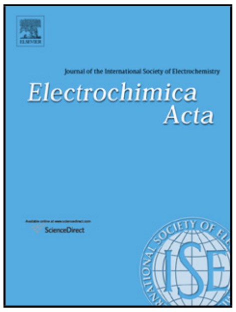

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Electrochemical degradation of bisphenol A in chloride electrolyte - Factor analysis and mechanisms study

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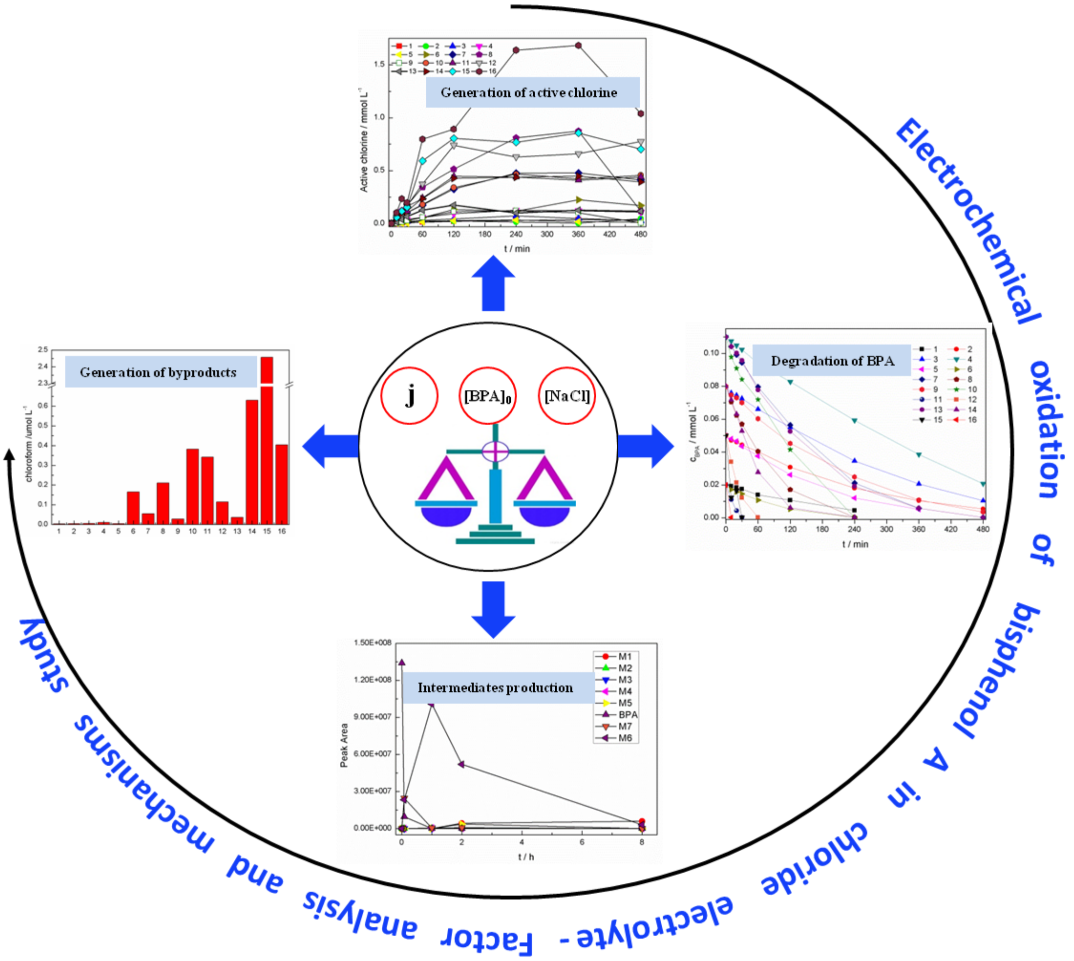
Graphic Abstract



Graphic Abstract

Highlights

- First study of BPA degradation in chloride electrolyte with Pt anode.
- Order of significance for *k*: j > initial BPA concentration > NaCl concentration.
- Cl-DBPs were analyzed concretely with the chlorine evolution for the first time.
- Mechanism was studied based on quantitative analysis of the fate of intermediates.

Abstract: Electrochemical oxidation technology is a powerful method in the degradation of recalcitrant organics, due to the high oxidizing ability of active chlorine and reactive oxygen species generated in the cell. However, influencing factor analysis and intermediates detection during the electrochemical removal of organics has not been extensively studied in the chloride electrolyte. In this study, an orthogonal test array design of $L_{16}(4)^3$ was carried on with Pt anode in NaCl electrolyte, using the typical endocrine disruptor bisphenol A (BPA) as the model pollutant. The influencing order of the three main factors for BPA degradation rate was current density > initial organic concentration > chloride concentration, based on the analysis of variance in this experiment. This emphasized the very significance of the active chlorine and hydroxyl radicals which were closely related with the potential of the system and the applied current density. Then both organic and inorganic Cl-byproducts were determined. The concentration of chloride decreased to 9.88 mM with an initial of 10 mM in the 480-min electrolysis and extremely low concentration of active chlorine was produced in this system (maximized at 0.037 mM) for the first set. Neither chlorate nor perchlorate was detected with the Pt anode. The factor of current density influenced greatest on the formation of chloroform due to the amount of active chlorine affected by the current density. Finally, intermediates generated in the electrolysis cell were concretely investigated. Compared with traditional chlorination, the amount of chlorinated-BPA (2, 2’-D_2CBPA and T_4CBPA) generated was relatively less (2.46 and 10.00 μM equiv BPA), which might be due to their fast simultaneously transformation in the electrochemical system. With the isopropylidene bridge cleavage of chlorinated-BPA, one-ring aromatic compounds (2,6-dichlorophenol, 2,6-dichloro-2,5-cyclohexadiene, 2,4,6-trichlorophenol) occurred at the same time. Finally, chlorinated-BPA was totally transformed and low molecular chlorinated compounds were detected to the end of the experiment. This is one of the very few studies dealing with chlorinated organic intermediates formed in chloride electrolyte, and thus these findings may have significant technical implications for electrochemical treatment of wastewater containing BPA.

Keywords: Bisphenol A; factor analysis; active chlorine; chlorine evolution

1. Introduction

Bisphenol A (BPA) is one of the highest-production-volume chemicals, three million tons each year all over the world, which is still increasing due to the strong demand and annual consumption worldwide in the plastics and epoxy resins manufacture [1-2]. It has already been found to be ubiquitously distributed in the natural environment and surface water [3]. BPA is a well-known endocrine disruptor and exhibits hormone-like properties [4]. Besides, it was determined that BPA showed the estrogenic, mutagenic effects, and acute toxicity to life body in the water [5]. As a result, efficient treatment method was in an urgent need to be developed for the degradation, detoxification and removal of BPA. Several processes have been carried on, including bacteria-mediated degradation [2,6], physical absorption [7-8] and advanced oxidation processes [9-12]. Biological degradation mainly depends on the metabolism of bacteria [2,6], which are time-consuming for organic removal in wastewater. Also, the regeneration of the absorption materials should be carefully considered, which was only a transfer rather than removal of the pollutants. Among these methods, advanced oxidation processes have been proved to be a promising method for BPA-like refractor organics. In particular, electrochemical oxidation is a promising environmentally clean process that is versatile, energy efficient and can be automated [10]. It has already shown excellent removal efficiency and mineralization ability for refractory organics, due to its advantages such as no need for chemical agents, the ability to work well at room temperature and control easily [12]. Recent research was carried on comparison of different kinds of modified anodes [13-14] in electrochemical removal of BPA and electrogenerated ferrous ion in activating oxidants [15-16] to degrade BPA in the electrolysis system. As part of the electrochemical process, organic compounds are broken down by means of the hydroxyl radical, the main active component with a high redox potential ($E_0 = 2.7$ V) formed through water oxidation at the surface of a high O_2-overpotential anode [17-18].

The electrode materials play a significant role in the electrochemical system, which has already been proved by many research [9,17]. Moreover, key influencing factors of current density, initial BPA concentration and electrolyte concentration, were also usually considered to investigate their effects on the electrochemical degradation in most of the related research. For example, Cui et al. [9] investigated the electrochemical degradation of BPA with Pt anode in 0.1 M Na_2SO_4 as the electrolyte, in comparison of boron-doped diamond (BDD), Ti/Sb-SnO_2 and Ti/RuO_2 anodes. Results showed that the Pt anode had a moderate ability to remove BPA. As the current density increased from 10 mA cm^{-2} to 50 mA cm^{-2}, the rate of BPA degradation accelerated by a factor of about 2 with a rapid increased charge consumption. Zaviska et al. [19] investigated the decomposition of BPA with three different anode materials (Ti/SnO_2, Ti/IrO_2, Ti/PbO_2) with a 2^3 Box-Behnken design, in which current density, electrolysis time and electrolyte (Na_2SO_4) concentration were selected as the objective factors.

It is of clearly consistence that higher current density, initial organic concentration and electrolyte concentration lead to more efficient organic degradation. However, it is not well known what factor of the three is the most crucial one and how about the order of these influencing factors in organic degradation. This is vitally important for providing references in the condition establishment of electrochemical oxidation of refractory organics. Besides, chloride exists ubiquitously in natural waters and the problem of organic and inorganic disinfection byproducts (DBPs) formation come out when organics are greatly oxidized in the electrochemical system [20]. Since these DBPs are high risks in water bodies whether recalcitrant organics in electrochemical chloride electrolyte is safe or not is still in question [21]. One of our previous papers has also proved that BPA has certain reactivity for DBP formation in electrochemical chloride-containing system [22]. Consequently, it is necessary to study the electrochemical degradation processes in chloride electrolyte rather than chloride-free electrolyte to minimize the gap, making the experimental results more practical.

This paper presents a study using Taguchi method for design of experiment (DOE) [23] to investigate the importance of different factors in the electrochemical degradation of BPA with a Pt anode. Selection of the three significant factors (current density, the electrolyte (NaCl) concentration, and the initial concentration of BPA) and their levels was based on the previous research of our group [17, 22]. An orthogonal test array design of $L_{16}(4)^3$ were carried on in this paper to determine the degree of significance for each process factors on BPA degradation based on the analysis of variance (ANOVA). More importantly, the byproducts and intermediates in the electrochemical degradation of BPA in the chloride electrolyte were analyzed concretely with the chlorine evolution for the first time and the mechanism of the process was proposed based on the quantitatively analysis of the fate of the produced intermediates.

2. Materials and methods

2.1. Chemicals

Bisphenol A (CAS: 80-05-7) was analytical standard material supplied by Sigma (St. Louis) with a purity of 99%. Organic solvent was HPLC grade supplied by Sigma (St. Louis). All other chemicals were analytical grade purchased from Beijing Chemical, and they were used without further purification. Solutions were prepared using deionized Milli-Q water (Millipore). The Pt electrode was provided by Ida Corporation, Tianjin.

2.2. Electrochemical degradation of BPA

Bulk electrolysis was carried out under galvanostatic conditions at room temperature (20 ^{o}C) in a 400 mL beaker equipped with Pt anode (1 cm^2) and stainless steel cathode. The electrode gap was set to 10 mm. NaCl was used as the electrolyte. The 250 mL electrolytic system was continuously stirred by a magnetic bar throughout the process. Samples were collected from the cell at prescribed intervals for chemical analysis. For each experiment, the Pt electrode was polished and then washed with deionized water.

2.3. Analytical procedures

Concentrations of BPA were monitored by an Agilent HP1100 HPLC instrument with a DAD detector and a ZORBAX SB-C18 column at 30 ^{o}C. The mobile phase comprised a mixture of methanol and water (70:30) at a flowing rate of 1 mL min^{-1}. The UV wavelength detector was set at 270 nm.

The concentration of active chlorine was determined by the N, N-diethyl-*p*-phenylenediamine (DPD) colorimetric method using a Unico (UV-4802) UV/VIS double-beam spectrophotometer according to the procedures described in a previous paper [24].

Prior to the analysis of DBPs, excess Na_2SO_3 (10 mM) was added to quench any residual oxidant in the sample. Chloroform was analyzed by purge and trap extraction (OI Analytical Model 4560) and by gas chromatography (Agilent 5890) equipped with electron capture detection (GC/ECD). Chloride, chlorate and perchlorate concentrations were measured with a Dionex DX-600 ion chromatography system equipped with an AS-50 autosampler, a GP-50 gradient pump, an anion self-regenerate suppressor ultra (ASRS-4 mm), an ED-25 conductivity detector, and a LC-20 chromatography enclosure. These detailed parameters were given in a previous paper [22]. These byproducts were quantified by the BPA calibration curve and their concentration was expressed as μM equivalent BPA (equiv BPA).

The intermediates of BPA degradation were obtained through a liquid-liquid solvent extraction to concentrate the samples. The extraction was carried out three times with dichloromethane in a 250 mL separating funnel. After extraction, the solvent was evaporated on a rotary evaporator to a known volume and was ready for analysis by gas chromatography (Agilent 6890) and mass spectrometry (Agilent 5973), using an HP-5MS (crosslinked 5% PH ME Siloxane) column with a length of 30 m and a film thickness of 0.25 mm. The conditions for GC were illustrated in [17].

Toxicity tests were performed using luminescent bacterium *V. fischeri* (No. 13L4152, Model Water, USA) according to the ISO 11348-3 (2007) [25], and the reduction of luminescence was measured using a Microtox Model 500 analyzer after the bacteria was exposed to the test chemical solutions for 15 min.

2.4. Design and analysis of orthogonal array $L_{16}(4)^3$

As the current density, initial concentration of BPA, the electrolyte concentration would influence the degradation rate, four levels for each factor were selected in this experiment based on our previous research [9, 17, 19, 22]. The pH value was fixed at 7 during the experiment. The $L_{16}(4)^3$ table of orthogonal design was used to test the electrochemical degradation rate of BPA and the formation of byproducts under the assigned experimental conditions (Table 1).

[Insert "Table 1" about here]

3. Results and discussion

3.1 Electrochemical degradation of BPA

Electrolysis was conducted under 16 different conditions according to Table 2. Fig. 1 shows the concentration decay of BPA in this orthogonal assay. BPA was degraded rather fast and completely for run 10, 15 and 16 in 30 min, while there was still BPA left in the 480-min electrolysis under conditions of run 2, 3 and 4. The role of different indicators on BPA degradation rate could be roughly concluded from the concentration trend. For example, the degradation rate of BPA was gradually increasing from run 1 to run 4, which was carried on with increasing chloride concentration from 10, 20, 30 to 40 mM. And thus it could be roughly judged that the BPA degradation rate was positively correlated with the chloride concentration in this experiment. It was estimated by Gallard et al. [26] that 4 mol of chlorine consumed per mol of BPA to achieve the complete degradation of BPA in the traditional chlorination process. In our experiment, the chlorine consumption was less than 1 mol per mol of degraded BPA, which was rather effective in BPA degradation.

[Insert "Fig. 1" about here]

[Insert "Table 2" about here]

[Insert "Table 3" about here]

Moreover, the concentration decays in Fig. 1 (Inset) fit well with a degradation kinetic equation related to a pseudo-first-order reaction of BPA and the degradation rate constants for BPA (*k*) were listed in Table 2. In order to accurately describe the influencing degree of the three important indicators on the BPA degradation rate, the ANOVA analysis was conducted (Table 3). SS is defined as the sum of the deviation squares, and F is the significance of the factors' influence on the results. Consequently, the factor of A (current density) with the highest F value, is the most important; and followed by factor C (initial concentration of BPA) and B (NaCl concentration). The value of the correlation coefficient (R^2 = 0.980) indicates that only 2.0% of the total variation could not be explained by the empirical model. According to Zaviska et al. [19], R^2 should be at least 0.80 for a good model fit. Since the R^2 value (0.980) of the fitted model in the present study for BPA removal was higher than 0.80, it could explain the whole influenced reaction well .

[Insert "Fig. 2" about here]

Recalcitrant organics can be removed much faster in the electrolyte containing chloride, in which both oxygen species and chlorine species work together with strong oxidizing ability [27]. Comparison experiments were conducted with Na_2SO_4 as the electrolyte and the results showed that degradation rate of BPA reached 61.3 % in 5 min electrolysis in chloride electrolyte and only 1.8 % with equivalent sulfate electrolyte (take the 16th group as an example and the figures were not given here). The contribution of the combined action in the chloride electrolyte was more significant in the electrochemical degradation of BPA. The reactive oxygen species (ROS, mainly including •OH) produced in electrolysis were predicted to play a significant role in electrochemical chloride-free system with Pt anode [9, 17, 18]. And it has been clearly proved that the formation of hydroxyl radicals, the most important species with the highest redox potential, is affected greatly with the current density applied in the electrolysis cell [18]. In the presence of •OH scavenger, either the organic degradation or microorganism inactivation was suppressed. Besides, the total concentration of active chlorine, containing dissolved gas (Cl_2), hypochlorous acid (HOCl) and/or the hypochlorite ion (OCl^-) [23], which were produced through discharge of Cl^- on the anode, was also closely related with the potential of the system and the applied current density [28]. As a result, the influence of the current density on the BPA degradation was the main factor. In the range of the current density investigated in this experiment, there is a positive correlation between *k* and j, however, the extent of increase is greatest in the scope of 30-40 mA cm^{-2} (Fig. 2). This is due to the reason that reactions related to both •OH and active chlorine occur very rapidly and effectively with high current density.

The factor of the initial BPA concentration is in the second position for this electrochemical oxidation experiment. *k* decreased gradually with the initial concentration increased from 0.02 mM to 0.11 mM (Fig. 2). This can be explained by the relatively limited oxidation capability of the electrolysis cell under a certain current density value, as the main contribution for the degradation is the active species generated by the electrochemical oxidation. Interestingly, the decrease turns slower when initial BPA concentration is 0.08-0.11 mM, indicating that organic degradation has been already out of mass-transfer control and this method is also applicable to cases with higher concentration of BPA. Besides, it has already been confirmed that BPA in a solution at neutral pH is easily absorbed to the Pt electrode surface, compared to acidic or alkaline media [29]. Then the electrochemical oxidation of BPA is greatly affected due to the electrode fouling by the formation of the electropolymerized film. As a result, it was put forward that low phenol concentration, which would not favor the film formation on the Pt anode surface should be promoted [30]. For the treatment of the real wastewater, many kinds of different organics often coexisted and would lead to the fouling of the electrode and then affect the efficiency of the purification treatment. As a result, how to cope with the fouling of the surface is extremely important for electrochemical oxidation process with Pt anode. It is already known that the electrode fouling was generated through the adsorption processes of the organic compounds on the surface of the Pt electrode [31] and this poison effect was much more serious for the aromatic organics [32]. Furthermore, the direct application of ultrasound or microwave was proved to be able to enhance the electrochemical oxidation performance by cleaning the surface instantly, in the form of breaking down the intermediates and suppressing their adsorption on the electrode surface [33-34]. Thus, the combination of these measures with electrochemical oxidation with Pt anode should be considered in real wastewater treatment, so as to mitigate the possible fouling and maintain the high efficiency of the electrolysis system.

A minimum chloride concentration of 10-20 mg L^{-1} is reported to be necessary for chlorine formation [35]. Also, chloride ions might adsorb on the surface of the electrode through the polarization curves study. Since the chloride concentration is usually high in this study (355-1440 mg L^{-1}) and higher chloride concentrations enhance the partial current density at the same potential, leading to better migration of the chloride ions to the active electrode sites [27]. So the concentration of active chlorine is always plentiful for this system, and the influence of NaCl concentration on BPA degradation is the least in the three. The predominating influence of chloride migration and active chlorine formation was the current density (or potential gradient at the anode), and then the mass transfer differences [36]. Comparison experiments were conducted with Na_2SO_4 as the electrolyte and the results showed that degradation rate of BPA reached 61.3 % in 5 min electrolysis in chloride electrolyte and only 1.8 % with equivalent sulfate electrolyte (take the 16th group as an example and the figures were not given here). The contribution of the combined reactions in the chloride electrolyte was more significant in the electrochemical degradation of BPA.

According to the reference [37], the current efficiency (CE) at a given time *t* was comparatively estimated from the following equation:

$$CE = 267FV\frac{(TOC)_0 - (TOC)_t}{8I\Delta t} \tag{1}$$

where $(TOC)_0$, $(TOC)_t$ are the total organic carbon (g L^{-1}) at times 0 and *t*(s), respectively; *V* is the volume of electrolyte (L); *I* is the current (A), F is the Faraday constant (96 487 C mol^{-1}).

CE values in 8-hour reaction were 6.54 %, 7.21 %, 7.72 %, 15.71 %, 2.38 %, 2.32 %, 7.55 %, 6.49 %, 4.34 %, 8.67 %, 4.16 %, 4.65 %, 8.79 %, 6.09 %, 8.09 % and 5.60 %, respectively for the 16 groups of electrochemical degradation of BPA. They were quite low due to the losses on the wires, the electrolytes, the mass transfer limiting and most importantly, the side reaction of oxygen evolution and the possible deactivation of the electrodes [32,38]. Definitely, CE values decreased with the increasing of the current density and increased with the chloride concentration in the electrolytes, which was the same with the present studies [22,37]. Moreover, the factor of the initial BPA concentration also obviously affected the current efficiencies in the studied Pt system.

3.2 Electrochemical generation of Cl-byproducts

One of our previous papers investigated the electrochemical production of chlorinated byproducts with the BDD anode [22]. To compare the characteristics of the two typical different anodes, chlorinated byproducts (including chloroform, chlorate and perchlorate), active chlorine, chloride ions were also determined with the Pt anodes in this experiment. Differently from the condition with the BDD anode, the chloride concentration decreased slowly during the 8-hour period in this experiment (Fig. 3(a)). Take the first group as an example, the chloride decreased from 10 mM to 9.88 mM in the 8-hour electrolysis with the Pt anode; while it decreased to nearly 1.0 mM with the same initial concentration in a BDD electrochemical cell [22]. It indicates that both the direct and the indirect oxidation of chloride are much slower in the Pt system.

Formation of the chloroform was determined and it followed a characteristic trend as reaction intermediate: there was an initial increase followed by a slow decrease or stable trend. The amount at 2 h of the 16 sets of experimental trials was given in Fig. 3 (b) (The interval point was selected due to the reason that the trend of chloroform was generally in the upward at 2 h for all the trials). ANOVA analysis showed that the factor of current density affected greatest in the formation of chloroform, indicating its significant role in available chlorine production, which reacted effectively with BPA and then transformed to the precursor of chloroform (figure not given here). Also, current density played an important role in other chlorinated byproducts, such as chlorate and perchlorate. Jung et al. [39] reported the generation of chlorate and perchlorate with Ti/Pt anode at a current density of 270 mA cm^{-2}, while none of chlorate or perchlorate was detected in our electrolysis experiment, which might be due to the relatively low current density and the different oxidation mechanism with the Pt electrolysis system [21, 24, 27].

Production of active chlorine was also determined in the orthogonal experiment (Fig. 3(c)). For the groups with 10 mM chloride concentration and low current density, the concentration of free active chlorine is negligible (maximized at 0.037 mM at 360 min). And the lower the initial chloride concentration, the less the transformation of chlorine, indicating the production of active chlorine was mass transfer control to a certain extent. Active chlorine yield increased with the increasing chloride concentration, which promoted reactions of chlorine with organics and other species and thus led to an increase of DBPs formation.

Finally, a balance of chlorine was conducted, including the chloride ions, the production of the active chlorine and the formation of Cl-products, and the data of the 16th group was described here (Fig. 3(d)). As the chloride concentration decreased from 40 mM to 35.92 mM in 480 min, the active chlorine displayed a characteristic trend of increasing first (1.68 mM at 360 min) and then decreasing (1.04 mM at 480 min); while the production of the Cl-products kept increasing. The Cl-products involved chloroform, and all the other Cl-containing intermediates generated during the electrochemical oxidation. Even in high levels of current density and chloride concentration, the depletion of chloride was much slower in the Pt system compared with our previous study with the BDD anode (90 % of the initial chloride was converted to other forms of chlorine in 480 min) [22].

[Insert "Fig. 3" about here]

3.3 Degradation mechanisms analysis

Hydroxyl radical is the main important species produced in the chloride-free electrochemical cell [21]. In the case of Pt anode, formation of a passivating film consisting mainly of chlorinated aliphatic acids poisons the anode surface and diminishes the removal efficiency [17]. Hermes and Knupp [10], and Cui et al. [9] have illustrated elaborately the degradation pathways of BPA with several anodes in Na_2SO_4 electrolyte solution. To the best of the author's knowledge, the mechanism of BPA degradation by electrochemical oxidation in chloride system has not yet been well reported. It is clear that no complete mineralization was achieved in the electrochemical experiments, as can be seen in the UV spectra (Fig. 4) and the GC/MS results.

[Insert "Fig. 4" about here]

The original UV–vis absorption peaks of initial BPA solution mainly consist of two peaks around 225 and 275nm (Fig. 4), and they are, respectively, ascribed to the presence of benzene ring and hydroxyl group in the BPA molecule [10]. And these two absorption bands were diminished very fast with the increase of the reaction time. Meanwhile, a new peak is observed around 230 nm, reflecting the formation of intermediates with aromatic rings [40-41]. As the electrolysis proceeded, these signals gradually decreased but not disappeared, indicating that the aromatic intermediates still in the solution exist in very low concentrations [10].

Due to its endocrine-disrupting properties, BPA is suspected to represent a danger for a wide range of living organisms. However, there is no report about the estrogenicity of chlorinated BPA compared with the original BPA in the electrochemical cell. As a result, the acute toxicity of the samples was determined through the electrochemical degradation of BPA (Inset of Fig. 4). With a luminous inhibition rate of 56.64% for the initial BPA concentration (0.02 mM), the luminous inhibition rate decreased to negative values rapidly with the undergoing of the electrochemical oxidation in 30 min. This was in accordance of the HPLC detection and the UV-visible spectra of BPA which was degraded rather rapidly. And after that the acute toxicity disappeared with a luminous inhibition rate of a minus value even the electrolysis experiment lasted for as long as 720 min. It has been assumed that and the present data have proved the assumption that chlorination of BPA weakened its acute toxicity [41] and demonstrated the applicability of this electrochemical technology for the treatment of BPA solutions without formation of more dangerous compounds at the end of the process.

The main intermediates detected in the electrochemical degradation of BPA in chloride electrolyte with the Pt anode were listed in Table 4. As for the acute toxicity of chlorinated BPA, the oral LD50 values for M7 are 7432 and 5050 mg/kg for rats and mice, respectively, lower than those for BPA (3250 and 2500 mg/kg) [42]. Further, considering the extremely trace amounts of the intermediates and their toxicity characteristics, the luminous inhibition rate decreased rapidly in the whole process [43]. A similar trend was reported in the $S_2O_8^{2-}$/UV-C treatment of BPA for the acute toxicity determination with the *V. fischeri* bioassay, in which a rapid and steady reduction in toxicity was observed [44]. Deborde and von Gunten [45] reported that oxidation, addition and electrophilic substitution reactions are possible pathways for active chlorine with organic compounds, while usually only electrophilic attack is significant from a kinetic point of view. Moreover, the two electron-rich centers of the structure in BPA can be easily attacked by the active radicals produced in the electrolysis system [10]. As illustrated above, the main important species of the hydroxyl radical produced in the chloride-free electrochemical cell has an extremely great reaction rate constant (around 10^9 M^{-1} s^{-1}) with both the organic compounds and chlorine in the electrolyte [46-47]. As a result, although the rate constant of active chlorine with BPA is 3×10^4 M^{-1} s^{-1} [26], the intermediates were almost chlorinous in the chloride-containing electrolysis system.

[Insert "Table 4" about here]

As a result, the first step is electrophilic substitution on the aromatic ring. Notable organochlorines were formed and detectable at 5 min such as dichloroBPA (M6) (mainly 2, 2'-D_2CBPA, due to the reason that this intermediate has a fragment ion at m/z 153 and lack those at m/z 119 and 187, while each aromatic ring bears on chlorine atom [42]) and tetrachloroBPA (T_4CBPA, M7) when the reaction started immediately (Fig. 5 (a)). Either trichloroBPA (T_3CBPA) or monochloroBPA was detected in this experiment, which might be due to the reason that the reaction of electrophilic substitution of chlorine occurred quite fast due to the plentiful chorine in this system; or the extraction procedure was ineffective to detect the very low concentrations of these byproducts. And chlorine reactivity is limited to particular sites (mainly activated aromatic systems) and small modifications in the parent compound's structure are expected for the primary attack [45]. The identified chloride-containing intermediates were also detected in traditional chlorination systems [26, 42]. It was reported that D_iCBPA (2, 2'-D_2CBPA and 2, 6-D_2CBPA) and T_4CBPA in the traditional chlorination of 5 μM BPA reached their maximum of 2.5 μM equiv BPA, respectively, in the few research about the quantity analysis of intermediates [26]. In our electrochemical oxidation of BPA (0.02 mM) with Pt anode, 2, 2'-D_2CBPA and T_4CBPA concentration reached a maximum of 2.46 and 10.00 μM equiv BPA, respectively, which is rather lower compared with traditional treatment. It might be due to that the chlorine enhances the production of these byproducts and also contributes to their further transformation meantime, which occurred with a fast rate in the electrolysis system.

[Insert "Fig. 5" about here]

These chlorinated BPAs were then transformed into one-ring aromatic compounds through the isopropylidene bridge cleavage. Fig. 5 showed the rapid formation of benzoic byproducts followed by slower disappearance of M6 and M7 with the electrolysis time. 2,6-dichlorophenol (M3), 1,4-dione, 2,6-dichloro-2,5-cyclohexadiene (M4), 2,4,6-trichlorophenol (M5) were detected in this experiment (Fig. 5 (b)). The formation of M3 was quite fast and reached its maximum value at the 5 min, which was half-decreased in 120 min and then nearly keeping stable in the next 360 min. M4 and M5 were formed relatively slowly from the initial 5 min of the electrolysis and then largely increased (maximized at 120 min) while the concentration of M6 and M7 decreased at the same time. Yamamoto and Yasuhara [42], who studied the traditional chlorination of BPA, also found this compound as a degradation product. It was found that the rate constants of chlorination reactions of phenol were gradually decreased with the number of chlorine substituted on the aromatic ring. For example, the rate constant of chlorination of chlorophenol to dichlorophenol was in the range of $2.17\text{-}2.42\times10^{3}$ $M^{-1}s^{-1}$, while it decreased to $1.94\text{-}3.03\times10^{2}$ $M^{-1}s^{-1}$ in its further chlorination to trichlorophenol [45]. As a result, the formation of M5 was delayed obviously compared with that of M3.

Finally, the aromatic ring opened and low molecular chlorinated compounds were formed. In this study, 2,3-dichloro-2-methyl-butane (M1) was detected since 60 min after the electrolysis started, and 1,3-dichloro-2-propanone (M2) was not produced until the 120 min of the reaction. M1 achieved its peak value at 120 min and then decreased partially to the end of the experiment. For M2, it kept an increasing trend during the whole 480 min of the electrolysis, indicating its continuous generation in the system.

Above all, there were some common intermediate structures between traditional chlorination and electrochemical oxidation with chloride electrolyte in this study; however, the two processes exhibited their own different reaction mechanism.

4. Conclusions

In the studied electrochemical system with the Pt anode, factor effects on BPA degradation rate was in the order of current density > initial BPA concentration > chloride concentration, based on the ANOVA of the $L_{16}(4)^3$ orthogonal test array design. Further, it was found that the oxidation of chloride was much slower and neither chlorate nor perchlorate was detected in this Pt system, while current density influenced greatest in the formation of chloroform due to the amount of active chlorine affected by the current density. Besides, the acute toxicity decreased to negative values rapidly in 30 min. According to the intermediates detected from GC/MS, it was concluded that with the generation of chlorinated-BPA (2, 2'-D_2CBPA and T_4CBPA), their transformation to one-ring aromatic compounds (2,6-dichlorophenol, 2,6-dichloro-2,5-cyclohexadiene, 2,4,6-trichlorophenol) occurred at the same time. Finally, to the end of the experiment (480 min), chlorinated-BPA was totally transformed and low molecular chlorinated compounds were detected.

Acknowledgments

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Figure captions

Fig.1. Degradation of BPA in the $L_{16}(4)^3$ orthogonal design

Fig. 2. Main effect plot of the mean values for the three influencing factors

Fig.3. Chorine evolution during the electrochemical oxidation with the $L_{16}(4)^3$ orthogonal design. (a) concentration of chloride, (b) active chlorine generated in the electrolysis, (c) chloroform formation at 2 h, (d) chlorine distribution at different intervals of the 16th group experiment.

Fig.4. UV-visible spectra for bisphenol A solution degradation by electrochemical degradation with Pt anode. Inserted: acute toxicity variation during the electrolysis. (current density: 40 mA cm^{-2}, initial BPA concentration: 0.02 mmol L^{-1}, chloride concentration: 40 mmol L^{-1})

Fig.5. Degradation of BPA and formation of intermediates in the electrochemical oxidation with Pt anode (current density: 40 mA cm^{-2}, initial BPA concentration: 0.02 mmol L^{-1}, chloride concentration: 40 mmol L^{-1})

Fig.1.

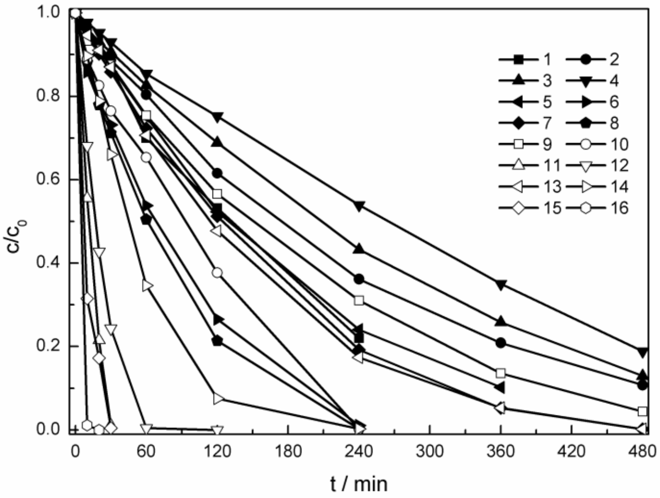

c/c$_0$
t / min
0.0
0.2
0.4
0.6
0.8
1.0
0
60
120
180
240
300
360
420
480
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Fig. 2.

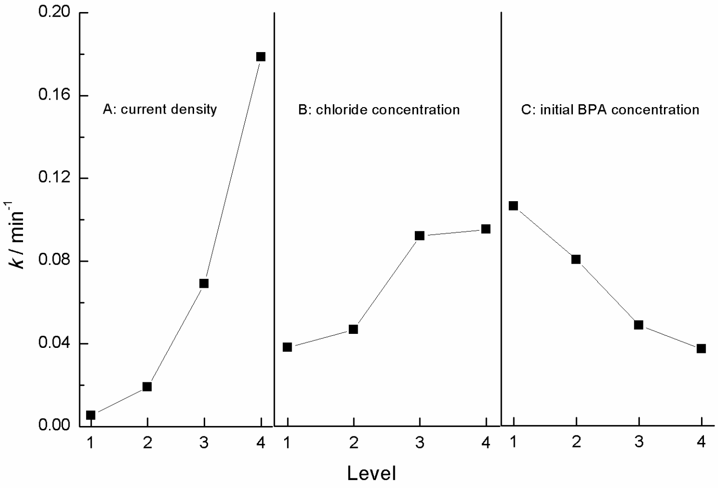

k / min^{-1}
0.00
0.04
0.08
0.12
0.16
0.20
A: current density
B: chloride concentration
C: initial BPA concentration
1
2
3
4
Level

Fig.3.

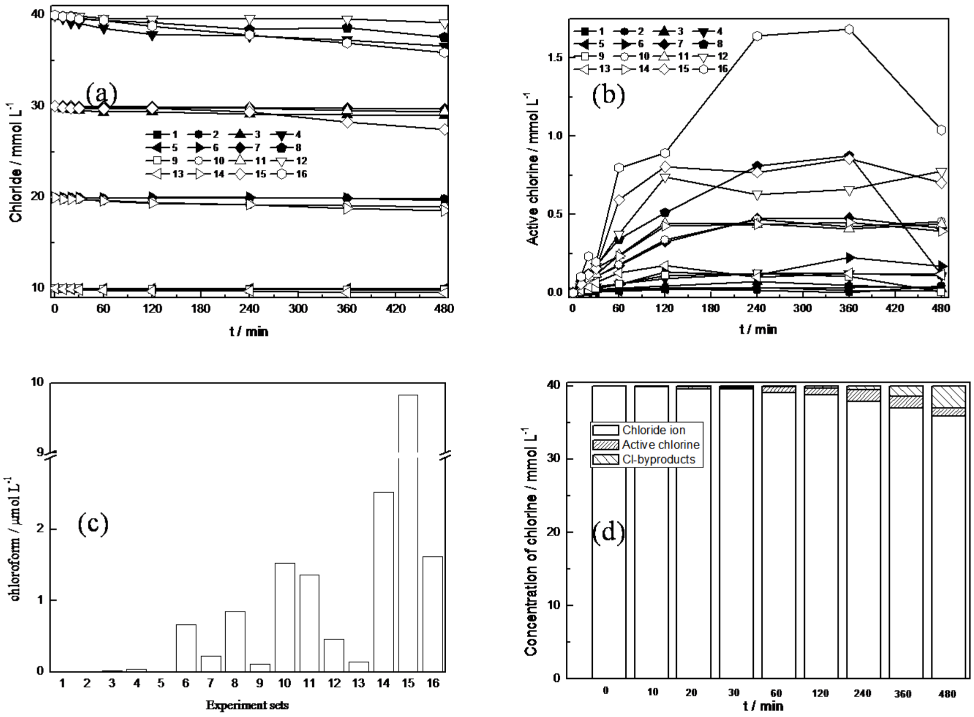

(a)
Chloride / mmol L^{-1}
t / min
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(b)
Active chlorine / mmol L^{-1}
t / min
(c)
chloroform / μmol L^{-1}
Experiment sets
(d)
Concentration of chlorine / mmol L^{-1}
Chloride ion
Active chlorine
Cl-byproducts
t / min

Fig.4.

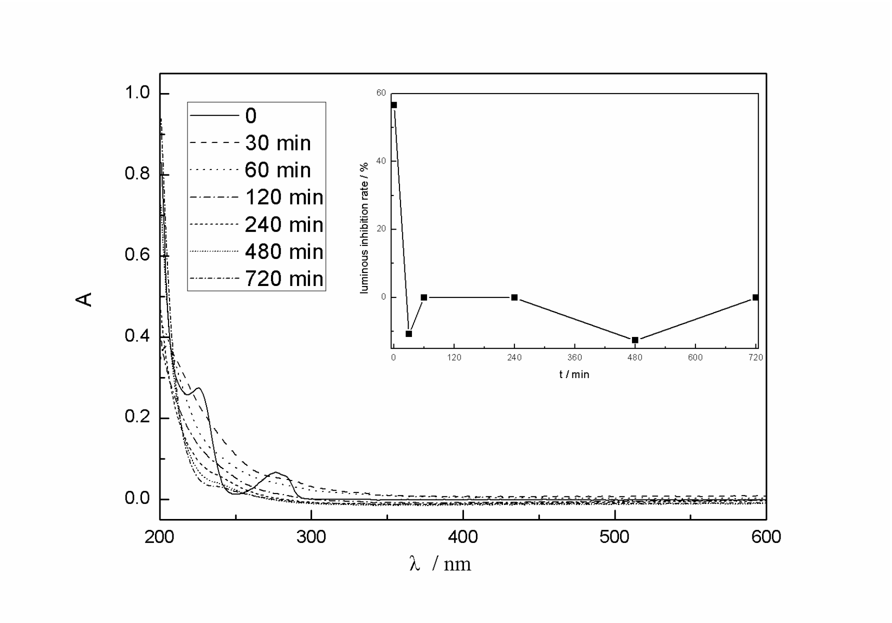

A
λ / nm
0
30 min
60 min
120 min
240 min
480 min
720 min
luminous inhibition rate / %
t / min

Fig.5.

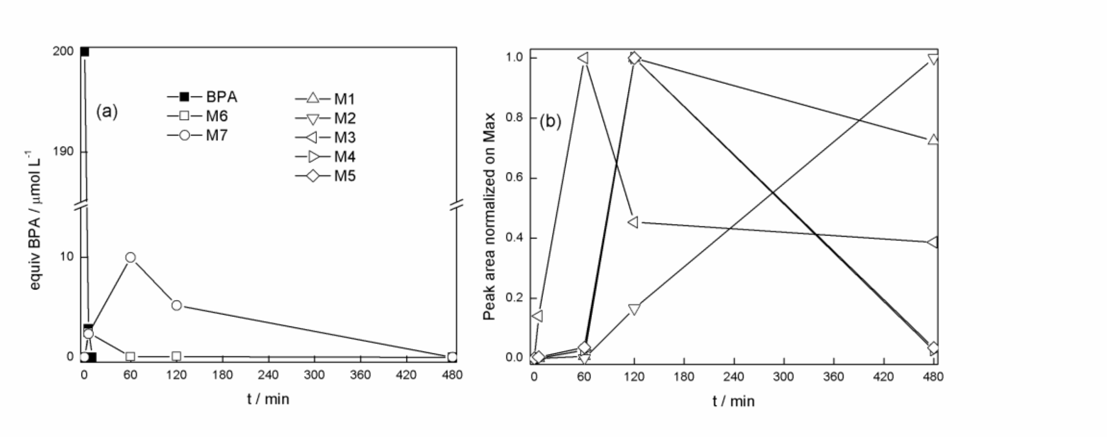

(a)
equiv BPA / μmol L⁻¹
200
190
10
0
BPA
M6
M7
M1
M2
M3
M4
M5
0
60
120
180
240
300
360
420
480
t / min
(b)
Peak area normalized on Max
1.0
0.8
0.6
0.4
0.2
0.0
0
60
120
180
240
300
360
420
480
t / min

Table 1 The $L_{16}(4)^3$ orthogonal array applied for BPA degradation

Level	A	B	C
	Current density (mA cm^{-2})	NaCl concentration (mmol L^{-1})	Intial BPA concentration (mmol L^{-1})
1	10	10	0.02
2	20	20	0.05
3	30	30	0.08
4	40	40	0.11

Table 2 The $L_{16}(4)^3$ orthogonal array and results applied for BPA degradation

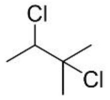
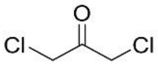
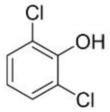
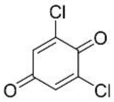
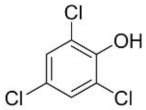
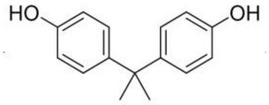
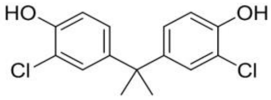
Run	A(mA cm^{-2})	B (mmol L^{-1})	C (mmol L^{-1})	k_i-BPA (min^{-1})	CE(%)
1	10	10	0.02	0.009	6.54
2	10	20	0.05	0.005	7.21
3	10	30	0.08	0.004	7.72
4	10	40	0.11	0.003	15.71
5	20	10	0.05	0.015	2.38
6	20	20	0.02	0.018	2.32
7	20	30	0.11	0.011	7.55
8	20	40	0.08	0.032	6.49
9	30	10	0.08	0.018	4.34
10	30	20	0.11	0.024	8.67
11	30	30	0.02	0.143	4.16
12	30	40	0.05	0.091	4.65
13	40	10	0.11	0.110	8.79
14	40	20	0.08	0.140	6.09
15	40	30	0.05	0.210	8.09
16	40	40	0.02	0.255	5.60

Table 3 ANOVA analysis of the $L_{16}(4)^3$ orthogonal array [a]

Source	SS	Df	F	$F_{0.05}$	Significant
A	0.074	3	108.052	3.49	0.00
B	0.011	3	15.507		0.003
C	0.012	3	17.158		0.002

[a] $R^2 = 0.980$

Table 4 Main intermediates detected in the electrochemical degradation of BPA in chloride electrolyte

No	Retention time / min	Chemical name	Molecular formula
M1	8.83	2,3-dichloro-2-methylbutane	
M2	11.93	1,3-dichloro-2-propanone	
M3	19.78	2,6-dichloro-phenol	
M4	20.97	1,4-dione, 2,6-dichloro-2,5-cyclohexadiene	
M5	24.32	2,4,6-trichloro-phenol	
BPA	39.68	4,4'-(1-methylethylidene)-bisphenol	
M6	40.43	4,4'-isopropylidene-bis(2-chlorophenol)	
M7	43.75	4,4'-(1-methylethylidene)-bis(2,6-dichlorophenol)