes the predominant species of ferrate(VI) and BPA ionization would occur because of its pK_a value (pK_{a1} = 9.2, pK_{a2} = 11.3), resulting in the generation of numerous phenolic hydroxyl groups and an increase in the fraction of BPA^{2-} [13,20]. The increase of electron density on the benzene ring enhances unfavorable repulsions between FeO_4^{2-} anions and BPA^{2-} anions, explaining the slow down of BPA degradation by ferrate(VI) between pH 7.0 and 11.0.

3.1.3. Effect of temperature

As shown in Fig. 3, the reaction rate constant k_{app} of BPA degradation by ferrate(VI) increased significantly from 2.5×10^3 to 1.7×10^4 mol^{-1} L s^{-1} with increasing temperature from 283 to 323 K, which indicated that the degradation of BPA by ferrate(VI) was strongly dependent on temperature. However, this temperature increase did not significantly alter the total removal of BPA after a 30 min reaction, as illustrated in Fig. S4. This result could be attributed to the complex effect of temperature on BPA degradation by ferrate(VI). While the collision frequencies between ferrate(VI) and BPA are enhanced with increasing temperature, increasing the elimination rate of BPA [17], the stability of ferrate(VI) reduced and self-decomposition enhanced, which is detrimental to BPA removal [40].

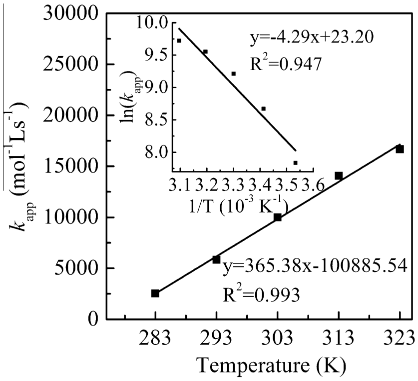

Fig. 3. Effect of temperature on the reaction rate constant (k_{app}). Inset: Arrhenius plot of ln(k_{app}) vs. 1/T. (Experimental conditions: BPA concentration = 4.4 μmol/L; the molar ratio [Fe(VI)]/[BPA] = 5.7; initial pH = 7.0.)

As shown in Fig. 3, there was a linear increase of k_{app} with temperature ($R^2 = 0.99$) as well as the Arrhenius plot of $\ln k_{app}$ vs. $1/T$ ($R^2 = 0.95$). According to the Arrhenius equation, the activation energy (E_a) in this study was calculated to be 35.71 kJ/mol, which is much lower than 48.7 kJ/mol reported for the degradation of BPA by permanganate [21].

3.2. Identification of intermediates and the possible degradation pathway

The identification of intermediates from the oxidation of BPA by ferrate(VI) was evaluated by GC/MS–MS, and the results are shown in Table S1 and Fig. S5. Table S1 summarizes the main fragment ions (m/z) and abundance (%) of reaction products in comparison to the NIST data library. Fig. S5 displays the MS/MS spectra of the intermediates observed during the oxidation reaction. Twelve intermediates with shorter retention times than BPA, indicating higher polarity, were observed in this study and five of them have also been identified by Li et al. [35], such as styrene, maleic acid, 1-(4-methyl phenyl) ethanone, p-isopropenyl phenol and p-isopropyl phenol. Nine of these twelve reaction products had aromatic rings, including styrene, hydroquinone, α-methylstyrene, 2-phenyl propenal and 1-(4-methyl phenyl) ethanone. Based on the twelve identified intermediate products, the possible degradation pathways of BPA by ferrate(VI) are proposed schematically in Fig. 4. This shows that the total degradation of BPA underwent dehydroxylation, cleavage of C–C bonds, OH group addition, elimination reactions and oxidation [35].

The degradation of BPA by ferrate(VI) oxidation can be divided into two possible pathways related to the bonds broken. The first pathway is dehydroxylation, by which the two C–O bonds were cleaved and the two hydroxyl groups departed from BPA molecule, resulting in the formation of (2-methyl-1-phenyl-1-propenyl) benzene. Subsequent cleavage of the aromatic ring connecting C–C bond produces (1-methyl vinyl) benzene and styrene, which each contains a single benzene ring. These intermediates are further oxidized to generate 2-phenyl propenal, 1,4-pentadien-3-ketone and maleic acid. The second pathway is initiated by the cleavage of the two phenyl groups in BPA and leads to the formation of p-isopropyl phenol, p-isopropenyl phenol and phenol (not detected in this study. It might due to the two electron-donating hydroxyl group in BPA molecular, which increases the electron density on each benzene ring and made the C–C bond connecting the two benzene rings more vulnerable [35]. These reaction products can continue to be oxidized by ferrate(VI), generating 2-phenyl isopropanol, 1-(4-methyl phenyl) ethanone, hydroquinone, benzoquinone, 1,4-pentadien-3-ketone, and maleic acid. As shown in Fig. 4, the two hypothesized degradation pathways were not isolated from each other and the intermediates, which are produced by the first pathway and contain two aromatic rings, can also be degraded by ferrate(VI) along the second pathway.

3.3. Toxicity analysis

While BPA is known to be toxic, its toxicity may change during the ferrate(VI) oxidation process due to the formation of intermediates. In this study, the relative inhibitory luminosity rate of *V. fischeri* was used to evaluate the toxicity variation during BPA degradation process by different dosages of ferrate(VI). The relative inhibitory rate (T%) is calculated from Eq. (2), where E_0 and

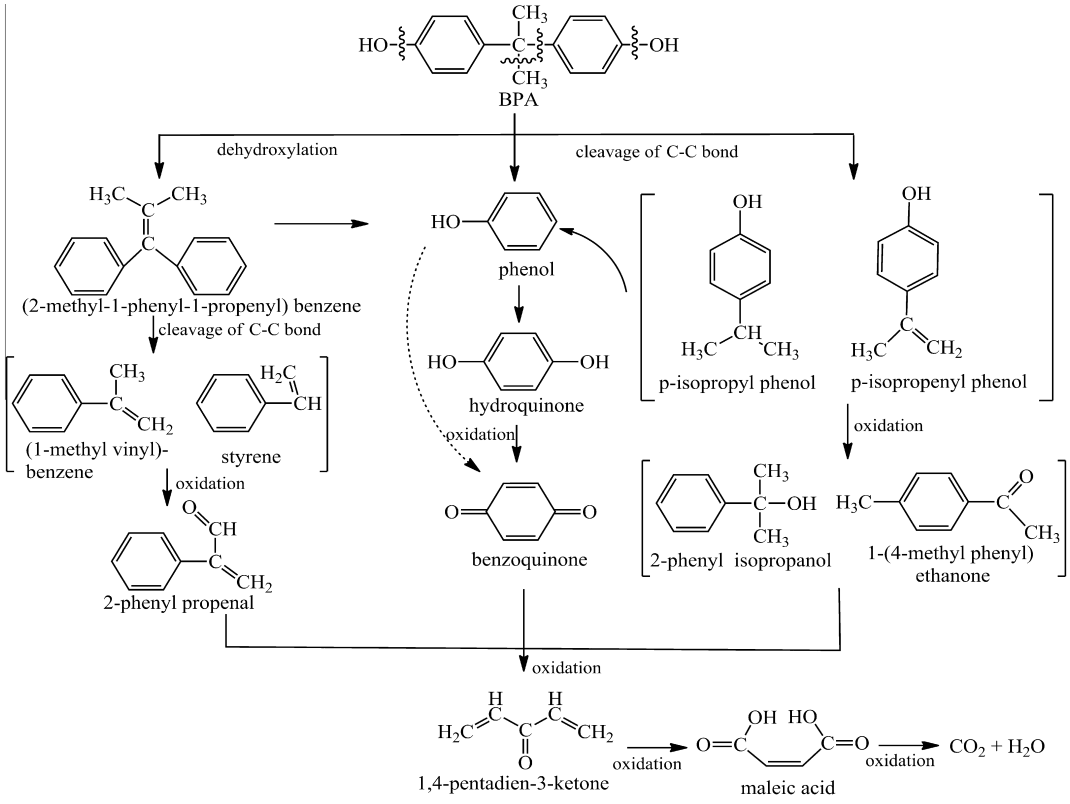

Fig. 4. The proposed BPA degradation pathway by ferrate(VI) oxidation.

E represent the normalized bioluminescence intensities of the control and the sample, and the results are shown in Fig. 5.

$$\text{Relative inhibitory rate} \quad (T\%) = \frac{E_0 - E}{E_0} \times 100\% \qquad (4)$$

While BPA degradation was rapidly completed within 10 min with almost total BPA removal achieved at ferrate(VI) dosages $\geqslant$ 35.0 μmol/L, toxicity exhibited a hysteresis effect. Fig. 5 shows that the relative inhibitory rate rapidly increased at the start of the oxidation reaction and peaked within the first 5 min. Subsequently, it decreased gradually but not completely stopped even when oxidation time was prolonged to 60 min. This hysteresis effect could be attributed to the generation of more toxic intermediates, especially those containing aromatic rings. UV scanning of samples within the range of 200–360 nm at different reaction times was conducted to explain the toxicity variation, as illustrated in Fig. S6. The absorbance of the treated water increased during the first 10 min and then decreased with reaction time, reflecting the generation of large amounts of intermediates. The variation of the absorbance in the typical benzenoid band, between 240 and 280 nm, indicated the existence of substituted functional groups in phenyl rings, such as conjugated double bonds, unsaturated carbonyl, etc. The generation of these intermediates might cause the increase of toxicity. In addition, it is seen from Table S1 that the identified reaction products included a series of aromatic intermediates, such as benzoquinone (LD50: 25 mg/kg;

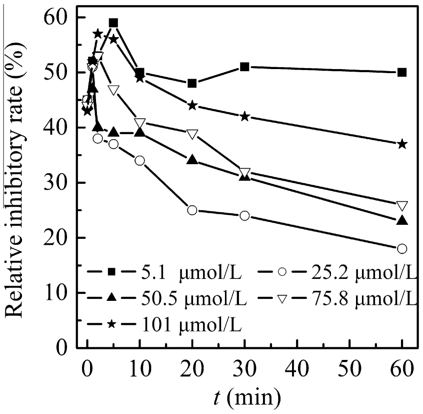

Fig. 5. Variations of toxicity during BPA oxidation process (Experimental conditions: $[BPA]_0$ = 4.4 μmol/L; initial pH = 7.0; temperature = 298 K.).

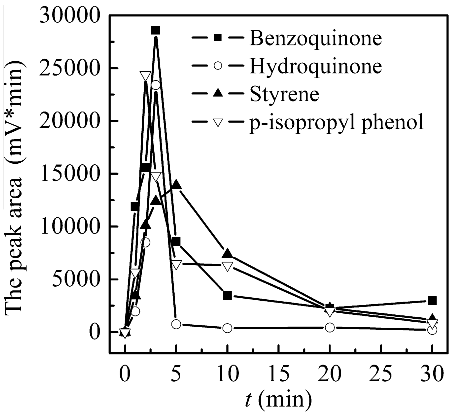

Fig. 6. Changes of the peak areas of intermediates during BPA oxidation process (Experimental conditions: BPA concentration = 4.4 μmol/L; the molar ratio [Fe(VI)]/[BPA] = 5.7; initial pH = 7.0; temperature = 298 K.).

oral dose, mouse), hydroquinone (245 mg/kg), styrene (316 mg/kg), p-isopropyl phenol (875 mg/kg) and 2-phenyl propenal (2220 mg/kg), which were all more toxic than BPA (2400 mg/kg) [45,14]. With further degradation and mineralization of these intermediates, lower toxicity and even nontoxic products were generated, which resulted in the decrease of toxicity. Thus, the variation in the intermediate content, shown in Fig. 6, which corresponds to the areas of the absorption peak for four of the more toxic intermediates, further explains the changes in toxicity. It is noteworthy from Fig. 6 that all of these intermediates achieved maximum absorbance at around 2–5 min and then decreased substantially up to 30 min, which clearly matched the variation of toxicity.

Fig. 5 also displayed that with increasing ferrate(VI) doses above 25.2 μmol/L, toxicity of the treated water increased gradually and was consistent with other studies and probably due to the over production of metallic parts [46]. The control experiments using the final reduction product of ferrate(VI), Fe(III), as shown in Fig. S7, indicated that Fe(III) was slightly detrimental to luminous bacteria with the increase of dosage.

4. Conclusion

The degradation of BPA by ferrate(VI) has been systematically investigated in this study and the major conclusions drawn from it are summarized as follows:

(1) BPA can be effectively degraded by ferrate(VI) oxidation. About 97.5% BPA removal was achieved at a ferrate(VI) to BPA molar ratio of 8.0 with an initial BPA concentration of 4.4 μmol/L, initial solution pH of 7.0, temperature of 298 K and contact time of 10 min.

(2) Reactions between ferrate(VI) and BPA obeyed pseudo-second order kinetics. Factors, including ferrate(VI) to BPA molar ratio, the initial pH and temperature, had significant effects on both of the BPA removal and the kinetic constants.

(3) Twelve intermediate compounds were identified, allowing the proposal of possible pathways for BPA degradation by ferrate(VI) oxidation. These pathways can be divided into two based on the type of the initial bond breaking. BPA undergoes a series of steps, including dehydroxylation, cleavage of C–C bond, elimination reactions and oxidation, to achieve the final mineralization.

(4) Toxicity tests conducted with *V. fischeri* delineated that compared with BPA degradation, toxicity reduction exhibits a hysteresis effect, which requires a long time to fall below the toxicity of BPA. An increase in toxicity during the initial stages of treatment was observed and attributed to the generation of more toxic intermediates, such as benzoquinone, hydroquinone, styrene, p-isopropyl phenol etc. Further degradation of these intermediates by ferrate(VI) resulted in the eventual gradual decrease in toxicity.

Acknowledgement

The authors would like to appreciate the supports of Urban Water Pollution Control and Management Generic Technology Integrated Program (2012ZX07206-002).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2014.09.071.

References

[1] T. Suzuki, Y. Nakagawa, I. Takano, K. Yaguchi, K. Yasuda, Environmental fate of bisphenol A and its biological metabolites in river water and their xeno-estrogenic activity, Environ. Sci. Technol. 38 (2004) 2389–2396.

[2] V.A. Santhi, N. Sakai, E.D. Ahmad, A.M. Mustafa, Occurrence of bisphenol A in surface water, drinking water and plasma from Malaysia with exposure assessment from consumption of drinking water, Sci. Total Environ. 427–428 (2012) 332–338.

[3] D.A. Crain, M. Eriksen, T. Iguchi, S. Jobling, H. Laufer, G.A. LeBlanc, L.J. Guillette, An ecological assessment of bisphenol-A: evidence from comparative biology, Reprod. Toxicol. 24 (2007) 225–239.

[4] T. Yamamoto, A. Yasuhara, H. Shiraishi, O. Nakasugi, Bisphenol A in hazardous waste landfill leachates, Chemosphere 42 (4) (2001) 415–418.

[5] V. Bindhumol, K.C. Chitra, P.P. Mathur, Bisphenol A induces reactive oxygen species generation in the liver of male rats, Toxicology 188 (2003) 117–124.

[6] I.A. Lang, T.S. Galloway, A. Scarlett, W.E. Henley, M. Depledge, R.B. Wallace, D. Melzer, Association of urinary bisphenol A concentration with medical disorders and laboratory abnormalities in adults, J. Am. Med. Assoc. 300 (2008) 1303–1310.

[7] S.C. Laws, S.A. Carey, J.M. Ferrell, G.J. Bodman, R.L. Cooper, Estrogenic activity of octylphenol, nonylphenol, bisphenol A and methoxychlor in rats, Toxicol. Sci. 54 (2000) 154–167.

[8] A. Hatef, S.M.H. Alavi, A. Abdulfatah, P. Fontaine, M. Rodina, O. Linhart, Adverse effects of bisphenol A on reproductive physiology in male goldfish at environmentally relevant concentrations, Ecotoxicol Environ. Saf. 76 (2012) 56–62.

[9] S. Saiyood, A.S. Vangnai, P. Thiravetyan, D. Inthorn, Bisphenol A removal by the Dracaena plant and the role of plant-associating bacteria, J. Hazard. Mater. 178 (1–3) (2010) 777–785.

[10] J. Li, B. Zhou, Y. Liu, Q. Yang, W. Cai, Influence of the coexisting contaminants on bisphenol A sorption and desorption in soil, J. Hazard. Mater. 151 (2–3) (2008) 389–393.

[11] I.B. Toledo, M.A.F. Garcia, J.R. Utrilla, C.M. Castilla, Bisphenol A removal from water by activated carbon. Effects of carbon characteristics and solution chemistry, Environ. Sci. Technol. 39 (2005) 6246–6250.

[12] R.A. Doong, S.M. Chang, C.W. Tsai, Enhanced photoactivity of Cu-deposited titanate nanotubes for removal of bisphenol A, Appl. Catal. B Environ. 129 (2013) 48–55.

[13] C.Z. Jia, Y.X. Wang, C.X. Zhang, Q.Y. Qin, S.Q. Kong, Photocatalytic degradation of bisphenol A in aqueous suspensions of titanium dioxide, Environ. Eng. Sci. 29 (7) (2012) 630–637.

[14] N. Lu, Y. Lu, F.Y. Liu, K. Zhao, $H_3PW_{12}O_{40}/TiO_2$ catalyst-induced photodegradation of bisphenol A (BPA): kinetics, toxicity and degradation pathways, Chemosphere 91 (2013) 1266–1272.

[15] D.Y.E. Kusvuran, Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry, Chem. Eng. J. 220 (2013) 6–14.

[16] F.J. Rivas, Á. Encinas, B. Acedo, F.J. Beltrán, Mineralization of bisphenol A by advanced oxidation processes, J. Chem. Technol. Biotechnol. 84 (4) (2009) 589–594.

[17] X.J. Yang, P.F. Tian, C.X. Zhang, Y.Q. Deng, J. Xu, J.L. Gong, Y.F. Han, Au/carbon as Fenton-like catalysts for the oxidative degradation of bisphenol A, Appl. Catal. B Environ. 134–135 (2013) 145–152.

[18] R.J. West, P.A. Goodwin, Evaluation of ready biodegradability of bisphenol-A using the OECD 301F: manometric respirometry test, Dow Company Report. (1997).

[19] J. Lee, B.C. Lee, J.S. Ra, J. Cho, I.S. Kim, N.I. Chang, H.K. Kim, S.D. Kim, Comparison of the removal efficiency of endocrine disrupting compounds in pilot scale sewage treatment processes, Chemosphere 71 (2008) 1572–1592.

[20] K. Lin, W.P. Liu, J. Gan, Oxidative removal of bisphenol A by manganese dioxide: efficacy, products, and pathways, Environ. Sci. Technol. 43 (2009) 3860–3864.

[21] J.J. Yang, G. Wen, J. Zhao, X.L. Shao, J. Ma, Oxidation of bisphenol A by permanganate: reaction kinetics and removal of estrogenic activity, Water Sci. Technol. 67 (2013) 1867–1871.

[22] C. Wang, L. Zhu, M. Wei, P. Chen, G. Shan, Photolytic reaction mechanism and impacts of coexisting substances on photodegradation of bisphenol A by Bi_2WO_6 in water, Water Res. 46 (3) (2012) 845–853.

[23] M. Moslemi, S.H. Davies, S.J. Masten, Empirical modeling of bromate formation during drinking water treatment using hybrid ozonation membrane filtration, Desalination 292 (2012) 113–118.

[24] R.M.R. Keykavoos, H. Ma, P. Jones, J. Soltan, Mineralization of bisphenol A by catalytic ozonation over alumina, Sep. Purif. Technol. 107 (2013) 310–317.

[25] J.Q. Jiang, B. Lloyd, Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Res. 36 (6) (2002) 1397–1408.

[26] G. Erzsébet, F. Tamás, B. Katalin, V. Csaba, V. Balázs, Z. Gyula, Ferrate treatment for inactivation of bacterial community in municipal secondary effluent, Bioresour. Technol. 107 (2012) 116–121.

[27] G.A.K. Anquandah, V.K. Sharma, V.R. Panditi, P.R. Gardinali, H. Kim, M.A. Oturan, Ferrate(VI) oxidation of propranolol: kinetics and products, Chemosphere 91 (1) (2013) 105–109.

[28] B. Yang, G.G. Ying, J.L. Zhao, S. Liu, L.J. Zhou, F. Chen, Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care

products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents, Water Res. 46 (7) (2012) 2194–2204.

[29] B. Yang, G.G. Ying, Oxidation of benzophenone-3 during water treatment with ferrate(VI), Water Res. 47 (7) (2013) 2458–2466.

[30] N.J.D. Graham, T.T. Khoi, J.Q. Jiang, Oxidation and coagulation of humic substances by potassium ferrate, Water Sci. Technol. 62 (4) (2010) 929.

[31] Y.Y. Eng, V.K. Sharma, A.K. Ray, Ferrate(VI): green chemistry oxidant for degradation of cationic surfactant, Chemosphere 63 (10) (2006) 1785–1790.

[32] V.K. Sharma, Oxidation of inorganic contaminants by ferrates (VI, V, and IV)-kinetics and mechanisms: a review, J. Environ. Manage. 92 (4) (2011) 1051–1073.

[33] V.K. Sharma, Potassium ferrate(VI): an environmentally friendly oxidant, Adv. Environ. Res. 6 (2) (2002) 143–156.

[34] C. Li, X.Z. Li, N. Graham, A study of the preparation and reactivity of potassium ferrate, Chemosphere 61 (4) (2005) 537–543.

[35] C. Li, X.Z. Li, N. Graham, N.Y. Gao, The aqueous degradation of bisphenol A and steroid estrogens by ferrate, Water Res. 42 (1–2) (2008) 109–120.

[36] P. Zhang, G. Zhang, J. Dong, M. Fan, G. Zeng, Bisphenol A oxidative removal by ferrate (Fe(VI)) under a weak acidic condition, Sep. Purif. Technol. 84 (2012) 46–51.

[37] J.M. Schroyer, L.T. Ockerman, Stability of the ferrate(VI) ion in aqueous solution, Anal. Chem. 23 (9) (1951) 1312–1314.

[38] Water quality, Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test)-Part 2: Method using liquid-dried bacteria; ISO 11348-2; International Organization for Standardization: Geneva, Switzerland, 2007.

[39] Q. Han, H. Wang, W. Dong, T. Liu, Y. Yin, Suppression of bromate formation in ozonation process by using ferrate(VI): batch study, Chem. Eng. J. 236 (2014) 110–120.

[40] W.F. Wagner, J.R. Gump, E.N. Hart, Factors affecting the stability of aqueous potassium ferrate(VI) solutions, Anal. Chem. 24 (9) (1952) 1497–1498.

[41] Q. Han, W.Y. Dong, H.J. Wang, T.Z. Liu, F.Y. Sun, Y.L. Ying, X.L. Yan, Effects of coexisting anions on decolorization of azo dye X-3B by ferrate(VI) and a comparative study between ferrate(VI) and potassium permanganate, Sep. Purif. Technol. 108 (2013) 74–82.

[42] V.K. Sharma, Oxidation of inorganic compounds by ferrate(VI) and ferrate(V): one-electron and two-electron transfer steps, Environ. Sci. Technol. 44 (2010) 5148–5152.

[43] G.A.K. Anquandah, V.K. Sharma, D.A. Knight, S.R. Batchu, P.R. Gardinali, Oxidation of trimethoprim by ferrate(VI): kinetics, products, and antibacterial activity, Environ. Sci. Technol. 45 (2011) 10575–10581.

[44] G.R. Xu, Y.P. Zhang, G.B. Li, Degradation of azo dye active brilliant red X-3B by composite ferrate solution, J. Hazard. Mater. 161 (2009) 1299–1305.

[45] ChemIDplus Adv. Specialized Information Services. <http://chem.sis.nlm.nih.gov/chemidplus/>.

[46] M. Bistan, T.T.A. Pintar, Catalytic and photocatalytic oxidation of aqueous bisphenol A solutions: removal, toxicity, and estrogenicity, Ind. Eng. Chem. Res. 51 (26) (2012) 8826–8834.