Assessment of solar-assisted electrooxidation of bisphenol AF and bisphenol A on boron-doped diamond electrodes

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ABSTRACT

Bisphenol (BP) analogues in wastewater effluent and groundwater pose a potential threat to human health due to their ability to disrupt steroidogenesis. A new solar-assisted electrochemical process (SECP) was developed and evaluated for the degradation of BP analogues. The effects of quenchers, current density, initial pH, supporting electrolyte, and aqueous matrix on the removal kinetics of bisphenol AF (BPAF) and bisphenol A (BPA) were investigated. The kinetic constants of BPAF, BPA, and bisphenol S (BPS) in the SECP with irradiation intensity of 500 mW cm−2 were 0.017 ± 0.002 min−1, 0.022 ± 0.002 min−1, and 0.012 ± 0.001 min−1, respectively. The changes in the degradation rates of BPAF, BPA, and BPS in the presence of quenchers indicated the relative contribution of hydroxyl radical (•OH) oxidation, anodic electrolysit, and singlet (1O2) oxygenation in the degradation of BPs in the SECP. The enhanced rate of generation of •OH and 1O2 was observed in the SECP compared with those in the conventional electrochemical system. The identification of the transformation products (TPs) of BPAF demonstrated that hydroxylation, ring cleavage, β-scission, and defluorination were the major processes during the oxidation in the SECP. The conversion to fluoride ions (76%) and mineralization of total organic carbon (72%) in the SECP indicated further degradation of TPs. The results from this study improved our understanding of the degradation of BP analogues in the electrooxidation irradiated by solar light and help to establish the application potential of the SECP for the effective degradation of emerging contaminants in wastewater.

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1. Introduction

Bisphenol (BP) analogues have been widely used in the manufacture of paper products, polycarbonate plastics, epoxy and phenolic resins, and beverage containers [1]. Bisphenol A (BPA) is the most frequently used BP analogue with an annual production of 5.5 million tons in 2010. It can be globally detected in natural water, sludge, sediments, air, soils, wildlife, and human body fluids [2,3]. The estrogen-like effect of BPA has raised public health concern, and therefore, the application of BPA has been restricted by several organizations. Consequently, other BP analogues, including bisphenol AF (BPAF) and bisphenol S (BPS), were developed and introduced in the market as an alternative to BPA [3]. The analysis of plasma and blood samples of Chinese participants showed that the mean concentrations of BPA, BPS, and BPAF were 0.4 ng/mL, 0.15 ng/mL, and 0.073 ng/mL, respectively [4]. However, recent studies have indicated similar or even stronger toxicity of BP analogues, compared with that of BPA. It was reported that the BP analogues were capable of disrupting endocrine steroidogenesis [5,6]. Due to the stability and bioaccumulation properties of the BPs [6], various types of treatment technologies were employed for their removal from wastewater, surface water, and groundwater. One of the widely used technologies to degrade BPs in surface...
water is the advanced oxidation process (AOP), which is based on the generation of active radicals. AOPs employed to degrade BPs in previous studies include photocatalytic oxidation [7], photo-oxidation with hydrogen peroxide (H₂O₂) [8], catalysis oxidation with peroxymonosulfate (H₂SO₅) [9], and manganese dioxide oxidation [10].

Electrochemical advanced oxidation process (EAOP), as environmentally friendly technology, has attracted greater attention and non-selectively applied for the degradation of organic compounds [11]. Especially, boron-doped diamond (BDD) anodes demonstrated strong oxidation capability for the degradation of different pollutants from wastewater via generation of heterogeneous and homogeneous hydroxyl radicals (•OH) [12], sulfate radicals [13], or active chlorine [14] in the EAOP. The degradation rate constant of 0.318 min⁻¹ and current efficiency of 54.93% for BPA removal was obtained at 40 mM NaCl and pH 8 by the BDD anodic oxidation, which was higher when compared to that by the platinum (Pt) anodic oxidation [14]. The in situ active species generated in the EAOP include H₂O₂ in electro-Fenton (EF) process and active chlorine species, involving free chlorine, hypochlorous acid (HClO), and hypochlorite ion (ClO⁻) in the electrooxidation process [11,14,15]. In addition, free radicals can also be generated through the activation process of oxidants (including H₂O₂, HSO₅⁻, persulfate, HClO, and chloramine) by ultra-violet (UV) or solar irradiation [16–19]. Previous studies have focused on the coupling of the EAOP with photolysis and sonolysis process (known as photoelectrolysis and sonoelectrolysis) to enhance the formation of radicals and other active species, thus improving the degradation efficiency of EAOP [20].

The EAOP studies based on the in-situ generation of free chlorine by the anodic oxidation [15,21], H₂O₂ via the EF reaction [22,23] and photosensitive anode [24,25] were extensively investigated to use in combination with the photo process to enhance the formation of active oxidative species. With the presence of chloride (Cl⁻), sulfate (SO₄²⁻), phosphate (PO₄³⁻), and carbonate (CO₃²⁻) ions in the synthetic matrix, the UV irradiation process enhanced the performance of BDD electrode oxidation, with the stronger effect of UV observed at the current density of 10 mA cm⁻², compared to that at 77.5 mA cm⁻² [26]. It was possible to produce •OH by coupling dimensionally stable anode (DSA®) responsible for the formation of free chlorine species with UV irradiation for enhanced removal and mineralization process [27]. However, the formation of chlorine organic by-products, such as chlorate (ClO₃⁻), perchlorate (ClO₄⁻), by the photo-electrochemical process using DSA and BDD with UVC light led to serious concerns in the presence of Cl⁻ [28]. The degradation of BPA has been investigated using EF, photo electro-Fenton (PEF), and solar photo electro-Fenton (SPEF) processes with BDD anode and air-diffusion cathode. The mineralization of BPA was achieved at pH 3.0 and followed the order EF < PEF < SPEF [29]. The viability of the SPEF process for the removal of herbicide bentazon was also confirmed in the urban wastewater, indicating that sunlight was superior to UVA light because of its greater irradiance as compared to UV and contribution of visible photons [30]. Therefore, the application of a low-cost solar source, replacing the UV lamp to provide photons, in a photo-assisted EF process at the pilot plant scale of 100 L was considered [31]. Moreover, the photo-electrocatalytic processes with TiO₂/ITO film anode [24] and PbO₂/SnO₂-Sb₂O₅/Ti/Ti/TiO₂ electrode [25] had been previously carried out to efficiently degrade BPA and fenuron, respectively. These bifunctional electrodes served as the photocatalyst and the anode with high photocatalytic activity in the photocatalytic electrochemical process. However, BDD had no photocatalytic property subjected to light irradiation. Little information is available on the enhanced oxidation of BPA and BPAF by the solar-assisted BDD electrooxidation process in the absence of Cl⁻.

The objectives of this work are: 1) to investigate the degradation performance of BPs in SO₄²⁻ electrolyte under solar-assisted electro-oxidation process (SECP) with BDD anode; 2) to elucidate the removal mechanism by the investigation of radical and nonradical oxidation; 3) to evaluate the influence of electrochemical factors on the removal efficiency, and 4) to propose the oxidation pathway and identify the transformation products (TPs) in the SECP and electrochemical system with BDD anode.

2. Materials and methods

2.1. Materials

The one-side coated BDD/Si electrodes (Neocat SA, Switzerland) and graphite felt (Beijing Jixing Co. Ltd, China) were applied as anode and cathode in the electrochemical system, respectively. Commercially available 4,4'- Hexafluoroisopropylidene) diphenol (BPAF), 4,4'-((propane-2,2-diyl) diphenol (BPA), 4,4'-Sulfonyldiphenol (BPS), sodium nitrate, sodium sulfate, sodium bicarbonate, methanol (MeOH), tert-butanol (TBA), phenol, ascorbic acid, 2,2,6,6-tetra methylpyperidine-1-oxyl (TEMPO) and 5,5-dimethyl-1-pyrrroline N-oxide (DMPO) of analytical grade were purchased from Aladdin Co. Ltd, China. The electrolyte media were prepared with deionized (DI) water (18.25 MΩ cm⁻¹) collected from a Milli-Q system. The biologically treated effluent was collected from a wastewater treatment plant (WWTP) in Harbin, and its characteristics are provided in supplementary information (SI, Table S1).

2.2. Experiment set-up

A pyrex dish made of borosilicate glass was used as the cell for SECP with the effective volume of 100 mL. The batch experiments for SECP were carried out under the constant current density of 5 mA cm⁻² provided by a galvanostatic DC power (Agilent Co., USA) and irradiated under a lamp (Newport Co., USA). GC400 filter was used so that the lamp power simulated the spectral output of the sun. The sunlight was irradiated from the upper side of the electrodes (Fig. S1). The distance between the electrodes was set as 2.5 cm, and the working area of electrodes was 6.25 cm² (2.5 × 2.5 cm). The target compounds (BPAF, BPA, or BPS) of 5 µM were spiked as the model BP pollutants in the DI water or WWTP effluent before electrolysis. The quenching experiments were conducted with excess MeOH, TBA, or phenol to evaluate the roles of •OH, sulfate radical, and singlet oxygen (¹O₂) in the solution. At desired time intervals, 0.9 mL samples were collected in vials, and a 0.1 mL solution of 10 mM ascorbic acid was added to the vials to quench the residual oxidative species. All the experiments were conducted at the stirring condition and repeated three times under room temperature (25°C).

2.3. Analytical methods and calculation procedures

High-performance liquid chromatography (HPLC) was used to determine BPAF, BPA, and BPS in the samples. The TPs of BPAF in the SECP were identified by a quadrupole time-of-flight mass spectrometry (QTOF-MS) coupled with HPLC system. The radicals and ¹O₂ were identified by electron paramagnetic resonance (EPR) spectroscopy. The specific operating conditions of HPLC, HPLC-QTOF-MS, and EPR were presented in SI (Text S1). The concentration of fluoride ions was detected by ion chromatography ( Dionex ICS3000, USA) with an AS11-HC (4 × 250 mm) anion exchange column and potassium hydroxide (KOH) eluent. The total organic carbon (TOC) was measured using a carbon analyzer (Multi N/C 3100, Analytik Jena, Germany). The samples collected from batch experiments with actual wastewater were filtered by 0.22 µm
membranes filters before analysis. The calculation of energy consumption was also given (Text S1).

3. Results and discussion

3.1. Enhanced degradation of BP analogues in the SECP

The degradation of BPAF, BPA, and BPS in the SECP with a reaction time of 60 min was compared with the conventional solar and conventional electrochemical systems to evaluate the improvement in the degradation performance, as shown in Fig. 1. No degradation of three BP analogues was observed in the conventional solar system. The removal efficiency of $64 \pm 5\%$, $76 \pm 4\%$, and $52 \pm 5\%$ for BPAF (Fig. 1a), BPA (Fig. 1b), and BPS (Fig. 1c) was observed in the SECP after 60 min of electrolysis, respectively. On the other hand, only about $40 \pm 4\%$, $44 \pm 4\%$, and $26 \pm 3\%$ removal efficiencies for BPAF, BPA, and BPS were observed in the conventional electrochemical system (BDD system), respectively. The removal efficiency of BPA achieved $98 \pm 1\%$, $64 \pm 3\%$, and $3 \pm 2\%$ in the SECP, BDD system, and solar system with the prolonging of electrolysis time to 120 min, respectively. The synergistic interaction on the BDD and solar system was confirmed based on the removal efficiencies of BP analogues in three systems, rather than a simple addition of electrooxidation and irradiation processes. The removal of BP analogues in the SECP was enhanced with the increase in irradiation intensity from $300 \text{ mW cm}^{-2}$ to $500 \text{ mW cm}^{-2}$, with the pseudo-first-order removal kinetic constants for BPAF increasing from $0.01 \pm 0.0005 \text{ min}^{-1}$ to $0.017 \pm 0.002 \text{ min}^{-1}$, BPA increasing from $0.012 \pm 0.001 \text{ min}^{-1}$ to $0.022 \pm 0.002 \text{ min}^{-1}$, and BPS increasing from $0.006 \pm 0.0005 \text{ min}^{-1}$ to $0.012 \pm 0.001 \text{ min}^{-1}$ (Fig. 1d), respectively.

The removal of BP analogues in the BDD system and SECP subjected to the same irradiation intensity was in the order BPS < BPAF < BPA (Fig. 1d). The higher susceptibility of BPA than BPAF and BPS towards the oxidation in the BDD system and SECP was due to the stronger electron-donating effect of the alkyl substituent (-CH$_3$ group) (Fig. 1b) than the -CF$_3$ (Fig. 1a) and -SO$_2$ (Fig. 1c) groups on the aromatic ring. Both the $pK_a$ values of BPA (9.6 and 11.3) were higher compared to those of BPAF (9.13 and 9.74) and BPS (7.42 and 8.03), respectively [4,32]. Based on the respective $pK_a$ values, the biodegradation rate of BPA in the natural environment was higher than that of other BP analogues (BPAF and BPS) [33,34]. The removal of BPA, BPAF, and BPS were also reported in the MnO$_2$ system, and the removal efficiency followed the same order BPS < BPAF < BPA [10].

3.2. Removal mechanism of BP analogues

The quenching experiments were conducted to evaluate the role of reactive solution-phase oxygen species in the SECP. The effect of scavengers for BP analogues removal is shown (Fig. S2). The corresponding removal rate constants are summarized and illustrated in Fig. 2. The degradation rate constants of three BP analogues decreased to $0.006 \text{ min}^{-1}$, $0.005 \text{ min}^{-1}$, and $0.003 \text{ min}^{-1}$ for BPAF, BPA, and BPS, respectively, in the presence of $0.01 \text{ M TBA}$ in the SECP (Fig. 2). The degradation constants obtained in this case were almost similar to those obtained in the presence of $0.01 \text{ M MeOH}$. The saturated alcohols scavengers react rapidly with solution-phase radicals [35], at the rate constants of $3.8 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ (k

![Fig. 1. Removal plots of (a) BPAF, (b) BPA, (c) BPS during the SECP compared with solar and BDD system under irradiation intensity of 500 mW cm$^{-2}$, and (d) removal rate constants in the BDD system and SECP under different irradiation intensities of 300 mW cm$^{-2}$, 400 mW cm$^{-2}$, and 500 mW cm$^{-2}$ (Experimental conditions: 5 mM of initial pollutants, 30 mM of SO$_4^{2-}$, pH 6.8, and current density of 5 mA cm$^{-2}$).

![Fig. 2. Effect of different scavengers on the removal rate constants of BPAF, BPA, and BPS in the SECP (Experimental conditions: 5 mM of initial pollutants, 30 mM of SO$_4^{2-}$, pH 6.8, current density of 5 mA cm$^{-2}$, and irradiation intensity of 500 mW cm$^{-2}$).]
BDD, •OH) and 9.7 \times 10^8 \text{ mol} \cdot \text{s}^{-1} (k_{\text{MeOH}, \cdot \text{OH}}) in the presence of 0.01 M TBA and 0.01 M MeOH, respectively [36]. This indicated the contribution of •OH in the solution for the degradation of BP analogues in the SECP. The degradation of BPA in the BDD system was related to the generation of •OH originating from the physisorbed •OH at the BDD surface (Eq. (1)) [29,37,38]. It was reported that BDD could also produce peroxy sulfate and further sulfate radical with the SO$_4^-$ electrolyte [26,39], however, no difference in quenching results was observed in the presence of TBA and MeOH scavengers with the reaction rate constants of 4.0 \times 10^5 \text{ mol} \cdot \text{s}^{-1} (k_{\text{TBA, SO}_4^-}) and 1.1 \times 10^7 \text{ mol} \cdot \text{s}^{-1} (k_{\text{MeOH, SO}_4^-}), respectively (Fig. 2), indicating that there was no clear evidence of free sulfate radicals during scavenger experiments in this SECP.

**EPR spectra with (a) DMPO and (b) TEMPO observed in the SECP and BDD system (Experimental conditions: 30 mM of SO$_4^-$, pH 6.8, current density of 5 mA cm$^{-2}$, 10 mM of DMPO/TEMPO, and irradiation intensity of 500 mW cm$^{-2}$ in the SECP).**

\[
\text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD}(\cdot\text{OH}) + \text{H}^+ + e^- \tag{1}
\]

Similar rate constants were observed for BPAF degradation in the SCEP and BDD system when the quenching was carried out with TBA or MeOH (Fig. S2a). Thus, the increase in BPAF degradation in the SECP was probably due to the enhanced generation of •OH scavengers with the SO$_4^-$ electrolyte [26,39], however, no difference in quenching results was observed in the presence of TBA and MeOH scavengers with the reaction rate constants of 4.0 \times 10^5 \text{ mol} \cdot \text{s}^{-1} (k_{\text{TBA, SO}_4^-}) and 1.1 \times 10^7 \text{ mol} \cdot \text{s}^{-1} (k_{\text{MeOH, SO}_4^-}), respectively (Fig. 2), indicating that there was no clear evidence of free sulfate radicals during scavenger experiments in this SECP.

3.3. Effect of operating conditions on the removal of BPAF and BPA

3.3.1. Effect of current density

The current density influenced the electrochemical process by controlling the rate of formation of •OH (Eq. (1)). The degradation of BPAF and BPA was carried out at different current densities of 1 mA cm$^{-2}$, 2 mA cm$^{-2}$, 5 mA cm$^{-2}$, and 10 mA cm$^{-2}$ in the SECP (Fig. S3). The degradation rate constants of BPAF and BPA increased with the increase in the current density, as shown in Fig. 4. These results are consistent with the results obtained during the photocatalytically-assisted electrooxidation of 0.1 mM fenuron in SO$_4^-$ electrolyte [25]. The pseudo-first-order kinetic rate constants of BPAF increased from 0.007 \pm 0.001 min$^{-1}$ to 0.024 \pm 0.0025 min$^{-1}$ and are linearly related to the increase in applied current density, i.e. from 1 mA cm$^{-2}$ to 10 mA cm$^{-2}$ (Fig. 4). Similarly, the removal of BPA in the SECP was also enhanced by the increase in current density, with the corresponding removal rate constants increasing from 0.008 \pm 0.001 min$^{-1}$ to 0.041 \pm 0.0085 min$^{-1}$.

3.3.2. Effect of pH

Fig. 5 shows the effect of pH on the removal of BPAF and BPA. There was no significant change in the removal of BPAF and BPA in
the SECP with the increase in pH from 4 to 10. This was in agreement with the result observed during 2,4-D herbicide removal in the photoelectro-peroxone process [43] and fenuron removal in the photocatalytically-assisted electrooxidation [25]. In the previous studies, contradictory results in terms of change in pollutant removal with varying pH in the electrochemical system were reported, which can be ascribed to different removal mechanisms and pollutants characteristics [46,47]. In alkaline conditions, the decrease in the generation of \( \bullet \text{OH} \) was explained by their conversion to oxygen (Eq. (2)) that led to a decrease in the removal efficiency. In contrast, there can be an enhanced generation of \( \bullet \text{O}_2 \), leading to greater pollutant removal [19,48]. The pH-independent nature of BPAF and BPA removal in the SECP could guarantee the effectiveness of the SECP over a wide pH range.

\[
2\bullet \text{OH} \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^-
\]  

(2)

3.3.3. Effect of supporting electrolyte

Electrolyte plays an important role in the electrochemical system to provide the necessary ionic strength and conductivity for electrolysis [49]. The effect of different electrolytes and \( \text{SO}_4^{2-} \) concentration on the removal rate of BPAF and BPA in the SECP was investigated, and the results are shown in Fig. 6. \( \text{SO}_4^{2-} \), bicarbonate (\( \text{HCO}_3^- \)), and nitrate (\( \text{NO}_3^- \)) salt solutions were selected as electrolytes to support the electrolysis and avoid the generation of chlorinated products. These electrolytes were used in the SECP to carry out electrolysis processes at the same ionic strength. The presence of \( \text{HCO}_3^- \) and \( \text{NO}_3^- \) demonstrated a negative influence on the removal of BPAF (Fig. 5a) and BPA (Fig. 5b), compared to that of \( \text{SO}_4^{2-} \). The similar inhibitory effect of anions (Fig. 6a) was also observed in the previous studies [25,50]. \( \text{HCO}_3^- \) ions could scavenge \( \bullet \text{OH} \) to generate other radicals [51]. The reaction rate constants for BPA degradation in the presence of carbonate radicals (\( \bullet \text{CO}_3^- \)) with BPA \( (k_{\text{BPA, \bullet CO}_3^=} = 2.28 \times 10^{10} \text{mol}^{-1} \text{s}^{-1}) \) was much lower than that in the presence of \( \bullet \text{OH} \) \( (k_{\text{BPA, \bullet OH}^=} = 1.02 \times 10^{16} \text{mol}^{-1} \text{s}^{-1}) \) [52], thus decreasing the removal rate of BPs.

The effect of different \( \text{SO}_4^{2-} \) concentrations on the removal rate was also investigated. The current density of 5 mA cm\(^{-2}\) was fixed for different \( \text{SO}_4^{2-} \) concentrations in the SECP to provide the same electrical charge at different electrolyte conditions. The optimal removal efficiency of BPAF (Fig. S4a) and BPA (Fig. S4b) was obtained using 30 mM \( \text{SO}_4^{2-} \) as the supporting electrolyte. When the corresponding removal rate constants of BPAF and BPA were calculated at different \( \text{SO}_4^{2-} \) concentrations, maximum removal was observed at 30 mM (Fig. 5b). Similar results were observed in the study by Dai et al. [53]. The result might be explained that increasing electrolyte concentration at a low level would increase ionic strength in aqueous solution and enhance the probability of collision between the particles in the system [53]. However, \( \text{SO}_4^{2-} \) ions at higher concentration would possibly impede the migration of pollutants to the electrode surface, produce persulfate thus significantly scavenging \( \bullet \text{OH} \) [54], and slow down the removal rate of the organic pollutants.

3.4. Identification of transformation products and degradation pathway of BPAF

The TPs of BPAF in the SECP and BDD system were identified by HPLC-QTOF-MS. The \( m/z \) values, chemical formulae, and possible structures of TPs are given (Table S2), with the corresponding MS profile and fragment pattern shown in Fig. S6. Similar reactions, including electron transfer, hydroxylation, and defluorination took place in SECP and BDD system based on whether radical oxidation, anodic electrolysis, and \( \text{O}_2 \) oxygenation were involved. However, the differences in the contributions by radical and nonradical oxidation in the SECP and BDD system resulted in the formation of different TPs. Based on the detected TPs, the possible degradation pathway of BPAF by SECP and BDD system is presented in Fig. 7.

Two reaction chains based on the susceptible sites on the
phenolic ring and isopropylidene bridge of BPAF are shown (Fig. 7).

Three major proposed schemes that describe the reactions in the SECP and BDD system (Schemes S1–3). The proposed pathway of hydroxylation can modify the phenolic ring via direct electron transfer and radical attachment (Scheme S1). Electron transfer promotes the formation of phenolic-BPAF radical cations, which can be further transformed into catechol-BPAF radical. The catechol-BPAF radical can be further oxidized by O₂ to generate hydroxybenzene TPs (PA1). Similar reactions involving the hydroxylation of the phenolic ring were also observed in the previous studies based on •OH reactions with BPAF and BPA [52,55], where hydroxyl-BPAF and hydroxyl-BPA were identified. The iso- propylidene bridge on BPAF and PA2 can be modified to produce formyl acids (PB2 and PB3). Besides, hydroxybenzene TP can undergo the β-scission process [1,10], resulting in the formation of catechol derivative (PB4) and ketones (PA5).

As the oxidation of TPs continues further, carbon dioxide (CO₂) and water (H₂O) are finally formed, and the fluoride ions are released into the solution. About 76% fluorine from BPAF was released as fluoride ions in the SECP at 210 min, when compared with 6% fluorine released in BDD system (Fig. S5). The defluorination process takes place along with the oxidation, was confirmed by the presence of fluoride ions [55]. Higher concentration fluoride ions were observed in the SECP, thus confirming the enhanced defluorination in the SECP. The TOC removal efficiency in the SECP and BDD system was 72% and 59% in 240 min (Fig. S5), revealing greater degradation of the TPs to smaller molecular weight compounds in the presence of solar irradiation. Thus, hydroxylation, ring cleavage, β-scission, and defluorination are major reactions involved during the degradation of BPAF by the SECP.

The temporal profiles of BPAF TPs are presented in Fig. 8 to demonstrate the differences in the formation of TPs in the SECP and BDD system, mainly because of the differences in the roles played by •OH and ¹O₂ in two systems. Among the TPs (Table S2), PA3 (C₁₄H₁₀F₆O₂), PB2 (C₁₃H₉F₃O₂), PB4 (C₈H₁₀O₃), and PB3 (C₈H₁₇F₃O₈) were observed only in the SECP (Fig. S7a), and the increasing trend of PA4 (C₁₄H₁₀F₆O₃) was observed only in the BDD system (Fig. S7b).

The remaining TPs, as given in Table S2, were detected in both the systems at different temporal concentrations (Fig. 8). Besides PA2 (C₁₅H₁₀F₅O₅), PA5 (C₃F₃OH), PAB5 (C₁₂H₇F₃O₁₀), and PC1 (CHF₃) (Fig. 8b and d), seven other TPs exhibited higher concentrations in the SECP than those in the BDD system, indicating the greater capability of the SECP in oxidizing organics. Moreover, the concentration of eight TPs in the SECP increased initially and then decreased after attaining peak value, indicating smaller molecular TPs were generated with the electrolysis time. However, PA5, PAB4 (C₁₄H₁₁F₄O₃), and PC1 continued to increase in both the systems. Compared with those in the SECP, there was a higher accumulation of PA4, PA5, PAB5, PC1 in the BDD system (Fig. 8 and Fig. S7). Moreover, fewer fluoride ions were released into the BDD system, which was consistent with the previous result (Fig. S5).

3.5. Removal of BPAF in WWTP effluent

The radical-based AOPs are always non-selective to organic matters and influenced by pH, organics, and inorganic ions existing in actual wastewater [57]. The natural organic matters (NOM), PO₄³⁻ and HCO₃⁻ in actual wastewater might compete for adsorption with targeted pollution at anode and scavange free radicals in the system, thus lowering the degradation efficiency of target pollutants [48]. The WWTP effluent (characteristics presented in Table S1) was used to evaluate the efficacy (Fig. S8) and electrical consumption (Fig. S9) of the SECP and BDD system. The removal efficiency of BPAF in WWTP effluent of 24 ± 4% and 18 ± 5% at 60 min in the SECP and BDD system consumed the electrical energy of 3.43 kWh m⁻³ and 3.50 kWh m⁻³, respectively. The removal rate constants of BPAF in both systems are shown in Fig. 9. Compared with that in electrolyte prepared in DI water, the removal rate constants of BPAF in the SECP and BDD system significantly decreased to 0.005 ± 0.0005 min⁻¹ and 0.003 min⁻¹, respectively in the WWTP effluent spiked with BPAF (Fig. 9). Lower conductivity and ionic concentration in the WWTP effluent may be responsible for the poor removal performance of BPAF [49] and higher electrical consumption (Fig. S9).

The removal of BPAF from the effluent in the presence of 30 mM SO₄²⁻ was inhibited in the SECP and BDD system, with the rate constants of 0.011 ± 0.001 min⁻¹ and 0.006 ± 0.0005 min⁻¹, respectively. This was attributed to the presence of various components such as organics, alkalinity, etc. in the actual effluent [58]. It should be noted that the BPAF removal rate constant in the SECP was higher than that in the BDD system for the same actual effluent. Thus, the SECP was efficient to remove BP pollutants in
actual effluent with adequate ionic strength and conductivity. For the consideration of the application of this SECP, additional study is needed to evaluate the toxicity risk of TPs generated in actual effluent in the SECP.

4. Conclusions

This study investigated the performance, kinetics, mechanisms, and pathway of BPAF degradation in the SECP, compared with those in the BDD system. It indicated that the SECP could be applied as an efficient system to remove BP analogues in wastewater with adequate ionic strength and conductivity. The following conclusions can be drawn:

(1) The degradation performance of all three BP analogues (BPAF, BPA, and BPS) was enhanced in SO$_4^{2-}$ electrolyte in the BDD system subjected to solar irradiation, with the removal kinetics in the order BPS $<$ BPAF $<$ BPA in the BDD system and SECP subjected to the same irradiation intensity. The pseudo-first-order kinetic constants of BPAF, BPA, and BPS were determined to be $0.017 \pm 0.002$ min$^{-1}$, $0.022 \pm 0.002$ min$^{-1}$, and $0.012 \pm 0.001$ min$^{-1}$, respectively in the SECP with 500 mW cm$^{-2}$ irradiation intensity.

(2) The contribution of radical oxidation, anodic electrolysis, and singlet oxygenation was verified during the degradation of BP analogues in the SECP. The generation of $\bullet$OH and $^1$O$_2$ in the SECP was enhanced when subjected to solar irradiation.

(3) The current density had a positive influence on the rate of degradation of BPAF and BPA in the SECP. In contrast, the degradation kinetics in the SECP was not affected by a wide range of pH (4.0 to 10.0). HCO$_3^-$ and NO$_3^-$ electrolytes inhibited the degradation process, when compared with a SO$_4^{2-}$ electrolyte.
Based on the variation in TPs of BPAF detected in the SECP and BDD system, the degradation pathway involving a series of processes namely, hydroxylation, ring cleavage, β-scission, and defluorination was proposed. Higher fluoride conversion efficiency (76%) and enhanced mineralization of organics (72%) were achieved in the SECP, compared with that of 6% and 59% in the BDD system under similar conditions. The results obtained in this study provide a better understanding of the application potential of the SECP for the degradation of BP contaminants in wastewater.

Declaration of competing interest

The authors declare that they have no known conflict of interests or personal relationships that could have appeared to influence the work reported in this paper. I am one author signing on behalf of all co-authors of this manuscript, and attesting to the above.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ese.2020.100036.

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