Ferrate(VI) oxidation of tetrabromobisphenol A in comparison with bisphenol A

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A B S T R A C T
Ferrate(VI) (Fe(VI)) oxidative removal of various organic micropollutants mainly depends on the reactivity of Fe(VI) to target micropollutants and coexisting constituents present in source water. This study evaluated the potential of Fe(VI) oxidation of the brominated flame retardant tetrabromobisphenol A (TBBPA) by using reaction kinetics, products identification and toxicity evaluation, and investigated the influencing effects of humic acid and clay particles on Fe(VI) removal of TBBPA in comparison with bisphenol A (BPA). The obtained apparent second-order rate constants ($k_{app}$) for Fe(VI) reaction with TBBPA ranged from $7.9(\pm0.3) \times 10^3 \text{M}^{-1}\text{s}^{-1}$ to $3.3(\pm0.1) \times 10^4 \text{M}^{-1}\text{s}^{-1}$ with the half-life ($t_{1/2}$) ranging from 1.7 s to 419.3 s at pH 7.0-10 for an Fe(VI) concentration of 10 mg L$^{-1}$. Easier oxidation by Fe(VI) was observed for TBBPA than for BPA. Fe(VI) can destroy and transform the TBBPA molecule through $\beta$-scission reaction, yielding the chemical species of low bromine-substituted products. More importantly, the oxidation of TBBPA by Fe(VI) led to the loss of its multiple hormonal activities (androgenic, antiestrogenic and antiandrogenic activities). The organic component humic acid decreased the TBBPA and BPA reactions with Fe(VI), while the inorganic component montmorillonite had no effect on their removal within the tested concentrations. Increasing the Fe(VI) dosage can reduce the effects of soluble organic matter and clay particles present in source waters on the degradation process, leading to the complete removal of target micropollutants.

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1. Introduction

Ferrate(VI) (Fe(VI)) is an emerging environmentally friendly water treatment chemical due to its dual functions as an oxidant and a subsequent coagulant/precipitant as ferric hydroxide (Jiang and Lloyd, 2002; Sharma, 2002, 2011; Lee et al., 2004; Sharma et al., 2011). Fe(VI) can achieve a complete removal of various emerging organic micropollutants during water and wastewater treatment (Lee et al., 2009; Sharma, 2013). The removal efficiency mainly depends on the reactivity of Fe(VI) to target micropollutants and coexisting constituents present in source water (Lee and von Gunten, 2010). Fe(VI) has been known to react with electron-rich organic moieties, such as phenols, anilines, amines, and olefins through electrophilic oxidation mechanism (Hu et al., 2009; Lee et al., 2009; Yang et al., 2012; Sharma, 2010, 2013). The corresponding second-order reaction rate constants range from $1 \times 10^3$ to $10^4 \text{M}^{-1}\text{s}^{-1}$ in aqueous solution (Lee et al., 2009; Sharma, 2013). However, the coexisting constituents present
in source water are also responsible for a rapid Fe(VI) consumption, which determine its ability to remove organic micropollutants. For example, Zhang et al. (2012) have shown that humic acid and SiO$_2$ notably reduced the bisphenol A (BPA) removal, tert-butanol slightly decreased the BPA removal, and the existence of HCO$_3$ slightly enhanced the BPA removal by Fe(VI). Yang and Ying (2013) have shown that humic acid and SiO$_2$ removal by Fe(VI) treatment. Yang and Ying (2013) have shown that Fe(VI) had no effects on benzophenone-3 removal, while Cu$^{2+}$ enhanced the removal. However, NH$_4^+$, NO$_3^-$, Fe$^{3+}$, and Fe$^{2+}$ had no effects on benzophenone-3 removal within the tested concentrations. Lee and von Gunten (2010) also found that ammonia, nitrite, and bromide have little effects on the 17α-ethinylestradiol removal during Fe(VI) treatment of a secondary wastewater effluent at pH 8. Thus, the coexisting constituents present in source water play an important role in the removal of organic micropollutants by Fe(VI) treatment.

Suspended particles with a particle size ranging from 1 mm down to 1 µm are also an important coexisting constituent ubiquitous in surface water and wastewater. Suspended particles are an important carrier for some pollutants and pathogens. The smaller the particle size, the greater the total surface area per unit mass of particle, and resulting in the higher pollutant load that is likely to be carried (Gregory, 2006; Templeton et al., 2006). For example, the brominated flame retardant tetrabromobisphenol A (TBBPA) was detected in quantifiable levels in 15 of the 17 wastewater treatment plants’ sewage sludge samples, in a concentration range of not detected (nd)–472 ng/g dw (Gorga et al., 2013). Thus, activated sludge-associated TBBPA may still penetrate to the disinfection stage of tertiary treatment under certain circumstances. The detection of dissolved and particle-bound taste and odor compounds such as geosmin, b-ionone, 2-isobutyl-3-methoxy-4-ethyl-5-isoxazolinen, 2-isopropyl-3-methoxypyrazine and 2-methyl-isoborneol in the Swiss lake waters were found to affect the oxidation pretreatment for source water in the drinking water treatment process (Peter et al., 2009). Therefore, it is necessary to investigate the effects of suspended particles on the fate of emerging organic micropollutants during the oxidation treatment processes.

In this study, TBBPA was selected as the target compound as it is the most widely used brominated flame retardant in the world and has also been widely detected in surface water (Covaci et al., 2009; He et al., 2013). TBBPA is synthesized from BPA through bromination reaction, so they have very similar molecular structures and functional groups. Compared with BPA, TBBPA is characterized by a low to moderate water solubility, and a moderately high octanol/water partition coefficient which is dependent on ionization state at different pH solutions (Kuramochi et al., 2008). When released into the environment, TBBPA will have a tendency to partition into sediment and soil, to bind to suspended particles and to the lipid fraction of biota (He et al., 2019). Besides, humic acid (HA) and montmorillonite (MMT) are often used as the model organic and inorganic suspended particles in experiments (Templeton et al., 2008). Therefore, the objective of this study was to assess the potential of Fe(VI) oxidation of TBBPA by using reaction kinetics, products identification and toxicity evaluation. The reactivity of TBBPA with Fe(VI) was simultaneously compared with BPA, which has been in-depth researched by Lee et al. (2005a) and Li et al. (2008). Besides, the influences of suspended particles such as HA and MMT on Fe(VI) removal of TBBPA and BPA were investigated both in phosphate buffer solutions and natural waters.

2. Experimental section

2.1. Standards and materials

Chemical standards tetrabromobisphenol A (TBBPA, 99%) and bisphenol A (BPA, 99%) were purchased from Dr. Ehrenstorfer GmbH. Diammonium 2,2’-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS, 98%), and humic acid (HA) were purchased from Sigma–Aldrich; while montmorillonite K 10 (MMT) was from Acros Organics. Potassium ferrate (Fe(VI), >95%) was prepared by wet chemical synthesis (Delaude and Laszlo, 1996). Buffer chemicals and all other reagents used in the experiments were of analytical grade. All reaction solutions were prepared with Milli-Q water (>18 MΩ cm) from a Millipore Water Purification System. The stock solutions of Fe(VI) (0.5–1.0 mM) were freshly prepared by dissolving solid Fe(VI) in Milli-Q water (pH ≈ 9.2). The Fe(VI) stock solution was quickly filtered through a 0.45 µm hydrophilic polyethersulfone (PES) syringe filter (Shanghai ANPEL, China) and then standardized spectrophotometrically at 510 nm ($ε$ = 1150 M$^{-1}$ cm$^{-1}$). The stock solutions of TBBPA and BPA were prepared in methanol at the concentration of 100 mg L$^{-1}$. The stock solutions of HA and MMT were prepared in 10 mM phosphate buffer solutions (pH = 8.0) with their concentrations of 500 mg L$^{-1}$ and 1000 mg L$^{-1}$ respectively.

Surface water used in the experiments was sampled from the Zhujiang River in Guangzhou, South China. The initial pH, UV$_{254}$, UV$_{400}$, total organic carbon (TOC), conductivity, alkalinity and turbidity of the natural water sample were 6.98, 0.093, 0.016, 3.43 mg L$^{-1}$, 429 µS cm$^{-1}$, 3.15 mM (HCO$_3$) and 7.0 NTU, respectively. Part of the above water sample was filtered through a 0.45 µm cellulose-nitrate membrane to remove the suspended particles. The dissolved organic carbon (DOC) and turbidity of the filtered water sample was 3.04 mg L$^{-1}$ and 5.4 NTU. All the water samples were used within 24 h. Besides, the trace target pollutants in surface water did not interfere with the experiments because of the high spiked concentrations for TBBPA and BPA (2 µM).

2.2. Removal experiments of TBBPA and BPA at various Fe(VI) doses

The removal experiments of TBBPA and BPA with various Fe(VI) doses were performed in 10 mM phosphate buffer solutions (pH 7.0 and 8.0) and room temperature (24 ± 1 °C). In a series of 25 mL amber volumetric flasks, a target compound (2 µM) was firstly spiked into the buffer solution, and then the filtered and standardized stock solution of Fe(VI) was added or not added to yield various concentrations of 0–30 µM. The mixed solutions were shaken in order to have sufficient reaction. After 3 h reaction in the darkness, 1 mL of the reaction solution was sampled and quenched with 0.1 mL of a
The residual concentrations for TBBPA and BPA were then determined by the high performance liquid chromatography (HPLC) which was described later in Section 2.4. All removal experiments were performed in duplicate.

The effect of selected particles on Fe(VI) oxidation of TBBPA and BPA was evaluated by dosing various concentrations of HA or MMT (0–40 mg L\(^{-1}\)) to the reaction solutions used in the above removal experiments. When HA and MMT were spiked into the buffer solutions containing the target compounds of TBBPA or BPA, the experiments were further divided into two treatment groups: one followed with immediate addition of the Fe(VI) stock solutions to oxidation; the other with mixing of the solutions in a shaking incubator (SKY-211BG, 150 r min\(^{-1}\), 24 ± 1 °C) for 12 h, and followed with addition of Fe(VI) stock solutions to reaction. The mixing process by the shaking incubator was aimed to achieve the interaction of the selected particles with the target compounds as occurred in the actual water environment. After 3 h reaction in the darkness, the residual concentrations of TBBPA and BPA were determined by HPLC. The pH variation of all the experiments was found below 0.05 units.

2.3. Kinetic experiments of TBBPA oxidation by Fe(VI)

The kinetics of TBBPA oxidation by Fe(VI) were studied under pseudo-first-order conditions in the pH range of 7.0–10 (10 mM phosphate buffer solutions). In the 150 mL reaction mixture solutions, the initial concentration of Fe(VI) was 25 μM, and the concentration for TBBPA was 2 μM. The experiments were performed in a 200 mL beaker equipped with a magnetic stirrer (700 r min\(^{-1}\)) at the room temperature (24 ± 1 °C). The reactions were initiated by adding an aliquot of Fe(VI) stock solution to the suspensions containing TBBPA under rapid mixing. At certain time intervals, 5 mL of the reaction solution was sampled for the measurement of residual Fe(VI) concentrations using a ABTS method at 415 nm (Lee et al., 2005b), and 1 mL of the reaction solution was also sampled and quenched with a thiosulfate solution (5 mM, 0.1 mL) to measure residual concentrations of TBBPA by HPLC, then the apparent second-order rate constants (\(k_{\text{app}}\)) of Fe(VI) reaction with TBBPA were calculated by plotting the natural logarithm of the TBBPA concentrations with the Fe(VI) exposure (Yang et al., 2011a; Yang and Ying, 2013). All kinetic experiments were carried out in duplicate and the pH variation was below 0.1 units. Besides, the 150 mL kinetic reaction solutions were also quenched with 5 mL thiosulfate solution (5 mM) at a setting reaction time (0, 5, 10, 30, 50, 70 and 90 s) to identify the reaction products and evaluate the changes of hormonal activities.

Kinetic reaction experiments were also performed in natural water samples with and without filtration at pH 8.0 (20 mM borate buffer) to assess the effect of suspended particles in natural waters on Fe(VI) removal of TBBPA and BPA. Nevertheless, the difference with the above kinetic process was that the target compound was firstly spiked into the river water samples with and without filtration. Then the solutions were mixed in a shaking incubator for 12 h to have sufficient contact, and followed by addition of Fe(VI) to start the kinetic reaction. Preliminary experiments showed that the concentrations of the target compounds did not change during mixing (Data not shown).

2.4. Chemical analysis

The water samples were characterized as follows. The UV absorbance was measured with a Helios Alpha spectrophotometer (Thermo Spectronic, Cambridge, UK). The conductivity and pH values were determined using a Thermo Orion 5 star pH meter (Thermo Fisher Scientific, USA), which was calibrated using standard reagents (1314 μS cm\(^{-1}\) and pH 4.0, 7.0, and 10.0, Thermo China). TOC and DOC were measured using a Shimadzu TOC-V and TNM-1 analyzer (Shimadzu Scientific Instruments, Columbia, MD) (Yang et al., 2012; Yang and Ying, 2013). Alkalinity and turbidity were measured by standardized titrimetric analysis and spectrophotometric method respectively.

For the determination of the target compounds TBBPA and BPA, the quenched BPA reaction solutions were directly analyzed by HPLC, while TBBPA in the quenched reaction solutions was analyzed after extraction. Briefly, the quenched TBBPA reaction solutions were firstly extracted with dichloromethane (3 × 0.3 mL), then the extracts were concentrated under a gentle nitrogen, and re-dissolved in 0.5 mL acetonitrile for HPLC analysis. The instrument used for analysis of TBBPA and BPA was an Agilent 1200 series HPLC equipped with a diode array detector (DAD) and a fluorescence detector (FLD). Chromatographic separation was performed on a Zorbax Eclipse XDB-C18 column (150 × 4.6 mm, 5 μm). The column temperature was set at 30 °C. The mobile phase consisted of acetonitrile and Milli-Q water (80:20 for TBBPA and 60:40 for BPA) at a flow rate of 1 mL min\(^{-1}\). The injection volume was 100 μL. The UV wavelength for TBBPA detection was 210 nm. The excitation wavelength and emission wavelength of FLD for BPA detection was 230 nm and 305 nm respectively. The limit of quantitation was 50 μg L\(^{-1}\) for TBBPA, and 10 μg L\(^{-1}\) for BPA. The recovery of extractions ranged between 80.4% and 91.5% independent of the solution pH values (7.0–10) (Fig. S1 and Fig. S2).

For reaction products identification and hormonal activities transformation, 150 mL quenched reaction solutions were adjusted to pH 2 with 1 M HCl. Reaction products were extracted by vigorous shaking with 3 × 20 mL dichloromethane. Each extract was passed through an anhydrous Na\(_2\)SO\(_4\) column to remove water. The extract was concentrated under a rotary evaporator and re-dissolved in 1 mL methanol, then filtered through a 0.22 μm nylon syringe filter into 2 mL amber glass vial which was kept at −20 °C until analysis. The recovery rate for the TBBPA was about 73–82% during this extraction process.

The reaction products of TBBPA were analyzed by rapid resolution liquid chromatography–tandem mass spectrometry (RRLC–MS/MS). The RRLC-MS/MS instrument used in this analysis was an Agilent 1200 series RRLC connected to an Agilent 6460 triple quadrupole mass spectrometer, with an Agilent Zorbax SB-C18 column (100 × 3 mm, 1.8 μm). The mobile phase consisted of (A) Milli-Q water and (B) methanol, which was run at a flow rate of 0.3 mL min\(^{-1}\). The gradient was programmed as follows: 30% B at 0 min, increased to 80% at 25 min, kept in 80% B to 45 min, and the post time was 5 min. The column
Second-order rate constants for the reaction of Fe(VI) with TBBPA, BPA and 4-bromophenol as a function of pH (7.0–10) at the room temperature (24 ± °C). Kinetic data for BPA and 4-bromophenol are calculated from Lee et al. (2005a, b).

Fig. 1 – Apparent second-order rate constants and associated model simulation for the reaction of TBBPA, BPA and 4-bromophenol with Fe(VI) as a function of pH (7.0–10) at the room temperature (24 ± °C). Kinetic data for BPA and 4-bromophenol are calculated from Lee et al. (2005a, b).

The reaction temperature was set at 40 °C. The mass spectrometer was operated under negative electrospray ionization with MS² Scan mode and Product Ion mode. MS² Scan mode had a fragmentor voltage of 135 V with mass scan range of 50–1200 amu. Product Ion mode had a fragmentor voltage of 135 V and collision energy of 24 V with mass scan range of 50–800 amu. The ionization source conditions were listed as follows: the drying gas flow 3 mL min⁻¹ at 350 °C, sheath gas flow 12 mL min⁻¹ at 350 °C and the nebulizer pressure 40 psi.

2.5. Bioassays

Multiple hormonal activities (estrogenic and androgenic activities, antiestrogenic and antiandrogenic activities) were measured for the extracts of reaction solutions during Fe(VI) oxidation of TBBPA by using our previously developed in vitro recombinant yeast bioassays (Zhao et al., 2011). In brief, the yeast with human estrogen receptor (hER-α) gene integrated into expression plasmid was used for yeast estrogen screen (YES) and yeast antiestrogen screen (YAES) bioassays, and the yeast with human androgen receptor (hAR-α) gene integrated into expression plasmid was used for yeast androgen screen (YAS) and yeast antiandrogen screen (YAAS) bioassays. Standard chemicals 17β-estradiol, dihydrotestosterone, tamoxifen and flutamide were used as the positive control for YES, YAS, YAES and YAAS (Fig. S3). The potency of hormonal activity of a sample was calculated from the ratio of median effective concentration (EC50) of the sample and the EC50 of the corresponding positive control with a four-parameter log-logistic model using SigmaPlot 10.0 software. The levels of these hormonal activities were then expressed as 17β-estradiol equivalent (EEQ), dihydrotestosterone equivalent (DEQ), tamoxifen equivalent (TEQ), and flutamide equivalent (FEQ), respectively.

3. Results and discussion

3.1. Kinetics for the reaction of TBBPA with Fe(VI)

Second-order reaction rate law (Eq. (1)) was used to describe the Fe(VI) oxidation of TBBPA in the phosphate buffer solutions (Lee et al., 2005a, 2009; Yang et al., 2011a; Yang and Ying, 2013). The second-order rate constants (k_app) were determined under pseudo-first-order conditions with Fe(VI) concentrations in excess to TBBPA and calculated by using Eq. (2). The values of k_app for the reaction of Fe(VI) with TBBPA as a function of pH (7.0–10) are presented in Fig. 1. The k_app of the reaction decreased with increasing pH values. These pH-dependent variations in k_app could be quantitatively modeled by species-specific reactions between Fe(VI) species and TBBPA species by using Eq. (3), which was programmed by using the least-squares nonlinear regressions in the software SigmaPlot 10.0. Consequently, the species-specific second-order rate constants (k) of the reaction between HFeOt and the neutral or the dissociated TBBPA are listed in Table 1 and shown in Fig. 1 (R² = 0.99). Kinetic data for BPA and 4-bromophenol were calculated from Lee et al. (2005a) as a comparison to TBBPA (Fig. 1, Table 1).

- \[ \text{d}[\text{TBBPA}] / \text{dt} = k_{\text{app}}[\text{Fe(VI)}] \cdot [\text{TBBPA}] \] (1)

\[ \text{ln}([\text{TBBPA}] / \text{[TBBPA]}_0) = -k_{\text{app}} \int_0^t [\text{Fe(VI)}] \text{dt} \] (2)

\[ k_{\text{app}}[\text{Fe(VI)}] \cdot [\text{TBBPA}] = \sum_{i=1}^{2} \sum_{j=1,2,3} k_i \cdot x_i \cdot [\text{Fe(VI)}] \cdot [\text{TBBPA}] \] (3)

The k of the reaction between HFeOt and the dissociated TBBPA, BPA and 4-bromophenol was greater than the reaction.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKₐ</th>
<th>Reacting species</th>
<th>k₁₂/k₁₃</th>
<th>k(Ph 7)</th>
<th>k(Ph 8)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrabromobisphenol A(TBBPA)</td>
<td>7.5</td>
<td>HFeO⁺ + XH₂⁻</td>
<td>1.1(±0.1) × 10⁴</td>
<td>7.9 × 10³</td>
<td>2.6 × 10³</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>HFeO⁺ + XH⁻</td>
<td>1.8(±0.1) × 10⁴</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HFeO₄⁻ + X⁻</td>
<td>1.9(±0.07) × 10⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bisphenol A(BPA)</td>
<td>9.6</td>
<td>HFeO₃⁻ + XH₂⁻</td>
<td>8.2(±0.1) × 10⁷</td>
<td>6.4 × 10²</td>
<td>4.1 × 10²</td>
<td>Lee et al. (2005a, b)</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>HFeO₃⁻ + XH⁻</td>
<td>8.0(±0.2) × 10⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HFeO₄⁻ + X⁻</td>
<td>2.6(±0.2) × 10⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-bromophenol</td>
<td>9.34</td>
<td>HFeO₄⁻ + XH⁻</td>
<td>8.0(±0.4) × 10⁷</td>
<td>8.6 × 10³</td>
<td>8.7 × 10³</td>
<td>Lee et al. (2005a, b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HFeO₄⁻ + X⁻</td>
<td>1.2(±0.04) × 10⁸</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
between HFeO₄⁻ and the neutral compounds (Table 1), which indicates the reaction between HFeO₄⁻ and the dissociated target compounds controls the overall reaction. The obtained k value for the reaction of HFeO₄⁻ with each of TBBPA's acid-base species was $1.1(±0.1) \times 10^4$ M⁻¹ s⁻¹ ($k_{11}$), $1.8(±0.1) \times 10^4$ M⁻¹ s⁻¹ ($k_{12}$) and $1.9(±0.07) \times 10^4$ M⁻¹ s⁻¹ ($k_{13}$) respectively. The $k_{11}$ and $k_{13}$ of dissociated TBBPA with HFeO₄⁻ are lower than the ones of BPA with HFeO₄⁻. Since an aromatic ring is substituted with halogens, the reactivity of the substituent decreases due to a decreased electron density of the ring. However, the $k_{12}$ of neutral TBBPA with HFeO₄⁻ is higher than that of BPA, this may be due to the oxidation mechanism which is different from direct attack at the ring. Thus, the $k_{	ext{app}}$ value of Fe(VI) reaction with TBBPA was greater than that of the BPA in the pH range of 7.0–9.0, but TBBPA had a less $k_{	ext{app}}$ value than the BPA in the pH range of 9.0–10. Moreover, the $k_{	ext{app}}$ values for both TBBPA and BPA reaction with Fe(VI) are greater than that of the 4-bromophenol, indicating that the reactivity of these compounds with Fe(VI) can be enhanced by the introduction of substituent groups into benzene ring.

TBBPA showed a more appreciable reactivity with Fe(VI). The obtained $k_{	ext{app}}$ for Fe(VI) reaction with TBBPA ranged from $7.9(±0.3) \times 10^3$ M⁻¹ s⁻¹ to $3.3(±0.1) \times 10^4$ M⁻¹ s⁻¹ with the half-life ($t_{1/2}$) ranging from 1.7 s to 419.3 s at pH 7.0–10 for an Fe(VI) concentration of 10 mg L⁻¹ (Fig. 1). The $t_{1/2}$ for Fe(VI) reaction with TBBPA (1.7 s, pH 7.0) is magnitude lower than that of the permanganate (29.8 s, pH 7.0) (Pang et al., 2014), manganese dioxide (1.79 min, pH 4.5) (Lin et al., 2009) and photochemical life ($t_{1/2}$) ranging from 1.7 s to 419.3 s at pH 7.0

Experimental conditions: pH = 7.1 and 8.0, T = 24 ± 1 °C, [TBBPA/BPA] = 2.0 μM, and contact time 3 h.

### 3.2. Removal of TBBPA and BPA by Fe(VI)

Removal of TBBPA and BPA at various Fe(VI) doses was investigated in pH 7.0 and 8.0 phosphate buffer solutions. Fig. 2 shows the relative changes in the residual concentrations of TBBPA and BPA as a function of the Fe(VI) dose (0–30 μM). The residual concentrations of TBBPA and BPA decreased with the increasing dose of Fe(VI). The dosed amount of Fe(VI) for oxidation of TBBPA was much lower than that used for BPA either at pH 7.0 or 8.0. For example, 12.5 μM of Fe(VI) can completely remove TBBPA in the pH 7.0 buffer solution, but more than 30 μM of Fe(VI) was needed for BPA removal, which illustrated the easier oxidation of TBBPA molecule than BPA by Fe(VI). This may be because TBBPA had a higher $k_{	ext{app}}$ value in pH 7.0 and 8.0 than that of BPA (Table 1). Besides, the dosed amounts of Fe(VI) for removal of TBBPA and BPA were higher at pH 7.0 more than at pH 8.0 (Fig. 2). For example, 7.5 μM Fe(VI) was required to completely remove TBBPA at pH 8.0, but 12.5 μM Fe(VI) was required at pH 7.0. This can be explained by the higher stability of the Fe(VI) in the phosphate solution at pH 8.0, which resulted in a higher Fe(VI) exposure, and a lower Fe(VI) dosage for the removal of TBBPA and BPA in pH 8.0.

### 3.3. Oxidation products

The oxidation products of Fe(VI) reaction with TBBPA at different sampling times (0–90 s) were tentatively identified by using RRLC-MS/MS (Table 2, Fig. S4 and Table S1). Table 2 lists the primary molecular ions, product ions, relative abundances and proposed structures of the 2 products (A and B) and parent compound TBBPA. The two products A and B had a molecular ion peak at m/z of 308.9 and 322.9 and product ions 290.9, 80.9 and 78.8 (Fig. S6), which were considered as 4-(2-hydroxyisopropyl)-2,6-dibromophenol and 4-(2-methoxylisopropyl)-2,6-dibromophenol, respectively (Feng et al., 2013; Pang et al., 2014). But it should be noted that products A and B were also presented at trace levels in the initial reaction solution (0 s). During the Fe(VI) oxidation process, A and B gradually increased and then decreased (Fig. S5). Thus, A and B could be considered as the reaction products. Besides, another 10 peaks were also presented in the chromatograms which have characteristic bromine isotope ions (Fig. S4, Table S1), corresponding to dibromo-, tribromo- and tetrabromo- compounds, but no meaningful chemical structures were proposed. These 10 peaks may be the oxidation products of TBBPA or impurities and their potential oxidation products. Consequently, the detection of a large number of low bromine-substituted products that are important for further Fe(VI) oxidative degradation.

The oxidation products of BPA by Fe(VI) have been studied by Li et al. (2008) using LC-MS/MS and GC-MS/MS techniques. In the previous study, nine products were identified as 4-isopropanolphenol, p-isopropanolphenol, p-isopropenylphenol, oxalic acid, propanedioic acid, 4-isopropyl-cyclohexa-2,5-dienone, p-hydroxyacetophenone, styrene, and (1-phenyl-1-butetyl)benzene. Because the electron donating hydroxyl group increases the electron density of each aromatic ring, causing the bond connecting with two aromatic rings to be more vulnerable. So, the initial oxidation step for BPA by Fe(VI) was considered to be the bond cleavage of the two phenyl groups by Fe(VI) attack, yielding p-isopropanolphenol, phenol, 4-isopropanolphenol, and (1-phenyl-1-butenyl)benzene. These intermediate products can be further degraded by Fe(VI) oxidation, producing styrene, p-hydroxyacetophenone, 4-isopropyl-cyclohexa-2,5-dienone, propanedioic acid, and
oxalic acid. Although the parent compound BPA could be completely removed within less than 5 min, the oxidation products would still persist in the final reaction solutions (Li et al., 2008).

On the basis of the kinetic information, products identification and the mechanism of Fe(VI) reaction with BPA, a plausible reaction scheme for Fe(VI) oxidation of TBBPA was proposed in Fig. 3. Initially, Fe(VI) oxidizes the phenol moiety of TBBPA by one electron transfer generating a phenoxyl radical and Fe(V) as the first step (Rush et al., 1995; Huang et al., 2001; Li et al., 2008; Yang et al., 2011b). The phenoxy radical is stabilized by electron resonance within the phenol ring and forms radical R1, which supported by the calculation of charge distribution and spin densities via molecular modeling (Lin et al., 2009; Feng et al., 2013; Pang et al., 2014). Radical R1 undergoes β-scission (cleavage between one of the benzene rings and the isopropyl group) and releases a new radical 2,6-dibromo-4-isopropylphenol carbocation (R2). R2 may react with water to form the product A, or substitution with the methanol cosolvent (stock solution was prepared in methanol) to yield the product B (Feng et al., 2013). The pathway of product A has been extensively reported in the oxidative degradation of TBBPA by permanganate, manganese dioxide, UV/Fenton, and UV irradiation (Eriksson et al., 2004; Lin et al., 2009; Zhong et al., 2012; Pang et al., 2014). For product B, this is probably not valid in a potential real water treatment. In addition, radicals R1 and R2 may be transformed to other low bromine-substituted products through further Fe(VI) oxidation.

### Table 2 – Main fragment ions (m/z) of TBBPA and products in total ion chromatogram identified by means of RRLC-ESI-MS/MS in negative mode.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
<th>m/z values (&lt;sup&gt;a&lt;/sup&gt;) (Relative abundance)</th>
<th>MS&lt;sup&gt;2&lt;/sup&gt; scan</th>
<th>Proposed structure&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.454</td>
<td>306.8(62.5%)/308.9 (100%)/310.9(62.5%)</td>
<td>308.9(4.4%)/290.9(100%)/80.9(16.4%)/78.8(19.7%)</td>
<td><img src="image" alt="Structure A" /></td>
</tr>
<tr>
<td>B</td>
<td>21.352</td>
<td>320.9(55.7%)/322.9(100%)/324.9(54.8%)</td>
<td>322.9(0.5%)/290.9(100%)/80.9(23.2%)/78.8(21.2%)</td>
<td><img src="image" alt="Structure B" /></td>
</tr>
<tr>
<td>TBBPA</td>
<td>28.720</td>
<td>538.7(23.8%)/540.7(83.3%)/542.8(100%)/544.7(82.5%)/546.7(20.6%)</td>
<td>542.8(100%)/527.6(1.8%)/462.4(0.3%)/460.7(0.3%)/447.7(3.6%)/445.7(3.3%)/419.6(1.1%)/417.6(0.6%)/288.9(0.7%)/80.9(1.1%)/78.8(1.0%)</td>
<td><img src="image" alt="Structure TBBPA" /></td>
</tr>
</tbody>
</table>

<sup>a</sup> Fig. S4 and Fig. S6.<br>
<sup>b</sup> The uncertain substituent positions of atoms are displayed in dotted line.<br>
<sup>c</sup> Molecular ion peak.

3.4. Changes in hormonal activities

The multiple hormonal activities (estrogenic and androgenic activities, antiestrogenic and antiandrogenic activities) for the extracts of reaction solutions during Fe(VI) oxidation were determined by using in vitro recombinant yeast bioassays, as shown in Table 3. TBBPA showed in vitro androgenic, antiandrogenic and anti-estrogenic activities, but no estrogenic activity as shown in Table 3, which is consistent with the previous studies (Kitamura et al., 2005; Christen et al., 2010;
Huang et al., 2013). During Fe(VI) oxidation process, the determined androgenic and antiandrogenic activities decreased with increasing reaction time, and the reduction of the androgenic and antiandrogenic activities was in proportion to the decreasing residual TBBPA concentrations (Fig. S7 and Fig. S8). This indicates that the determined androgenic and antiandrogenic activities are related to the levels of TBBPA, suggesting the reaction products exhibiting negligible androgenic and antiandrogenic activities. Besides, no estrogenic and antiestrogenic activities were found throughout the Fe(VI) degradation process, which indicates that the reaction products also have no estrogenic and antiestrogenic activities. Consequently, the oxidation of TBBPA by Fe(VI) could lead to the loss of its hormonal activities.

3.5. The effect of suspended particles on Fe(VI) oxidation

The influence of selected suspended particles (HA and MMT) on TBBPA/BPA removal during Fe(VI) treatment was investigated in pH 8.0 phosphate buffer solutions. There were no obvious difference in TBBPA/BPA concentrations pretreated with and without mixing process, indicating no sorption of HA and MMT with TBBPA/BPA occurred. Fig. 4 shows the relative changes in the residual concentrations of TBBPA/BPA as a function of particles doses. With the increasing amount of HA, the residual concentration of TBBPA/BPA was increased. For example, when adding 20 mg L⁻¹ of HA, the removal efficiency of TBBPA and BPA dropped from 70% to 33.2% and 28.4% respectively, indicating the spiked HA decreased the Fe(VI) removal of TBBPA/BPA. Nevertheless, the removal of TBBPA/BPA was not affected by the presence of MMT within the tested concentrations (0–40 mg L⁻¹). Therefore, when applying a lower dose of Fe(VI) for treatment, the dissolved organic matter would decrease the removal of target pollutants by Fe(VI), but clay minerals would have no significant effect.

The influence of natural particles on Fe(VI) removal of TBBPA/BPA was also investigated by kinetic oxidation experiments with the filtered and unfiltered natural water samples. Compared to the relatively lower dose of Fe(VI) used in the above batch experiments, the dosage of Fe(VI) (25 μM) was in excess to TBBPA/BPA. Along with the increasing reaction time, the residual concentrations of TBBPA/BPA by Fe(VI) in unfiltered and filtered water samples as well as phosphate buffer solutions decreased, showing similar trends (Fig. 5). But, the residual concentrations of TBBPA/BPA in the unfiltered water samples were slightly more than in the filtered water sample, indicating the presence of suspended particles in natural water can reduce the removal efficiency of TBBPA/BPA by Fe(VI) (Lee et al., 2009; Lee and von Gunten, 2010). Besides, the unfiltered natural water had initial TOC and turbidity of 3.4 mg L⁻¹ and 7.0 NTU, but the filtered water had the TOC and turbidity of 3.0 mg L⁻¹ and 5.4 NTU. So the residual concentrations of TBBPA and BPA in both filtered and unfiltered water samples were more than the phosphate buffer solutions because of the high dissolved organic matter in natural waters. Besides, other coexisting constituent such as inorganic ions and metal cations present in filtered and unfiltered water samples may be responsible for the above differences (Yang and Ying, 2013). Finally, Fig. 5 also shows that dosing more Fe(VI) can achieve complete removal of the target pollutants in the natural water. This is because the competition between target pollutants and dissolved organic matter can disappear rapidly after the electron-rich organic moieties present in dissolved organic matter are consumed by the selective oxidation of Fe(VI) by ferrate ion (Yeung et al., 2013).
oxidant Fe(VI) (Lee and von Gunten, 2010; Yang and Ying, 2013).

4. Conclusions

This study demonstrated that by Fe(VI) oxidation the brominated flame retardant TBBPA could be more easily removed than BPA. The determined $k_{app}$ of the Fe(VI) reaction with TBBPA was greater than that of BPA in the studied pH range. Based on the tentatively identified products, the Fe(VI) oxidation of TBBPA generates the main products of 4-(2-hydroxyisopropyl)-2,6-dibromophenol and 4-(2-methoxyisopropyl)-2,6-dibromophenol. The Fe(VI) oxidation process decreased the multiple hormonal activities (androgenic and antiandrogenic activities) of TBBPA, with no detectable estrogenic and antiestrogenic activities. It was shown that the natural organic matters such as HA in water would decrease the Fe(VI) reactions with TBBPA and BPA, while the inorganic particles such as clay minerals had no effect on the removal within the tested concentrations. Complete removal of organic compounds such as TBBPA can be achieved by increasing the Fe(VI) doses in order to reduce the effects of suspended particles present in natural waters.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.05.056.

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