Dual-electrode oxidation used for aniline degradation in aqueous electrolyte
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ABSTRACT
The electrochemical degradation of aniline in aqueous electrolyte has been studied by dual-electrode oxidation process using Ti/SnO₂−Sb₂O₅ for anodic oxidation and graphite cathode to produce H₂O₂ in situ. The linear voltammograms were employed to obtain reasonable anodic and cathodic potential values for the purpose of restraining side reactions. The influence of Fe²⁺ on aniline degradation was investigated under potentiostatic condition with a three-electrode system. It was found that an anodic potential range of 2.0 ± 0.1 V and a cathodic potential of −0.65 V could favor anodic oxidation and H₂O₂ generation. Anodic oxidation was accounted for aniline degradation in the absence of Fe²⁺, while in the presence of Fe²⁺ both electro-Fenton oxidation and anodic oxidation (dual-electrode oxidation) could degrade aniline effectively. When cathodic potential values were −0.65 and −0.80 V, the optimum Fe²⁺ concentration were 0.50 and 0.30 mM, respectively. 77.5% COD removal and 70.4% TOC removal with a current efficiency (CE) of 96–100% were achieved under the optimum conditions. This work indicates that dual-electrode oxidation process characterized by a high CE is feasible for the degradation of organic compounds.

Key words | aniline, anodic oxidation, degradation, dual-electrode, electro-Fenton

INTRODUCTION
In the past few decades, a large variety of advanced oxidation processes (AOPs) characterized by the in situ generation of hydroxyl radical (·OH) as the main oxidizing agent, have been proposed for the degradation of toxic and bio-refractory organics in wastewaters (Cañizares et al. 2007; Guinea et al. 2008). Among the various AOPs, electro-Fenton oxidation and anodic oxidation have attracted much attention in recent years, benefiting from their advantages such as versatility and environmental compatibility (Martinez-Huitie & Sergio 2006; Brillas et al. 2009).

In electro-Fenton process, H₂O₂ is continually electro-generated in acidic solutions by two-electron reduction of O₂ on the cathodes such as graphite, carbon-felt and carbon-polytetrafluoroethylene. When Fe²⁺ is presented as catalyst, Fenton reaction will take place in the contaminated solution, generating strong oxidizing ·OH to destruct the various organics. The mechanism of ·OH generation can be represented by the following equations (Özcan et al. 2008).

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}
\]

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \tag{2}
\]

Electro-Fenton oxidation process has been applied to treat many industrial wastewaters containing organic compounds including chlorophenol (Wang & Wang 2009), aniline (Sánchez-Sánchez et al. 2007), dyes (Wang et al. 2008), and so on. The main purposes of these studies were to investigate the removal efficiency using different electrodes under various conditions and demonstrate the viability of such technologies, usually paying less attention to the variations of H₂O₂ and Fe²⁺ in electro-Fenton reactions as well as the influence of anodic oxidation action. Moreover, further effort to enhance the current efficiency (CE) of pollutants removal is necessary since it is only about 10 ~ 50% according to the reported results (Panizza & Cerisola 2009b).
As another popular AOP, anodic oxidation has been thoroughly investigated using various anodes such as graphite, carbon fiber, Pt, IrO₂, RuO₂, PbO₂, SnO₂ and boron-doped diamond (BDD) (Martinez-Huitle & Sergio 2006). The degradation mechanism of organic compounds was proposed by Comninellis (Comninellis & Battisti 1996). According to this mechanism, organics degradation is ascribed to the oxidation of adsorbed ‘OH and/or higher oxide. The degradation will compete with the side reactions of producing O₂, which causes anodic process efficiency decreased. As a result of low CE, high energy consumption is required for an effective anodic oxidation. Unfortunately, almost all the available electrodes can not present an ideal CE for organics degradation. Though a high CE up to about 100% was obtained in some research using BDD as CE for organics degradation. Though a high CE up to about 100% was obtained in some research using BDD as anode (Rodriguez et al. 2009), the price of this electrode was unacceptable in view of extensive use in industry.

From the above discussion, much effort to enhance CE reducing treatment cost is still required both for electro-Fenton oxidation and anodic oxidation. It is well known that anodic reactions and cathodic reactions take place simultaneously in electrolysis system. But now in the studies on the two processes, the actions of work electrodes were investigated carefully, usually omitting the actions of counter electrodes. Few studies were conducted to destroy organic pollutants paying equal attention to anodic and cathodic actions.

This paper reported a study on the degradation of aniline by the dual-electrode oxidation process, in which electro-Fenton oxidation and anodic oxidation were united in one electrochemical system. The influences of potential, Fe²⁺ concentration on aniline degradation were investigated under potentiostatic conditions. The variations of H₂O₂ and Fe²⁺ concentration were also examined to learn more about the mechanism of this process.

**MATERIALS AND METHODS**

**Apparatus**

The electrolytic experiments were performed using an undivided cell with a volume of 250 ml, supplied with a magnetic stirrer and a CHI760D Electrochemical Workstation. A Ti/SnO₂–Sb₂O₅ electrode with an area of about 20 cm² was used as anode, two graphite sheets with an area of about 38 cm² was used as cathode, and a saturated calomel electrode (SCE) as a reference. The distance between anode and cathode was 15 mm. A small inflow pump was used to supply air.

Ti/SnO₂–Sb₂O₅ electrode was prepared by thermal decomposition method. Its contents of Sn and Sb were 2.0 and 0.20 mg cm⁻², respectively.

**Voltammetry experiments**

The linear voltammogram of Ti/SnO₂–Sb₂O₅ (2.4 cm²) was obtained using graphite (2.4 cm²) as the counter electrode and SCE as a reference. The measurement was performed in the unstirred solution containing 0.10 mol L⁻¹ Na₂SO₄ at pH 3.0 within a potential range of 0.5–2.5 V, using a linear sweep rate of 20 mV s⁻¹. The linear voltammogram curve of graphite electrode (9.6 cm²) was measured using Ti/SnO₂–Sb₂O₅ (9.6 cm²) as the counter electrode in the same conditions except a potential range of 0 to −1.0 V.

**Bulk electrolysis**

All electrolytic treatments were conducted in an open, undivided glass cell with 200 ml solution containing 180 mg L⁻¹ aniline and 0.10 mol L⁻¹ Na₂SO₄ at initial pH 3.0 under potentiostatic conditions. To investigate the influence of Fe²⁺, FeSO₄ was added into the solution. During the electrolysis, a stirring of 400 r min⁻¹ was provided by a magnetic bar and an air flow rate of 25 ml s⁻¹ was supplied by an inflow pump, at desired time the samples were collected for chemical analysis. In some experiments, the concentration of H₂O₂ or Fe²⁺ was determined promptly after the samples were taken. All the experiments were performed twice at 18 ± 2 °C.

**Chemicals and analytical methods**

All chemicals were either HPLC or analytical grade from Shanghai. All solutions were prepared with high-purity water with conductivity <6×10⁻² μS cm⁻¹. The pH values of solutions were adjusted by addition of H₂SO₄.

Aniline was determined by N-(1-naphthyl) ethylenediamine spectrophotometric method with a detection limit of 0.03 mg L⁻¹ (China national standard: GB11889-1989). H₂O₂ concentration was obtained by the light absorption of the titanium-hydrogen peroxide colored complex at λ = 410 nm with a detection limit of 1.2 mg L⁻¹ (Sánchez-Sánchez et al. 2007). Fe²⁺ was determined by 1, 10-phenanthroline spectrophotometric method (China national standard: HJ/T 345-2007). COD was determined by the dichromate closed reflux method with a high COD range (China national standard: GB11914-89). TOC was monitored using TOC-V CPH Analyzer (Japan).
CE was calculated using the following relationship (Scialdone et al. 2008):

\[
CE(\%) = \frac{\text{COD}_0 - \text{COD}_t}{8 \times I \times t} \times F \times V \times 100
\]  

(3)

Where COD₀ and CODₜ are chemical oxygen demands at times \( t = 0 \) and \( t \) (g L⁻¹), respectively, \( I \) is the current (A), \( F \) is the Faraday constant (96,487 C mol⁻¹), \( V \) is the electrolyte volume (L), and \( 8 \) is the oxygen equivalent mass (g eq⁻¹).

**RESULTS AND DISCUSSION**

**Voltammetry characteristics**

The linear voltammetry was used to obtain the anodic potential of oxygen-evolving and the reasonable cathodic potential for the reduction of \( \text{O}_2 \) generating \( \text{H}_2\text{O}_2 \). Figure 1(a) shows the anodic onset potential of oxygen-evolving is about 1.7 V for Ti/SnO₂–Sb₂O₅ electrode, much higher than graphite, Pt, IrO₂, RuO₂, etc (Panizza & Cerisola 2009a). This characteristic favors the electrochemical oxidation of organics because the side reaction of oxygen-evolving can be restrained effectively. In anodic oxidation process, the low anodic potential accompanied by low current will result in a poor degradation as well as the possible poisoning effect of anode (Rodgers et al. 1999). However, the high potential with high current will lead to a low CE because of \( \text{O}_2 \) generation. Therefore, it is logical to carry out anodic oxidation process with a compromise potential, at which an appropriate oxidation of \( \text{H}_2\text{O} \) generating \( \text{O}_2 \) takes place. According to Figure 1(a), the reasonable potential value is about 2.0 ± 0.1 V for Ti/SnO₂–Sb₂O₅ anode.

The voltammogram of graphite obtained in the presence of \( \text{O}_2 \) was shown in Figure 1(b). A reduction peak can be observed at about \(-0.3 \) to \(-0.8 \) V, which shows the presence of direct electron transfer between \( \text{O}_2 \) and the cathode surface, namely the reduction of \( \text{O}_2 \) generating \( \text{H}_2\text{O}_2 \) by Reaction (1). When the cathodic potential is more negative than \(-0.8 \) V, obvious current increasing caused by \( \text{H}_2 \) evolution from Reaction (4) can be observed. As a result, the CE of producing \( \text{H}_2\text{O}_2 \) substantially decreases, especially when the cathodic potential is more negative than \(-0.9 \) V. The ideal cathodic potential favoring the generation of \( \text{H}_2\text{O}_2 \) is about \(-0.65 \) V for graphite cathode.

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

(4)

**Aniline oxidation only by \( \text{H}_2\text{O}_2 \)**

Since \( \text{H}_2\text{O}_2 \) has a weak oxidizing ability, the possible degradation resulted from the single action of \( \text{H}_2\text{O}_2 \) must be considered. In an experiment, the electrodes were just immersed in the solution (pH 3.0) containing 0.10 mol L⁻¹ \( \text{Na}_2\text{SO}_4 \), 180 mg L⁻¹ aniline and 500 mg L⁻¹ \( \text{H}_2\text{O}_2 \) without potential externally imposed. It was found that \( \text{H}_2\text{O}_2 \) and aniline almost remain unchanged in 300 min, which indicates: (i) the single action of \( \text{H}_2\text{O}_2 \) without catalyst is not able to result in aniline degradation; (ii) the chemical rate of \( \text{H}_2\text{O}_2 \) decomposition is very slow and the decay of \( \text{H}_2\text{O}_2 \) caused by this action can be neglected.

**Aniline degradation in the absence of \( \text{Fe}^{2+} \)**

Figure 2(a) shows the evolution of aniline as a function of electrolysis time in the absence of \( \text{Fe}^{2+} \). The cathodic potentials were controlled constantly at \(-0.65 \), \(-0.80 \) and \(-1.00 \) V, while anodic potentials were 1.92–2.00, 2.00–2.0
and 2.10–2.25 V, respectively. More negative cathodic potential accompanied by more positive anodic potential and higher current could result in a relatively better removal. Since the single action of H₂O₂ was not able to oxidize aniline, aniline decay was ascribed to the anodic oxidation in the absence of Fe²⁺.

The evolution of H₂O₂ concentration was shown in Figure 2(b). As clearly seen, the accumulation of H₂O₂ is obviously higher at /C₀ = 0.65 V than those at /C₀ = 0.80 V and /C₀ = 1.00 V, conforming to the result given in Figure 1(b). In this process, while H₂O₂ was continually generated at the cathode, its destruction caused by several modes also took place. Generally, H₂O₂ decomposition was attributable to the following modes: the oxidation of H₂O₂ at the anode by Reaction (5), the reduction of H₂O₂ at the cathode by Reaction (6) and chemical decomposition in the bulk of solution by Reaction (7).

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad (5) \\
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow 2\text{H}_2\text{O} \quad (6) \\
2\text{H}_2\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (7)
\end{align*}
\]

Since H₂O₂ chemical decomposition was very slow and the reduction of H₂O₂ at the cathode required more negative cathodic potential than −1.00 V (Drogui et al. 2001; Agladze et al. 2007), the destruction of H₂O₂ was mainly ascribed to the anodic oxidation.

Aniline degradation by dual-electrode oxidation

During the course of anodic oxidation of aniline, H₂O₂ can be continually electro-generated at the appropriate cathodic potential confirmed by Figure 2(b). In this work, the influence of Fe²⁺ on aniline degradation in terms of aniline and COD removal was investigated at −0.65 and −0.80 V. Anodic average current densities were about 1.0 and 1.4 mA cm⁻², respectively. As can be seen from Figure 3, the addition of Fe²⁺ greatly enhanced the decay rate of aniline. When the cathodic potential was controlled constantly at −0.65 V, the aniline removal (\(1 - c_c/c_0\)) increased significantly as the initial Fe²⁺ concentration was increased from 0 to 0.50 mM. The aniline decay achieved from the initial concentration of 1.00 mM was similar as from 0.50 mM, which indicated that the optimum initial Fe²⁺ concentration was about 0.50 mM. However, the optimum concentration of 0.30 mM was obtained at −0.80 V, significantly lower than 0.50 mM. This difference might be explained by the fact that comparing with −0.80 V, the cathodic potential of −0.65 V was more favorable for H₂O₂ generation.

In the presence of Fe²⁺, both cathodic electro-Fenton oxidation and anodic oxidation accounted for aniline degradation, hence this process might be called dual-electrode oxidation. According to the variation of aniline concentration presented in Figures 3(a) and (b), the predominant mechanism for aniline degradation was electro-Fenton oxidation, while anodic oxidation was the secondary mechanism under the ideal condition of Fe²⁺ concentration, which could be further confirmed by the COD variation. Figure 3(c) presented the COD removal rate measured after the dual-electrode oxidation treatment for 600 min using varying amount of Fe²⁺. As can be seen, the addition of Fe²⁺ greatly enhanced COD removal and the maximum removal was achieved at 0.50 mM Fe²⁺ for −0.65 V as well as 0.30 mM for −0.80 V, which agreed with the results of aniline removal. As initial Fe²⁺ concentration was further increased beyond the optimum amount, slight decrease in COD removal rate was observed. It has been reported that an excess of Fe²⁺ would consume OH⁻ reducing the oxidation of organics (Brillas et al. 2007), which might
explain the decrease of COD removal with a large amount of Fe$^{2+}$. Additionally, an excess of Fe$^{2+}$ will lead to a high content of Fe$^{3+}$, hence it is easy to produce Fe(III)-oxalate complexes which are difficult to oxidize by $'\text{OH}$ (Anotai et al. 2006).

According to Figure 3(c), the COD removal obtained at $-0.80 \text{ V}$ was better in comparison with the results obtained at $-0.65 \text{ V}$. Although $-0.80 \text{ V}$ was not the best cathodic potential value for H$_2$O$_2$ generation, the anodic oxidation power in this condition was stronger thanks to more positive anodic potential accompanied by a higher current density. But it should be noted that the CE of $-0.80 \text{ V}$ was lower than that of $-0.65 \text{ V}$ due to the relatively violent side reactions.

Despite a large number of papers dealing with the degradation of organics by electro-Fenton process, the variations of H$_2$O$_2$ and Fe$^{2+}$ in the course of organics degradation were almost not paid attention. In fact, these variations are very important for learning more about the mechanism of electro-Fenton oxidation. Figure 3(d) shows the variations of H$_2$O$_2$ and Fe$^{2+}$ in the course of aniline degradation by dual-electrode oxidation with initial Fe$^{2+}$ concentration of 0.50 mM at $-0.65 \text{ V}$. H$_2$O$_2$ concentration increases from 0 to 8.2 mg L$^{-1}$ in the initial 120 min, almost remains unchanged in the following 120 min, and then increases slightly with the subsequent reaction time. In the presence of Fe$^{2+}$, the reasons for H$_2$O$_2$ variation become complicated because Fenton reaction and other radical reactions are involved in the course of organics degradation. The oxidation of Fe$^{2+}$ and the reduction of Fe$^{3+}$ co-existed in the process. Since H$_2$O$_2$ and Fe$^{2+}$ are the essential reactants for Fenton reaction, their variations are supposed to show a relativity to a certain extent, which can be confirmed by the fact that Fe$^{2+}$ concentration decreases while H$_2$O$_2$ concentration increases in the range of 360–600 min.

**Variations of COD removal, TOC removal and CE**

Figure 4 shows the variations of COD and TOC removal as a function of electrolysis time at $-0.65 \text{ V}$ with 0.50 mM Fe$^{2+}$. COD and TOC removal increased significantly with electrolysis time. After the treatment of 600 min, COD concentration decreased by 77.5% from initial 468 mg ml$^{-1}$ while TOC concentration decreased by 70.4% from initial 140 mg L$^{-1}$. The results showed that aniline removal rate was greater than COD and TOC removal rates, which...
During the electrochemical oxidation of aniline using Ti/SnO$_2$–Sb$_2$O$_5$ as the anode and graphite as the cathode, H$_2$O$_2$ could be accumulated significantly in the absence of Fe$^{2+}$. In this case, the aniline removal was owing to the anodic oxidation. To obtain an effective anodic oxidation and restrain the side reaction of oxygen-evolving, the anodic potential should be controlled at about 2.0 ± 0.1 V. The appropriate cathodic potential for H$_2$O$_2$ generation is about −0.65 V.

- The addition of Fe$^{2+}$ greatly enhanced aniline degradation and the optimum Fe$^{2+}$ concentration had a close relation to the electrode potential. Under the conditions of −0.65 V, pH 3.0 and 0.50 mM Fe$^{2+}$, 77.5% COD removal and 70.4% TOC removal were achieved. In the presence of Fe$^{2+}$, electro-Fenton oxidation was the main and anodic oxidation was the secondary mechanism for organics degradation.

- Thanks to the realization of dual-electrode oxidation in one electrolysis system and the effective restraining of side reactions, a high CE of nearly 100% was achieved, which indicated that this process might provide a promising technology for organic wastewater treatment.

**ACKNOWLEDGEMENTS**

The financial support of this work by the National Natural Science Foundation of China (No. 50808103) is gratefully acknowledged.

**REFERENCES**


