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Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode

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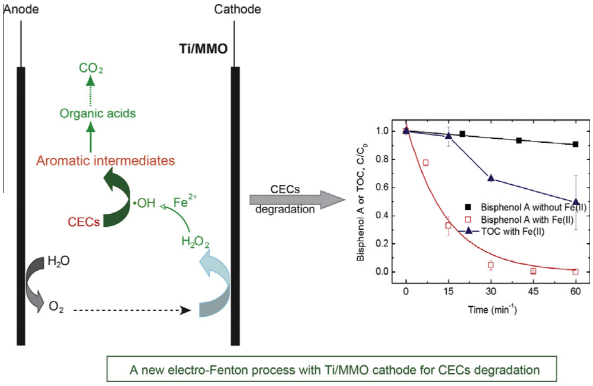
HIGHLIGHTS

- A new electro-Fenton process with Ti/MMO cathode is developed.
- Contaminants of emerging concerns are effectively degraded.
- Influence of operating parameters is investigated.
- Degradation mechanisms and pathways are proposed.
- Contaminants are quickly transformed to nontoxic aliphatic acids.

GRAPHICAL ABSTRACT



A new electro-Fenton process with Ti/MMO cathode for CECs degradation

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ABSTRACT

The performance of a new electro-Fenton process with Ti-based mixed metal oxides (Ti/MMO) cathode, a dimensionally stable electrode, is evaluated for degrading contaminants of emerging concerns (CECs) in aqueous solutions. Bisphenol A (422 $\mu g\ L^{-1}$) is completely degraded in an undivided cell using Ti/MMO as the cathode in the presence of 6.9 $mg\ L^{-1}$ Fe^{2+} within 20 min under conditions of pH 4 and 25 mA. Both bisphenol A degradation and H_2O_2 production increase with decreasing solution pH and increasing current. Ti/MMO cathode is effective for reducing O_2 to H_2O_2 and regenerating Fe^{2+} from Fe^{3+}. ·OH radicals are validated to be the predominant reactive oxygen species (ROS) contributing to bisphenol A degradation. This new electro-Fenton process is also effective for degrading bisphenol A, triclosan and ibuprofen even at a relatively high concentration of 5 $mg\ L^{-1}$. The partial removals of total organic carbon suggest a moderate extent of mineralization. The transformation pathways of the three CECs are proposed based on the intermediates identified by HPLC and GC–MS, showing that CECs are mainly transformed to nontoxic aliphatic acids. This study demonstrates that Ti/MMO can be used as the cathode in the electro-Fenton process for degrading CECs at trace levels in waters.

1. Introduction

Contaminants of emerging concern (CECs), such as endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs), are frequently detected in aquatic environments (Daughton and Ternes, 1999; Sumpter and Johnson, 2005; Schwarzenbach et al., 2006; Pal et al., 2010). CECs can cause severe adverse effects on humans and wildlife, therefore elimination of

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CECs is a major issue in environmental and health risk management (Daughton and Ternes, 1999; Sumpter and Johnson, 2005; Kidd et al., 2007). Traditional water and wastewater treatment processes are not designed to eliminate CECs, especially at the trace levels as those present in drinking water and aquatic environment (Sedlak et al., 2000; Jones et al., 2005). Current processes that have been proposed for removing CECs in wastewaters mainly include adsorption, biodegradation and membrane filtration (Bolong et al., 2009; Liu et al., 2009). The wide range categories of CECs suggest that they have varying susceptibility to different treatment processes. Therefore, the removal efficiencies of CECs by various treatment processes depend on their properties. Membrane filtration is effective but costly for removal of trace levels of CECs (Bolong et al., 2009). Developing cost-effective technologies for eliminating the harmful effects of various CECs is thus of great interest to the environmental field.

Advanced oxidation processes (AOPs), such as photocatalysis (Roseneeldt and Linden, 2004), ozonation (Zhang et al., 2008), chlorine dioxide (Van den Heuvel et al., 2006), Fenton-based process (Gözmen et al., 2003; Dirany et al., 2012) and other strong oxidants (Jiang et al., 2012), are reported to be effective for degrading CECs. Among the AOPs, electro-Fenton processes have attracted particular interests because hydroxyl radicals (·OH, oxidation potential of 2.8 V/NHE) are continuously generated from the combination of H_2O_2, which is produced from two-electron reduction of O_2 on the cathode (Eq. (1)), with Fe^{2+} added externally (Eq. (2)) (Gözmen et al., 2003; Brillas et al., 2009; Wang et al., 2010; Dirany et al., 2012; Sirés and Brillas, 2012). Regeneration of Fe^{2+} is also effective due to the reduction of Fe^{3+} on the cathode (Eq. (3), Brillas et al., 2009). ·OH radicals are the most powerful reactive oxygen species (ROS) that can oxidize organic contaminants unselectively at a diffusion-controlled rate. Gas-diffusion electrodes (GDEs) or porous carbon are most commonly used as the cathode in electro-Fenton processes to enhance H_2O_2 production (Brillas et al., 2009; Wang et al., 2010; Sirés and Brillas, 2012). However, these porous electrodes have a low mechanical and chemical stability suggesting a limit for practical and large-scale applications. In addition, as the concentrations of CECs in water are generally at a trace level of μg L^{-1} (Daughton and Ternes, 1999; Sumpter and Johnson, 2005; Schwarzenbach et al., 2006; Pal et al., 2010), production of H_2O_2 with concentration levels on the order of tens or hundreds of mg L^{-1} by GDEs cathode (Brillas et al., 2009) may not be advantageous or cost-effective.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^{\theta} = 0.695\,\mathrm{V/NHE} \qquad (1)$$

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + {}^{\cdot}OH + H_2O \qquad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (3)$$

Ti-based mixed metal oxides (Ti/MMO) are the most stable electrode materials that have been used as dimensionally stable electrodes (DSE) in large-scale industrial applications (Kong et al., 2009). In the environmental field, Ti/MMO is used as the anode to degrade organic contaminants in wastewaters (Zhou et al., 2012). Ti/MMO is also used as the cathode to reduce chlorinated and nitro compounds in groundwater (Gilbert and Sale, 2005; Petersen et al., 2007). However, Ti/MMO has never been used as the cathode for O_2 reduction in electro-Fenton processes because of its small specific surface area. As the oxidation potential of O_2 (0.695 V/NHE) is comparable with the chlorinated and nitro compounds that are reduced by Ti/MMO cathode (Gilbert and Sale, 2005; Petersen et al., 2007), it is rational to hypothesize that Ti/MMO has the potential to reduce O_2 for H_2O_2 production in aqueous solutions under controlled conditions. In the traditional electro-Fenton processes, O_2 is injected externally into the cathode surface to produce high concentrations of H_2O_2. Because concentrations of CECs in water are generally in a low level of several or tens of μg L^{-1} (Daughton and Ternes, 1999; Sumpter and Johnson, 2005; Schwarzenbach et al., 2006; Pal et al., 2010), the O_2 produced on the anode mostly contributes to production of H_2O_2 for CECs degradation (Oturan et al., 2001), thus avoiding the injection of O_2.

In this study, Ti/MMO was used as the cathode to reduce anodic O_2 for production of H_2O_2 under acidic conditions. The performance of this new electro-Fenton process was tested for degrading three CECs, namely bisphenol A, triclosan and ibuprofen. The effect of operating parameters on CECs degradation was evaluated using bisphenol A as a representative. The degradation mechanisms were elucidated by analyzing the predominant ROS produced in the process. The degradation pathways of the three CECs were ultimately proposed through identifying the main degradation intermediates using HPLC and GC–MS.

2. Materials and methods

2.1. Chemicals

Bisphenol A, 4-chlorocatechol (97%), 4-chlororesorcinol (98%), chloro-p-benzoquinone (95%) and 4-isobutylacetophenone were purchased from Sigma–Aldrich. Ibuprofen (99%), 2,4-dichlorophenol (99%), 4-ethylbenzadehyde (98%), resorcinol (98%), chlorohydroquineone (90%), catechol (99%) and benzoqinone (99%) were supplied by Acros. Triclosan (99.7%) was from Calbiochem and hydroquinone was from Fischer Sci. Deionized (DI) water (18.2 MΩ cm) obtained from a Millipore Milli-Q system was used in all the experiments. All the chemicals used in this study were above analytical grade.

2.2. Electro-Fenton degradation of CECs with Ti/MMO cathode

A 600-mL acrylic cell was used for the electro-Fenton degradation of CECs at ambient temperature (25 ± 1 °C). Two mixed metal oxide sheets (MMO, IrO_2/Ta_2O_5 coating on titanium mesh type, 3 N International, USA), with dimension of 85 × 15 × 1.8 mm (length × width × thickness), were used as the anode and the cathode with 42 mm spacing in parallel position. 410 mL of 2 mM Na_2SO_4 solution in DI water was transferred into the cell. Na_2SO_4 was used as the supporting electrolyte to simplify the background influence because of its inert nature. A low concentration of Na_2SO_4 (2 mM) was used to simulate the relatively clean waters containing CECs. Initial solution pH was adjusted by dilute H_2SO_4 and NaOH. Solution pH was not adjusted during treatment. Different initial Fe^{2+} concentrations were attained by addition of specific volume of Fe^{2+} stock solution. Specific volumes of bisphenol A, triclosan and ibuprofen stock solution were added independently to reach the required initial concentrations. Reactions were allowed to continue for 20 min to 1 h in the mode of constant current. Continuous stirring at 600 rpm was maintained using a Teflon-coated magnetic stirring bar. H_2O_2 production in the process was measured under identical conditions but in the absence of CECs and Fe^{2+}. The aqueous solution was taken out at regular time intervals and filtered through a 0.2-μm micropore membrane (Whatman) for analysis of CECs and their degradation products. Selected samples were analyzed for pH, soluble Fe^{2+}, total soluble iron, TOC and ·OH radicals.

2.3. Analysis

Bisphenol A, triclosan, ibuprofen and selected known degradation intermediates were measured by a 1200 Infinity Series HPLC (Agilent) equipped with a 1260 diode array detector (DAD), a

1260 fluorescence detector (FLD) and a Thermo ODS Hypersil C18 column (4.6 × 50 mm) and an Agilent Eclipse AAA C18 column (4.6 × 150 mm). Standard compounds were used for intermediates identification. The mobile phase was a mixture of acetonitrile and water (60:40, v/v) at the flow rate of 1 mL min^{-1}. The detection wavelengths for DAD were set at 210 and 278 nm simultaneously. The excitation and emission wavelengths for FLD were set at 278 and 320 nm, respectively.

H_2O_2 was measured at 405 nm by a spectrometer (Spectronic 20D+, Caley & Whitmore Corp.) after coloration with $TiSO_4$ (Eisenberg, 1943). The soluble Fe^{2+} concentration was determined at 510 nm using the 1,10-o-phenanthroline analytical method (Komadel and Stucki, 1988). Total soluble iron was determined after reduction of ferric ion by hydroxylamine hydrochloride. TOC concentration was detected by a TOC analyzer (TOC-L CPH, Shimadzu). ·OH radicals were assayed by electron spin resonance (ESR). 100 μL sample was taken immediately after the addition of 6.9 mg L^{-1} Fe^{2+} after 10 min electrolysis without contaminants under conditions of initial solution pH of 3 and current of 25 mA. The sample was immediately mixed with 25 μL of 0.2 M DMPO to form a DMPO-radical adduct, which was then measured by a Bruker EMX ESR spectrum with microwave bridge (receiver gain, 5020; modulation amplitude, 2 Gauss; microwave power, 6.35 mW; modulation frequency, 100 kHz; center field: 3525 G).

Aside from the standard compounds comparison by HPLC, intermediates identification was also performed by a GC (Varian 431) equipped with a capillary column (FactorFour™: VF-5 ms, 30 m × 0.25 mm, 0.25 μm) and a mass spectrometer (MS, Varian 220). After 15 min degradation, 400 mL of aqueous solution was acidified to pH < 2 by H_2SO_4 and extracted with 20 mL of chloroform (Murugesan et al., 2010). The extract was dried with anhydrous sodium sulfate. The US National Institute of Science and Technology (NIST) library was used for species identification. Standard compounds of selected intermediates were also used for the identification by HPLC.

3. Results and discussion

3.1. Validation of electro-Fenton process with Ti/MMO cathode

The production of H_2O_2 from the reduction of anodic O_2 on the Ti/MMO cathode was measured. It is recognized that H_2O_2 can be produced from the dimerization of ·OH on anode surface (Guinea et al., 2009) or the reduction of O_2 on Ti/MMO cathode. To evaluate the relative importance of anode and cathode on H_2O_2 production, a divided electrolytic system was employed. Fig. 1a shows that H_2O_2 accumulated significantly and negligibly in the presence and absence of O_2 in the cathodic compartment of a divided electrolytic system, respectively. This suggests that MMO cathode was able to reduce O_2 to H_2O_2, although the concentrations were relatively low (<1 mg L^{-1}). In comparison, no H_2O_2 accumulated in the anodic compartment under identical conditions (Fig. 1a), precluding the possibility of H_2O_2 production from the dimerization of ·OH on MMO anode. The current efficiency of Ti/MMO cathode for H_2O_2 production increased with increasing time but was less than 7% in the tested duration time (Fig. SM-1), which is much lower compared with those using GDEs (Brillas et al., 2000; Brillas and Casado, 2002).

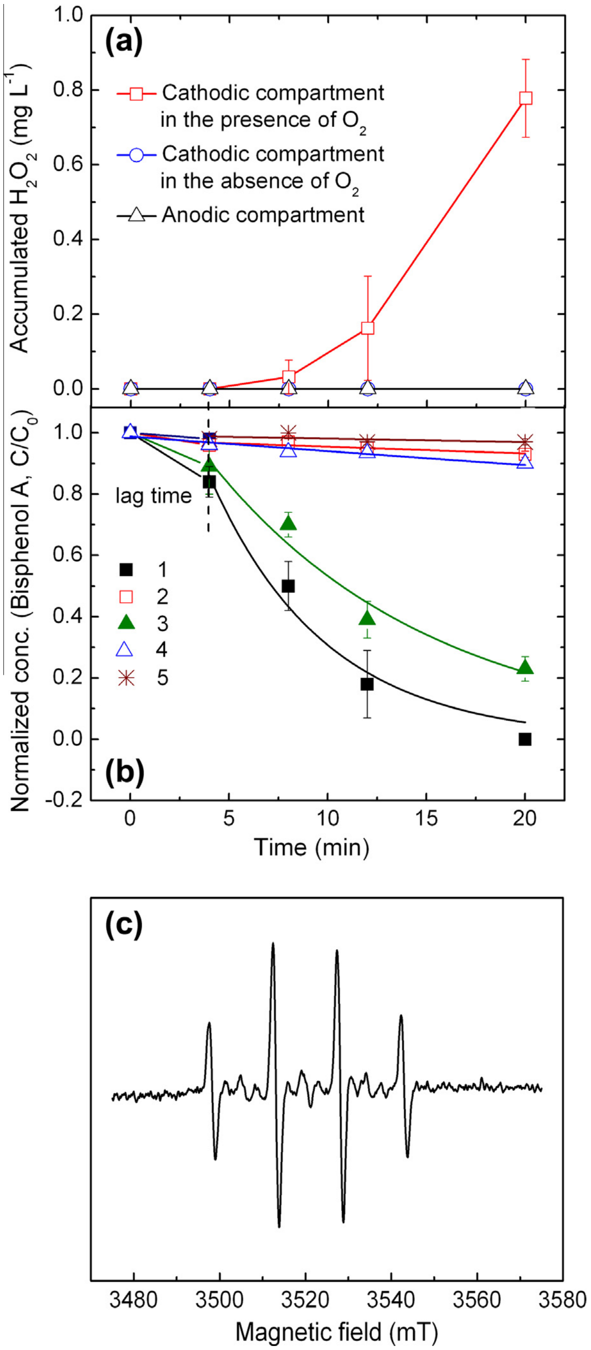


Fig. 1. (a) Production of H_2O_2 in the cathodic compartment of the divided cell, (b) degradation of bisphenol A under different conditions and (c) ESR signals for the electro-Fenton system. In (b), Curve 1: Degradation in the undivided cell; Curve 2: degradation in the anodic compartment of divided cell in the presence of Fe^{2+}; Curve 3: degradation after reversing the electrode polarity under condition 2; Curve 4: degradation in the cathodic compartment of divided cell in the absence of Fe^{2+} and O_2; Curve 5: degradation in the undivided cell after scavenging strong ROS by addition of 60 mM methanol. Unless otherwise specified, the degradation kinetics were based on 422 μg L^{-1} bisphenol A, 6.9 mg L^{-1} Fe^{2+}, solution pH of 3, 25 mA, and 2 mM Na_2SO_4 background electrolyte. Curves refer to pseudofirst-order kinetic fittings.

The degradation of bisphenol A was compared in the undivided and divided electrolytic system. Significant degradation was attained in the undivided electrolytic cell under conditions of 6.9 mg L^{-1} Fe^{2+}, pH 3, 25 mA and 422 μg L^{-1} initial concentration (Curve 1 in Fig. 1b). However in the divided electrolytic system, minimal degradation was observed in the anodic compartment with addition of Fe^{2+} (Curve 2 in Fig. 1b), ruling out the contribution of anodic oxidation and the production of H_2O_2 at the MMO anode. In comparison, the degradation was significant in the cathodic compartment in the presence of Fe^{2+} and O_2 (Curve 3 in Fig. 1b), which is consistent with the feature of cathodic electro-Fenton process. The minimal degradation in the cathodic compartment in the absence of Fe^{2+} and O_2 (Curve 4 in Fig. 1b) proves that bisphenol A cannot be reduced by the direct cathodic reduction. Therefore, we conclude that H_2O_2 was produced from the reduction of O_2 on Ti/MMO cathode, thereby contributing to bisphenol A degradation in the presence of Fe^{2+}.

The generation of ROS, presumably $\cdot$OH, was validated by radical scavenging experiments and ESR assay. Methanol is effective in scavenging strong oxidizing radicals such as $\cdot$OH (Guan et al., 2011). By the addition of 60 mM methanol to the undivided cell under conditions of 6.9 mg L^{-1} Fe^{2+}, pH 3 and 25 mA, the degradation of bisphenol A was completely inhibited (Curve 5 in Fig. 1b). This scavenging effect indicates that strong oxidizing radicals were responsible for the degradation. Moreover, ESR assay reveals the appearance of characteristic 1:2:2:1 signals with hyperfine coupling constants of $a^N = 14.9$ G and $a^H = 14.9$ G when Fe^{2+} was added to the electrolytic cell. These characteristic signals can be assigned to result from DMPO/$\cdot$OH adduct (Fig. 1c) (Guan et al., 2011; Ranguelova et al., 2012). As a consequence, $\cdot$OH radicals, which were produced from H_2O_2 and Fe^{2+}, are the predominant reactive oxygen species contributing to bisphenol A degradation. The above results validate that electro-Fenton process is successfully developed using Ti/MMO as the cathode.

3.2. Effect of Fe^{2+} concentration on bisphenol A degradation

Using bisphenol A as a representative of CECs, the effect of Fe^{2+} concentration on the electro-Fenton degradation of degradation of bisphenol A with Ti/MMO cathode was evaluated in the undivided cell. Fig. 2a shows that the degradation of bisphenol A is significantly affected by the concentration of Fe^{2+}. A slow degradation is observed within the initial 4 min, which can be ascribed to the time required for O_2 transport from the anode to the cathode surface. The degradation is fast after 4 min, following pseudofirst-order kinetics for all the reactions ($R^2 \geqslant 0.969$) except 0 mg/L Fe^{2+}. The degradation was negligible in the absence of Fe^{2+}, increased dramatically with increasing Fe^{2+} dosage from 0 to 6.9 mg L^{-1}, and started to decrease with the further increase to 13.7 mg L^{-1}. A good linear correlation between the degradation rate constants of bisphenol A and the Fe^{2+} dosage is observed when less than 6.9 mg L^{-1} Fe^{2+} was added (Fig. SM-2). This suggests that the concentration of Fe^{2+} in the tested range determines the generation of ROS and the degradation of bisphenol A. The soluble Fe^{2+} concentration increased with increasing Fe^{2+} dosage (Fig. 2b), which supplied more Fe^{2+} for the catalytic cycle of Fenton reaction (Eq. (2)). However, when Fe^{2+} was excess for the catalytic reaction, it competed with bisphenol A for ROS such as $\cdot$OH (Eq. (4)). The remarkable influence of Fe^{2+} on contaminant degradation is consistent with the feature of electro-Fenton processes (Brillas et al., 2009). The concentration of Fe^{2+} that is required for effective degradation is lower than or approximate with those reported (Brillas et al., 2009; Yuan et al., 2012), which is likely due to generation of low concentrations of H_2O_2.

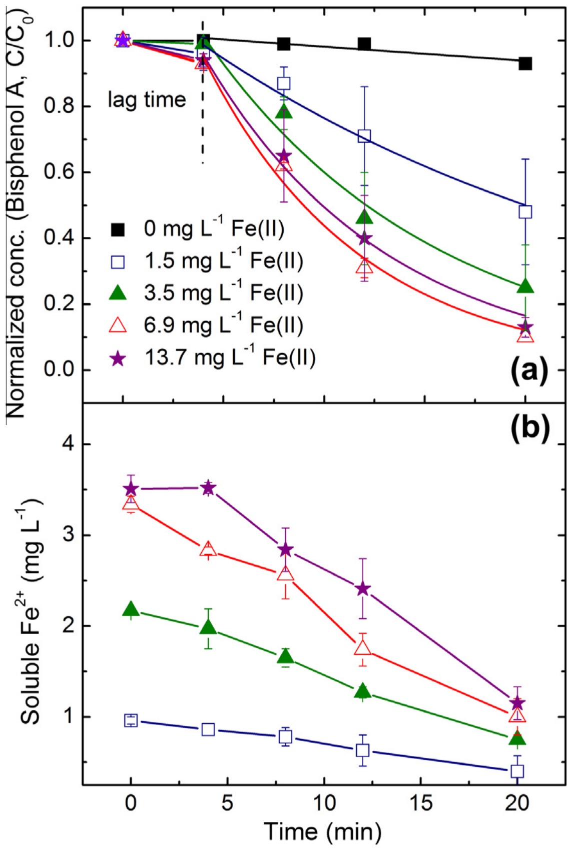


Fig. 2. Effect of Fe^{2+} dosage on (a) bisphenol A degradation and (b) soluble Fe^{2+} concentration variation. The degradation kinetics were based on 422 μg L^{-1} bisphenol A, initial solution pH of 4, 25 mA, and 2 mM Na_2SO_4 background electrolyte. Curves in (a) refer to pseudofirst-order kintic fitting.

$$\cdot OH + Fe^{2+} \rightarrow \cdot OH^{-} + Fe^{+} \quad k = 3.2 \times 10^{8}\, M\, s^{-1} \tag{4}$$

It is notable that soluble Fe^{2+} concentrations are approximate with the total soluble iron concentration (Fig. SM-3), implying the effective regeneration of Fe^{2+} from Fe^{3+}. This can be attributed to the reduction of Fe^{3+} on the Ti/MMO cathode because the regeneration of Fe^{2+} from Fe^{3+} is difficult in the conventional Fenton process (Brillas et al., 2009). The effective regeneration of Fe^{2+} from the reduction of Fe^{3+} on the Ti/MMO cathode (Eq. (3)) is validated by the production of Fe^{2+} using Fe^{3+} as the iron source (Fig. SM-4). Bisphenol A was efficiently degraded when Fe^{3+} instead of Fe^{2+} was used as the iron source (Fig. SM-4). It is noticed that degradation within the initial 4 min is much slower using Fe^{3+} than that using Fe^{2+} as the iron source. This difference is due to the lack of Fe^{2+} in the initial stage using Fe^{3+} as the iron source. Consequently, Ti/MMO can be used as the cathode for both H_2O_2 production and Fe^{2+} regeneration in the electro-Fenton process.

3.3. Effect of solution pH on bisphenol A degradation

Fig. 3a demonstrates that initial solution pH had a pronounced effect on the degradation of bisphenol A. The rate constant increased from 0020 ± 0.000 to 0.032 ± 0.001, 0.129 ± 0.014 and 0.172 ± 0.029 min^{-1} as the initial solution pH dropped from 7.3 to 5.5, 4.0 and 3.0, respectively. The solution pH decreased from the initial values of 7.3, 5.5 and 4.0 to 6.8, 4.4, and 3.9, respectively, and increased from the initial value of 3.0 to 3.1 after treatment. The optimal pH in the tested range for contaminant degradation by the new electro-Fenton process was about 3.0, which is in the range of pH 2.5–3.5 reported for electro-Fenton processes (Gözmen et al., 2003; Brillas et al., 2009; Wang et al., 2010; Dirany et al., 2012; Sirés and Brillas, 2012). Because of the much lower solubility constant of $Fe(OH)_3$ ($pK_{sp} = 38.55$) relative to $Fe(OH)_2$ ($pK_{sp} = 16.31$), regeneration of Fe^{2+} from Fe^{3+} becomes more difficult with the rise of pH due to Fe^{3+} precipitation. So, the concentration of soluble Fe^{2+} decreased quickly at pH 5.5 and was negligible at pH 7.3 (Fig. 3b). In the tested pH range, the soluble Fe^{2+} concentrations are close to the total soluble iron concentrations during the course of degradation (Fig. SM-5), which further supports that the Fe^{2+} can be effectively regenerated from the reduction of Fe^{3+} on the Ti/MMO cathode.

The production of H_2O_2 in the absence of Fe^{2+} was also measured in the tested range of solution pH. The cumulative concentration of H_2O_2 remarkably decreased with the rise of pH

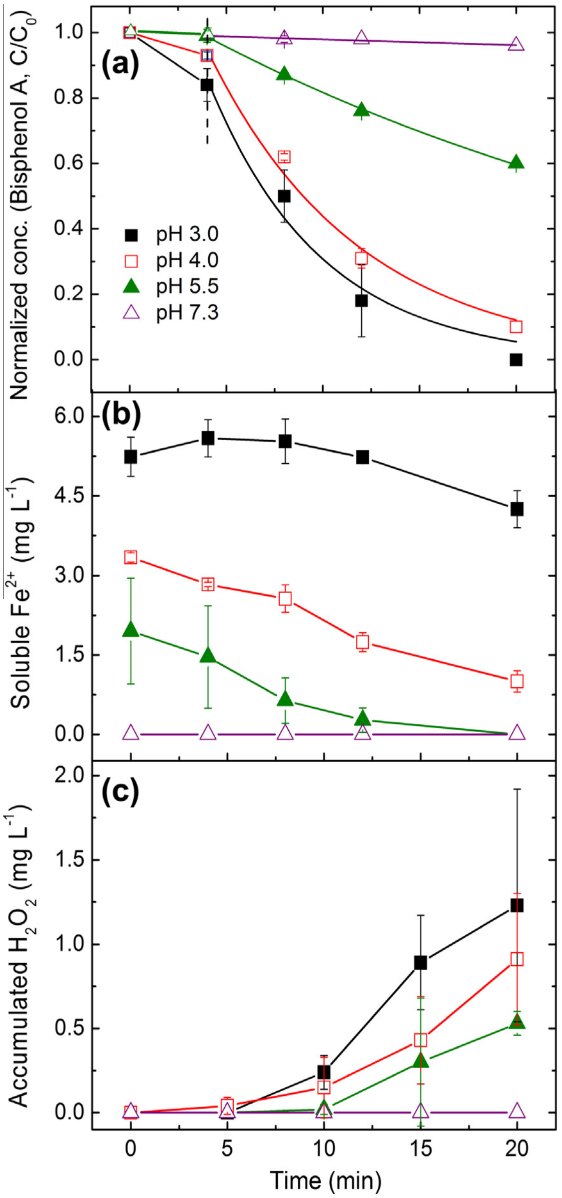


Fig. 3. Effect of initial solution pH on (a) bisphenol A degradation, (b) soluble Fe^{2+} concentration variation and (c) H_2O_2 production. The degradation kintics were based on 422 μg L^{-1} bisphenol A, 6.9 mg L^{-1} Fe^{2+}, 25 mA, and 2 mM Na_2SO_4 background electrolyte. Note in (c), no Fe^{2+} was added for H_2O_2 production. Curves in (a) refer to pseudofirst-order kinetic fitting.

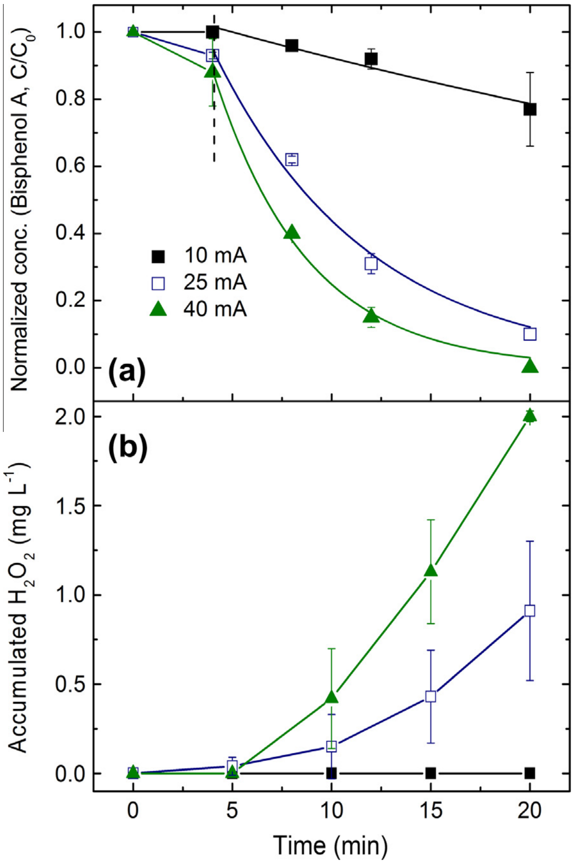


Fig. 4. Effect of current on (a) bisphenol A degradation and (b) H_2O_2 production. The degradation kintics were based on 422 μg L^{-1} bisphenol A, initial solution pH of 4, 6.9 mg L^{-1} Fe^{2+}, and 2 mM Na_2SO_4 background electrolyte. Note in (b), no Fe^{2+} was added for H_2O_2 production. Curves in (a) refer to pseudofirst-order kinetic fitting.

(Fig. 3c). This trend of pH influence on H_2O_2 production was also found in traditional electro-Fenton processes with porous cathode (Brillas et al., 2009). The cumulative concentration of H_2O_2 was always less than 1.3 mg L^{-1}, which is much lower compared with literature where GDEs are used as the cathode (Brillas et al., 2009; Wang et al., 2010). This implies that the Ti/MMO electrode is less effective for H_2O_2 production compared with GDE cathodes. The low cumulative concentration of H_2O_2 is consistent with the aforementioned low optimal dosage of Fe^{2+} required for bisphenol A degradation.

3.4. Effect of current on bisphenol A degradation

Both degradation of bisphenol A (Fig 4a) and production of H_2O_2 (Fig. 4b) are enhanced with increasing the current. As the solution was always exposed to air, the initial dissolved O_2 concentration can be assumed to be the saturated concentration under ambient conditions (0.25 mM). The Ti/MMO electrode used in this study is fabricated by coating IrO_2/Ta_2O_5 on titanium mesh. This type of Ti/MMO anode has a very low O_2 evolution potential (1.12 V vs SCE, Fig. SM-6), so the Faradic current efficiency for O_2 production on the Ti/MMO anode can be supposed to be 100% approximately. As a consequence, the maximum O_2 concentrations in the solution after 20 min electrolysis at 10, 25 and 40 mA were theoretically calculated to be 0.33, 0.45 and 0.57 mM, respectively. Although O_2 was continuously generated on the anode, it was also consumed on the cathode in the mean time. Some fractions of O_2 were even observed to evolve from the solution to the air at the high current of 40 mA. Therefore, supplying more O_2 at higher current may increase the reduction rate of O_2 on the Ti/MMO cathode, accelerating H_2O_2 production. Moreover, higher current may facilitate the electron exchange between the reactants, i.e., O_2, and the cathode surface when surface reaction limits, which further accelerates H_2O_2 production. As H_2O_2 concentrations were very low (Fig. 4b), H_2O_2 was less sufficient for contaminant degradation compared with the concentration of soluble Fe^{2+}. Consequently, the increase in H_2O_2 production with increasing the current significantly contributed to the degradation of bisphenol A.

3.5. Degradation of three CECs by the new electro-Fenton process with Ti/MMO cathode

The new electro-Fenton process with Ti/MMO cathode was further employed to degrade triclosan and ibuprofen. Bisphenol A was also degraded for comparison under identical conditions. The initial concentrations of the three CECs were set at a relatively high

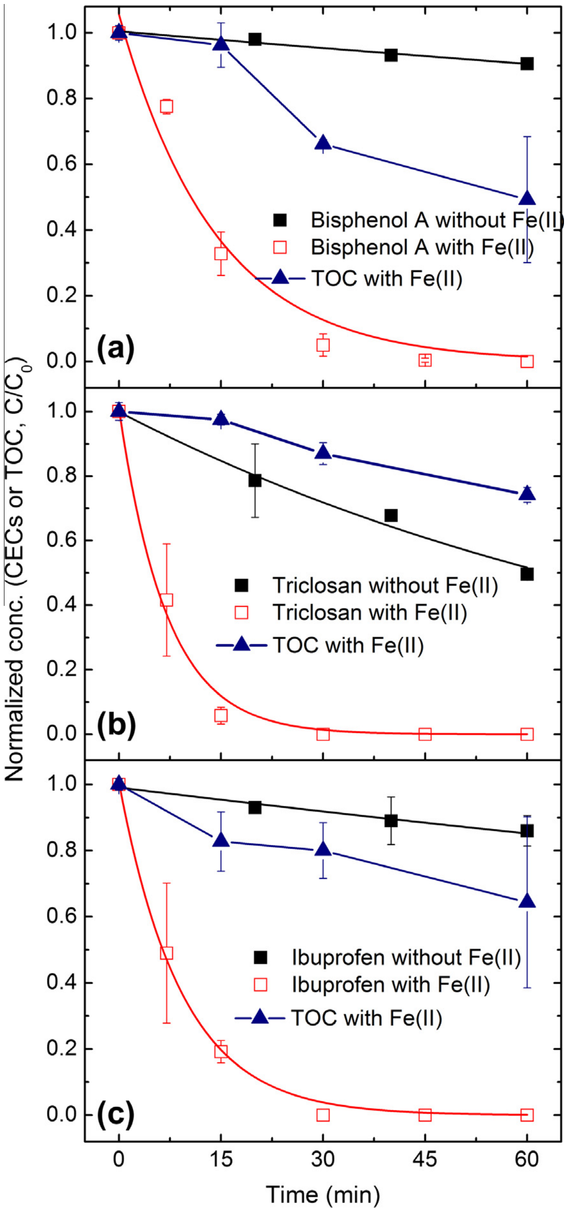


Fig. 5. Degradation of (a) bisphenol A, (b) triclosan and (c) ibuprofen individually by the new electro-Fenton process with Ti/MMO cathode. The degradation kintics were based on 5 mg L^{-1} individual CEC, 6.9 mg L^{-1} Fe^{2+}, initial solution pH of 3, 40 mA, and 2 mM Na_2SO_4 background electrolyte. Curves refer to pseudofirst-order kinetic fittings.

value of 5 mg L^{-1} to improve TOC measurement and intermediates identification. Fig. 5 presents the variations of CECs and TOC concentrations during the course of degradation under conditions of 6.9 mg L^{-1} Fe^{2+}, pH 3 and 40 mA. Control experiments in the absence of Fe^{2+} caused negligible removals of bisphenol A and ibuprofen but 51.4% removal of triclosan within 60 min. The significant removal of triclosan in the absence of Fe^{2+} can be ascribed to the reductive dechlorination on the Ti/MMO cathode (Gilbert and Sale, 2005; Petersen et al., 2007). By the addition of 6.9 mg L^{-1} Fe^{2+}, the removals of the three CECs were greatly enhanced. As summarized in Table SM-1, the pseudofirst-order rate constants for degradations of bisphenol A, triclosan and ibuprofen are 0.071 ± 0.011, 0.143 ± 0.013 and 0.109 ± 0.005 min^{-1}, respectively. The differences of the degradation rates are related to their chemical structures (See Fig. 6 for their structure). Triclosan has two electron-donating groups (–OH and –O–), which greatly activate the benzene ring. Ibuprofen has an *iso*-propionic acid group, in which the *tert*-carbon can be easily attacked by electrophilic ·OH radicals. Bisphenol A has only one electron-donating group (–OH) linked with the benzene ring. As a result, the degradation sequence of triclosan > ibuprofen > bisphenol A was obtained. The removals of bisphenol A, triclosan and ibuprofen attained 95%, 100% and 100%, respectively, for 30 min treatment (Table SM-1). This suggests that the new electro-Fenton process with Ti/MMO cathode is effective for degrading CECs even at a relatively high concentration of 5 mg L^{-1}.

TOC concentrations decreased slightly for degradations of the three CECs (Fig. 5), implying that CECs were mainly transformed to intermediates instead of CO_2. For 60 min degradation, the TOC removals only achieved 51.8%, 26.8% and 35.7% for degradations of bisphenol A, triclosan and ibuprofen, respectively (Table SM-1). The low removals of TOC can be attributed to the low concentrations of H_2O_2 and ·OH generated in the process. The partial removals of TOC for CECs degradation by electro-Fenton processes were also reported in literature (Gözmen et al., 2003; Skoumal et al., 2009). The mineralization current efficiencies (MCE) calculated from TOC variations were 22.7%, 6.1% and 15.7% for degradations of bisphenol A, triclosan and ibuprofen, respectively (Table SM-1), which were in the comparable level as reported using GDE cathodes (Brillas et al., 2000; Boye et al., 2003; Sirés et al., 2007).

3.6. Degradation pathways for the three CECs

As the three CECs were mostly transformed to intermediates by the new electro-Fenton process with Ti/MMO cathode, it is necessary to reveal the fate of these contaminants after treatment. So, the intermediates for degradations of the three CECs were identified by standard compounds comparison in HPLC as well as by GC–MS (See details in Sections SM-1–3). The intermediates identified are listed in Table 1. The degradation pathways are discussed in the following.

3.6.1. Bisphenol A

For the degradation of bisphenol A, the intermediates identified include 1,4-benzoquinone, hydroquinone and 4-isopropenylphenol (Table 1). The initial transformation pathway is depicted in Fig. 6a. Electrophilic attack of the carbon in aromatic ring by ·OH radicals produced 2-(4-hydroxyl-phenyl)-propyl carboncation and hydroquinone. Deprotonation of H^+ from 2-(4-hydroxyl-phenyl)-propyl carboncation produced 4-isopropenylphenol. Under the tested oxidizing conditions, hydroquinone converted to 1,4-benzoquinone. The proposed pathway of bisphenol A transformation is similar to that reported by electro-Fenton degradation using a carbon felt cathode (Gözmen et al., 2003). It is notable that all the intermediates disappeared after 60 min degradation (Fig. SM-7), suggesting the breakage of conjugate structures such as benzene ring. However, the low extent of mineralization indicates the accumulation of aliphatic acids (e.g., acetic acid, formic acid, etc.) which cannot be measured by HPLC at 210 nm (Gözmen et al., 2003). Although TOC removal was not great, accumulation of aliphatic acids suggests the elimination of toxicity since they can be biodegraded easily in the environment.

3.6.2. Triclosan

The intermediates for triclosan degradation were measured to be 4-chlorocatechol, 2,4-dichlorophenol and hydroxylated triclosan (Table 1). The initial transformation pathway is thus proposed in Fig. 6b. The phenolic ring of triclosan, which is activated by the two O-containing groups, was attacked by ·OH radicals, with production of hydroxylated triclosan. Hydroxylated triclosan was further oxidized to 2,4-dichlorophenol and chlorinated polyphenol. In

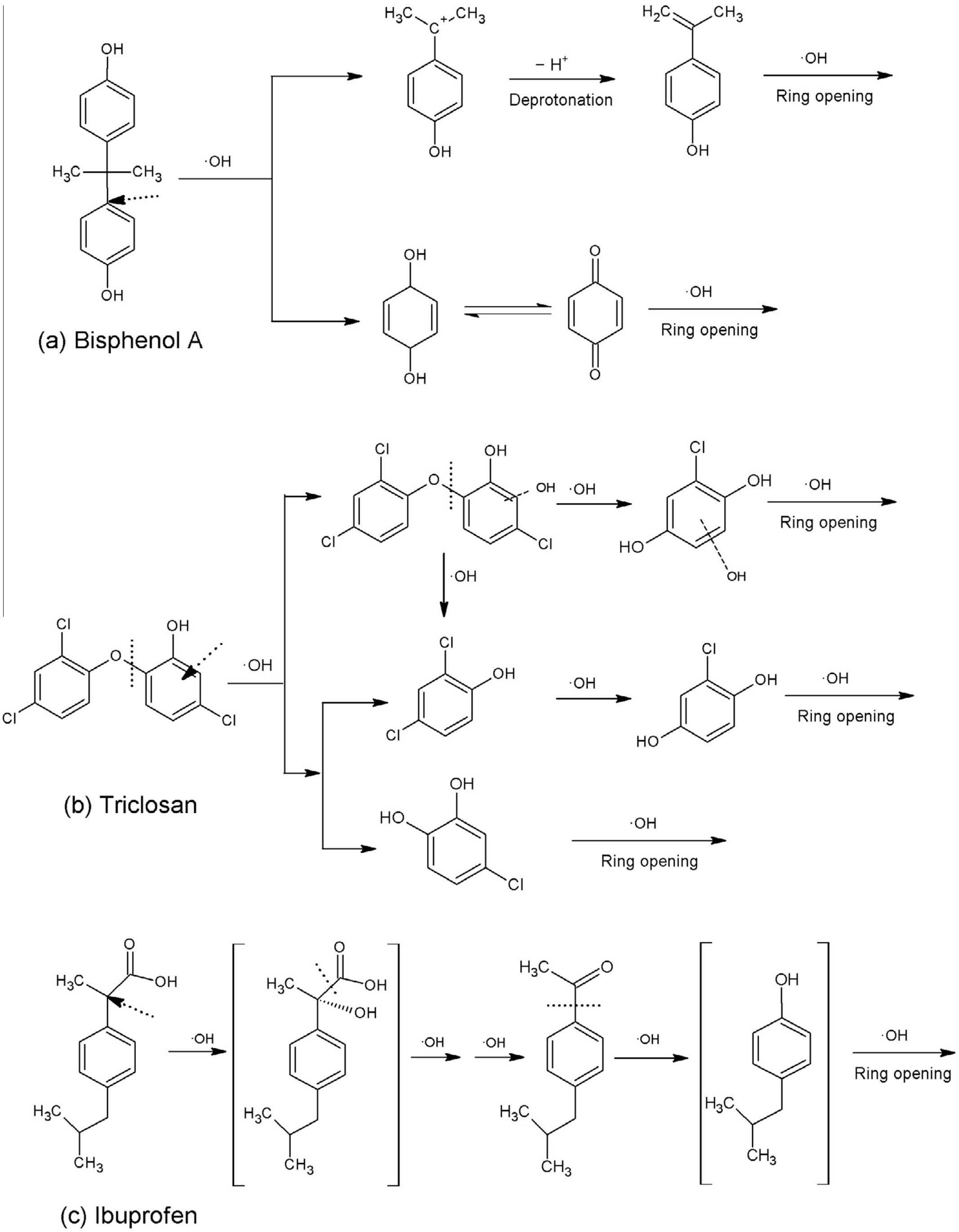


Fig. 6. Proposed initial pathways for degradations of (a) bisphenol A, (b) triclosan and (c) ibuprofen by the new electro-Fenton process with Ti/MMO cathode.

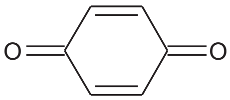
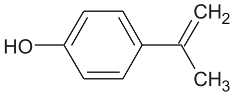
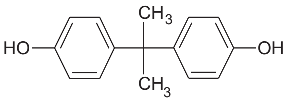
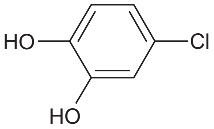
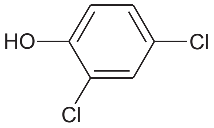
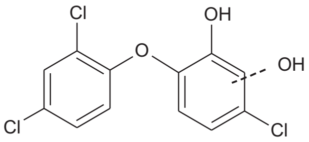
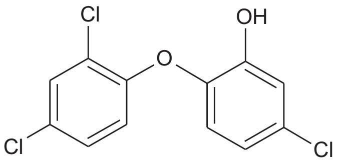
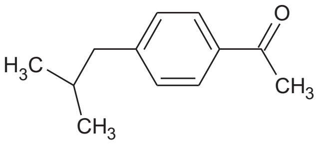
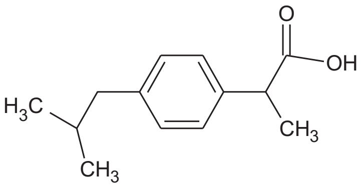
parallel, the cleavage of –O– bond generated 2,4-dichlorophenol and 4-chlorocatechol. The proposed pathway in this study is consistent with literature in which triclosan was degraded by electro-Fenton process with a GDE cathode (Sirés et al., 2007). Likewise, all these intermediates disappeared after 60 min degradation (Fig. SM-8). This also suggests the transformation of these intermediate compounds to aliphatic acids as only 26.8% TOC was removed after 60 min treatment.

3.6.3. Ibuprofen

For the degradation of ibuprofen, oxidation by ·OH generally goes through two pathways: (1) destruction of the propionic acid group produces consecutively 1-(1-hydroxyethyl)-4-isobutylbenzene, 4-isobutylacetophenone and 4-isobutylphenol, and (2) destruction of isobutyl substituent finally produces 4-ethylbenzaldehyde (Skoumal et al., 2009). However, the sole intermediate identified is 4-isobutylacetophenone (Table 1). The initial transformation pathway is then described in Fig. 6c. The C(2) in propionic acid group was preferentially attacked by ·OH in comparison with the C(1) in isobutyl substituent because of the stronger conjugate effect from carboxyl group and benzene. The pathway proposed in this study is somewhat different from that reported (Skoumal et al., 2009). The transformation of intermediates to aliphatic acids can be also suggested as the TOC removal was 35.7% after 60 min treatment.

As a summary, the three CECs can be effectively degraded by the new electro-Fenton process with Ti/MMO cathode, although H_2O_2 production on the Ti/MMO cathode is not as effective as on GDE cathodes that are commonly used in electro-Fenton processes.

Table 1
Intermediates identified for CECs degradation by the new electro-Fenton process with Ti/MMO cathode.

Compounds	Chemical structure	Methods
Bisphenol A		
1,4-Benzoquinone		HPLC
Hydroquinone		HPLC
4-Isopropenylphenol		GC–MS
Bisphenol A		HPLC and GC–MS
4-Chlorocatechol		HPLC
2,4-Dichlorophenol		HPLC and GC–MS
Triclosan		
Hydroxylated triclosan		Logical speculation
Triclosan		HPLC and GC–MS
Ibuprofen		
4-Isobutylacetophenone		HPLC and GC–MS
Ibuprofen		HPLC and GC–MS

The degradation led to accumulation of aromatic intermediates first. By prolonging the degradation time, these aromatic intermediates were then degraded to aliphatic acids and CO_2. As aliphatic acids are nontoxic and highly biodegradable, this new electro-Fenton process is environmentally friendly for degrading CECs. As the Ti/MMO cathode has a high mechanical and chemical stability and can be fabricated at large dimensions, this new electro-Fenton process could be promising for CECs degradation in practice. The weak acidity required for degradation is the barrier for the practical application of this process. Actually, the weak acidity is also required by traditional electro-Fenton processes (Brillas et al., 2009). In our recent investigations (Yuan et al., 2011; Yuan et al., 2013), a specially configured three-electrode electrolytic system that can automatically produce localized acidic condition in the reaction zone and neutral effluent after treatment was developed. This system may overcome the barrier of acidity requirement to some extent.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.09.051.

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