Advanced treatment of biologically pretreated coking wastewater by electrochemical oxidation using boron-doped diamond electrodes

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ABSTRACT

Electrochemical oxidation is a promising technology to treat biorefractory wastewater. Coking wastewater contains high concentration of refractory and toxic compounds and the water quality usually cannot meet the discharge standards after conventional biological treatment processes. This paper initially investigated the electrochemical oxidation using boron-doped diamond (BDD) anode for advanced treatment of coking wastewater. Under the experimental conditions (current density 20–60 mA cm\(^{-2}\), pH 3–11, and temperature 20–60 °C) using BDD anode, complete mineralization of organic pollutants was almost achieved, and surplus ammonia–nitrogen (NH\(_3\)-N) was further removed thoroughly when pH was not adjusted or at alkaline value. Moreover, the TOC and NH\(_3\)-N removal rates in BDD anode cell were much greater than those in other common anode systems such as SnO\(_2\) and PbO\(_2\) anodes cells. Given the same target to meet the National Discharge Standard of China, the energy consumption of 64 kWh kgCOD\(^{-1}\) observed in BDD anode system was only about 60% as much as those observed in SnO\(_2\) and PbO\(_2\) anode systems. Further investigation revealed that, in BDD anode cell, organic pollutants were mainly degraded by reaction with free hydroxyl radicals and electro-generated oxidants (S\(_2\)O\(_8\)\(^{2-}\), H\(_2\)O\(_2\), and other oxidants) played a less important role, while direct electrochemical oxidation and indirect electrochemical oxidation mediated by active chlorine can be negligible. These results showed great potential of BDD anode system in engineering application as a final treatment of coking wastewater.

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1. Introduction

Electrochemical oxidation has attracted wide attention as one of the environmental-friendly technologies in wastewater treatment processes. Other advantages of electrochemical oxidation include high efficiency in organic degradation, simple structure and easy control (Jüttner et al., 2000). Electrochemical oxidation of various refractory pollutants have been extensively studied, such as phenol (Feng and Li, 2003), chlorophenols (Rodgers et al., 1999), nitrophenols (Cañizares et al., 2004), dyes (Chen et al., 2003), surfactants (Panizza et al., 2005), and herbicides (Boye et al., 2006). Recently, electrochemical treatment of real wastewaters has also been studied, including landfill leachate (Cabeza et al., 2007; Cossu et al., 1998), textile dye effluents (Vaghela et al., 2005; Vlyssides et al., 1999), olive oil wastewater (Cañizares et al., 2006;
However, the high energy consumption of electrochemical oxidation limited its industrial application. It is well known that the current efficiency of an electrochemical oxidation process strongly depends on anode material. In recent decades, a lot of electrode materials have been examined to improve the effectiveness of oxidation and current efficiency, such as graphite (Awad and Abuzaid, 1999), platinum (Torres et al., 2003), IrO2 (Foti et al., 1999), RuO2 (Li et al., 2005), SnO2 (Zanta et al., 2003), PbO2 (Zhou et al., 2005), and boron-doped diamond (BDD) (Panizza and Cerisola, 2005) electrodes. The graphite and platinum electrodes had low current efficiencies and were easy to foul. The IrO2 and RuO2 electrodes had low reactivity for organic oxidation. The SnO2, PbO2, and BDD electrodes had high oxidation capacities for organic pollutants and high current efficiencies for organic oxidation, because hydroxyl radicals would be produced by water discharge at these electrodes. Among them, BDD electrode has attracted more attention recently, because it has several important technologically properties (Panizza and Cerisola, 2005; Zhu et al., 2008): an extremely wide potential window, corrosion stability in very aggressive media, an inert surface with low adsorption, a strong tendency to resist deactivation, and the robust oxidation capacity.

Coking wastewater is generated from coal coking, coal gas purification, and by-product recovery processes of coking. It contains inorganic pollutants (ammonium, sulfate, cyanide, thiocyanate, etc.) and organic contaminants (phenolic compounds, polynuclear aromatic hydrocarbons PAHs, nitrogen-, oxygen-, and sulfur-containing heterocyclic compounds, and so on) (Lim et al., 2003; Wang et al., 2002; Zhang et al., 1997). Most of these constituents are refractory, toxic, mutative, and carcinogenic. Pollution caused by coking wastewater is a serious problem in the world, especially in China. Because coal is the main energy source, there are many coke plants throughout China.

Conventional treatment of coking wastewater includes sedimentation, adsorption, iron salts, aeration, biological treatment (mostly the activated sludge process) (Zhang et al., 1997), and the anaerobic–anoxic–oxic (A1–A2–O) process (Zhang et al., 1997). These processes are still not efficient for the removal of organic pollutants. Although new biological reactors and processes have been developed and achieved good results, such as the sequencing batch reactor (SBR) (Yu et al., 1997), the anoxic–oxic (A–O) process (Yu et al., 2005), and the anaerobic–anoxic–oxic (A1–A2–O) process (Zhang et al., 1997), these processes are still not efficient enough to meet the strict requirements of the National Discharge Standard of China (COD < 150 mg L⁻¹, NH3–N < 25 mg L⁻¹) (Lai et al., 2008). Therefore, efforts on advanced processes for coking wastewater treatment are necessary.

For the aforementioned reasons, a conventional anaerobic–anoxic–oxic (A1–A2–O) process was incorporated with BDD anode system to further reduce the biological effluent COD to 150 mg L⁻¹ as required by the National Discharge Standard of China. Attributed to the high capacity to generate free hydroxyl radicals (Zhu et al., 2008), the BDD anodes have strong ability to mineralize a variety of bio-refractory pollutants, including phenols (Cañizares et al., 2005), dyes (Chen et al., 2003), surfactants (Panizza et al., 2005), polyacrylates (Bellagamba et al., 2002), and humic substances (Liao et al., 2008). Hence, the BDD anode system should be able to give a satisfied solution to the remained bio-refractory COD from the A1–A2–O process, which was mainly composed of humic substances (Lai et al., 2008, 2009).

This paper initially presented the feasibility of BDD anode system as an advanced treatment of coking wastewater. In order to optimize the electrochemical oxidation process using BDD anode, electrolysis of coking wastewater was carried out under different current density, pH, and temperature. Moreover, the effectiveness and energy consumption of BDD anode cell were compared to those of SnO2 and PbO2 anodes cells. Finally, the removal mechanisms of organic pollutants in BDD anode cell were investigated.

### 2. Materials and methods

#### 2.1. Preparation of electrodes

Ti/BDD (BDD) electrodes were prepared by microwave plasma-assisted chemical vapor deposition (CVD) (Zhu et al., 2007). Ti/SnO2–Sb (SnO2) electrodes were prepared by the thermal decomposition technique (Kong et al., 2007b). Ti/SnO2–Sb/PbO2 (PbO2) electrodes were prepared by electrodeposition method (Kong et al., 2007a). The surface morphology of the electrodes was examined by SEM (Quanta 200F).

#### 2.2. Bulk electrolysis

The raw coking wastewater was collected from a coking plant in Shanxi Province of China. An anaerobic–anoxic–oxic (A1–A2–O) process was used to treat this wastewater in our laboratory. The wastewater used in this work was the effluent of this A1–A2–O process. The characteristics of wastewater used in the experiments are listed in Table 1. In addition, the organic constituents of used wastewater have been analyzed using HPLC, GC-MS, ¹³C NMR, and MWD. The results showed that the biological effluent was primarily composed of humic substances (Lai et al., 2008, 2009).

Bulk electrolysis was performed in a one-compartment cell under galvanostatic conditions. The wastewater of 250 mL volume was stirred by a magnetic stirring bar in the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Coking wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>7.72</td>
</tr>
<tr>
<td>Chemical oxygen demand, COD</td>
<td>mgO2 L⁻¹</td>
<td>246</td>
</tr>
<tr>
<td>Total organic carbon, TOC</td>
<td>mg L⁻¹</td>
<td>78</td>
</tr>
<tr>
<td>Biological oxygen demand, BOD₅</td>
<td>mgO2 L⁻¹</td>
<td>15</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>mg L⁻¹</td>
<td>10</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg L⁻¹</td>
<td>52</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS cm⁻¹</td>
<td>2</td>
</tr>
</tbody>
</table>
electrolysis process. 0.2 M Na₂SO₄ were added into wastewater as supporting electrolytes. 1 M H₂SO₄ and NaOH were used to adjust the pH of solutions. The Ti/BDD, Ti/SnO₂–Sb, and Ti/SnO₂–Sb/PbO₂ electrodes with an exposed geometric area of 4 cm² were used as the anode, respectively. A stainless steel sheet with the same size was used as the cathode. The electrodes gap was set to be 10 mm. Constant temperatures were kept by thermostat bath. Samples were collected from the cell at various intervals for chemical analysis.

2.3. Analytical methods

The pH was determined using a pH meter (pH-201, Hanna Corporation, Italy). The total organic carbon (TOC) concentration was monitored using Multi TOC/TN Analyzer (Analytik Jena AG Corporation, Germany). The chemical oxygen demand (COD) was measured by a titrimetric method using dichromate as the oxidant in acidic solution at 150 °C for 2 h (Hach Corporation, USA). The biological oxygen demand (BOD₅) was determined by respirometric method (OxiTop IS6, Germany). NH₃–N concentration was obtained via a Nessler’s reaction using a 722S spectrophotometer (Shanghai Jingke, China). The concentration of chloride ion was detected using chloride ion selective electrode (PCL-1, Shanghai Luosu, China).

The acute toxicity of wastewater was assessed by growth inhibition test using the luminescent bacteria Photobacterium phosphoreum (T3 spp., Institute of Soil Science, Chinese Academy of Sciences) (Huang and Wang, 2007; Zhao et al., 2009). The difference in luminescence intensities of tested samples and reference with 10 μL P. phosphoreum suspension at 15 min exposure was determined by a photometer (DXY-2, Institute of Soil Science, Chinese Academy of Sciences, China), which was used to calculate the inhibition ratio of luminescence (Rᵢ) by:

\[ Rᵢ = 1 - \frac{Lₘ}{Lₗ} \]  

where \( Lₘ \) and \( Lₗ \) were the luminescence intensities of the sample and the reference (DI water), respectively. Before determination, NaCl was added into each water sample or reference to a 3% concentration (w/w) to keep the ionic strength be consistent with that of the nutrient medium.

Electrochemical measurements were performed using a CHI 760B electrochemical workstation (Shanghai Chenhua Corporation, China) in a conventional three-electrode cell at room temperature (25 °C). BDD electrodes with an exposed geometric area of 4 cm² were used as working electrodes. The counter electrode was a platinum plate with the same size. The saturated calomel electrode (SCE) was used as the reference electrode in a separate compartment with a Luggin capillary (all potentials are quoted against SCE).

2.4. Determination of energy consumption

The energy consumption (\( Eₑ \)) necessary to meet the National Discharge Standard was calculated using the following equation:

\[ Eₑ = \frac{1000UIt}{(COD₀ - CODₛ)V} \]  

where \( Eₑ \) is the energy consumption (in kWh kgCOD⁻¹), \( U \) is the voltage (in V), \( I \) is the current (in A), \( t \) is the time needed to meet the National Discharge Standard (in h), COD₀ is the initial COD of wastewater (in mg L⁻¹), CODₛ is the COD of National Discharge Standard (150 mg L⁻¹), and \( V \) is the volume of wastewater (in L).

3. Results and discussion

3.1. Electrochemical oxidation of coking wastewater at BDD anode with different operating parameters

In order to optimize the electrochemical oxidation of coking wastewater using BDD anode, the effects of current density (\( j \)), pH, and temperature (\( T \)) on TOC and NH₃–N removal were investigated.

Fig. 1 showed the evolution of TOC (a) and NH₃–N concentration (b) as a function of electrolysis time at different current density (20, 40, and 60 mA cm⁻²). The removal rates of...
TOC and NH$_3$–N increased with the increase of current density. As listed in Table 2, the reaction time ($t$) necessary to meet the National Discharge Standard at different current density were 3.19 h, 2.00 h, and 1.31 h, respectively. However, high current density led to low current efficiency, because side reaction (oxygen evolution) would be improved. As a result, the energy consumption ($E_s$) necessary to meet the National Discharge Standard was higher at larger current density. The $E_s$ at different current density were 50, 64, and 65 kWh kgCOD$^{-1}$, respectively (Table 2). Moreover, the service life of electrodes was shortened at high current density. Therefore, 20 mA cm$^{-2}$ was considered as the suitable current density.

Fig. 2 showed the evolution of TOC (a) and NH$_3$–N concentration (b) as a function of electrolysis time at different pH (3.10, not adjusted 7.72, and 9.98). In all cases, the removal rates of TOC were similar, and TOC was almost degraded completely after 10 h of electrolysis time. The surplus NH$_3$–N was almost completely removed in neutral and alkaline solutions, while it was hardly removed in acidic solution. The degradation of NH$_3$–N could be by direct oxidation (Reaction (3)) (Cabeza et al., 2007) and indirect oxidation (Reactions (4) and (5)) in the presence of Cl$^-$ (52 mg L$^{-1}$ in treated coking wastewater) (Panizza and Cerisola, 2004).

\[
\begin{align*}
2NH_4^+ + 6OH^- &= N_2 + 6H_2O + 2H^+ + 6e^- \quad (3) \\
2NH_4^+ + 3HClO &= N_2 + 3H_2O + 5H^+ + 3Cl^- \quad (4) \\
2NH_4^+ + 3ClO^- &= N_2 + 3H_2O + 2H^+ + 3Cl^- \quad (5)
\end{align*}
\]

Obviously, these three reactions were disfavored in acidic solution. Furthermore, hypochloric acid (HClO) was formed through oxidation of chloride in the wastewater (Reaction (6)) and disproportionation of chlorine (Reaction (7)) (Panizza and Cerisola, 2004). In basic solution, hypochloric acid dissociated to form hypochloric ion (ClO$^-$) (Reaction (8)). On the other hand, hypochloric acid had low stability in acidic solution and it would leave the cell as gaseous chlorine (Vaghela et al., 2005). Therefore, acid solution was not favorable to removal of NH$_3$–N.

\[
\begin{align*}
2Cl^- &= Cl_2 + 2e^- \quad (6) \\
Cl_2 + H_2O &= HClO + H^+ + Cl^- \quad (7) \\
HClO &= H^+ + OC\tilde{I}^- \quad (8)
\end{align*}
\]

Moreover, the energy consumption ($E_s$) necessary to meet the National Discharge Standard at different pH were very similar, i.e. 52, 50, and 54 kWh kgCOD$^{-1}$, respectively (Table 2). These results demonstrated that the pH of wastewater did not need to be adjusted before electrochemical treatment.

Fig. 3 showed the evolution of TOC (a) and NH$_3$–N concentration (b) as a function of electrolysis time at different temperature (30, 45, and 60 °C). As the increase of temperature, the removal rates of TOC and NH$_3$–N little increased, which might be attributed to the enhancement of reaction rate and mass transfer at higher temperature. Moreover,
lower energy consumption was achieved at higher temperature. The energy consumption ($E_s$) necessary to meet the National Discharge Standard at different temperature was 50, 41, and 42 kWh kgCOD$^{-1}$, respectively (Table 2). Since 45°C was an easy-to-obtain working temperature, the proper temperature was regarded as 45°C.

In summary, electrochemical oxidation using BDD anode was effective as an advance treatment of coking plant wastewater. In most investigated cases, organic pollutants and NH$_3$–N could be completely removed. Under the suitable conditions (20 mA cm$^{-2}$, pH not adjusted, and 45°C), the energy consumption ($E_s$) necessary to meet the National Discharge Standard was only 41 kWh kgCOD$^{-1}$, and the $E_s$ could be further decreased by optimizing the cell design. Therefore, the industrial application of this technology was very promising.

In addition, the toxicity of wastewater during electrochemical treatment was assessed by growth inhibition test using the luminescent bacteria P. phosphoreum (Fig. 4). During the process, the inhibition ratio of luminescence ($R_I$) was almost similar, which implied that the toxicity of wastewater was not increased by electrochemical treatment. As for the remained toxicity, it might be attributed to the inorganic pollutants (e.g. cyanide), and further investigation was needed.

3.2. Electrochemical oxidation of coking wastewater at BDD anode compared to at SnO$_2$ and PbO$_2$ anodes

Previous studies (Panizza and Cerisola, 2005; Zanta et al., 2003; Zhou et al., 2005) demonstrated that BDD, SnO$_2$, and PbO$_2$ anodes had high oxygen evolution potential and were effective for pollutants oxidation. In this study, for comparison, Ti/BDD (BDD), Ti/SnO$_2$–Sb (SnO$_2$), and Ti/SnO$_2$–Sb/PbO$_2$ (PbO$_2$) electrodes were prepared, and used as anodes in electrochemically advanced treatment of coking wastewater, respectively.

Fig. 5 shows the evolution of TOC (a), NH$_3$–N concentration (b), and pH (c) as a function of electrolysis time in BDD, SnO$_2$, and PbO$_2$ anodes cells under the same electrolysis conditions. The TOC removal rate in BDD anode cell was much greater than those in SnO$_2$ and PbO$_2$ anodes cells. At the end of treatment, TOC was almost completely removed in BDD anode cell, while TOC were only removed by 37% in SnO$_2$ anode cell and by 44% in PbO$_2$ anode cell (Fig. 5a). It meant that the mineralization capacity of BDD anode was much stronger than that of SnO$_2$ and PbO$_2$ anodes.

NH$_3$–N was almost completely removed in BDD anode cell, while only a little of NH$_3$–N was removed at initial stage in SnO$_2$ and PbO$_2$ anodes cells (Fig. 5b). The limitation of NH$_3$–N removal in SnO$_2$ and PbO$_2$ anodes cells was accounted for the decrease of solution pH during electrolysis process. It can be observed from Fig. 5c that the solution pH increased with the increase of electrolysis time in BDD anode cell, whereas pH value decreased with the increase of electrolysis time in SnO$_2$ and PbO$_2$ anodes cells. After electrolysis of 2 h, the pH in SnO$_2$
and PbO$_2$ anodes cells became less than 7. In above section, it was confirmed that acid solution was not favorable to removal of NH$_3$–N.

The energy consumption ($E_s$) necessary to meet the National Discharge Standard for BDD, SnO$_2$, and PbO$_2$ anodes were 64, 112, and 100 kWh kgCOD$^{-1}$, respectively. The $E_s$ for BDD anode was about 60% of those for SnO$_2$ and PbO$_2$ anodes.

The higher mineralization capacity and lower energy consumption for BDD anode might be attributed to its different degradation mechanism from SnO$_2$ and PbO$_2$ anodes. Our previous studies (Zhu et al., 2007, 2008) revealed that hydroxyl radicals mainly existed as free hydroxyl radicals at BDD anode. This type of hydroxyl radicals were difficult to combine with each other to produce oxygen (side reaction), and thus BDD electrode had the higher oxygen potential (2.25 V in 1 M H$_2$SO$_4$). Therefore, Ti/BDD anodes had stronger mineralization ability and higher current effectively. On the other hand, at PbO$_2$ and SnO$_2$ anodes, hydroxyl radicals mainly existed as adsorbed hydroxyl radicals. This type of hydroxyl radicals were easy to combine with each other to generate oxygen (side reaction), and consequently SnO$_2$ and PbO$_2$ electrodes had the lower oxygen evolution potential (1.30 and 1.75 V in 1 M H$_2$SO$_4$, respectively). Hence, SnO$_2$ and PbO$_2$ anodes had weaker mineralization capacity and lower current efficiency.

### 3.3 Removal mechanisms of organic pollutants in BDD anode cell

The removal of organic pollutants in BDD anode cell might be attributed to direct electrochemical oxidation on the anode surface, and indirect electrochemical oxidation mediated by hydroxyl radicals, peroxodisulfates (in the presence of SO$_4^{2-}$), or active chlorine (in the presence of Cl$^-$) (Cañizares et al., 2005; Zhu et al., 2008). In order to confirm that organic pollutants were mainly degraded by reaction with hydroxyl radicals during electrochemically advanced treatment of coking wastewater, further experiments were performed.

**Fig. 6** showed the cyclic voltammograms of coking wastewater at the BDD electrode. Compared to the blank (dotted lines), the current increased during potential +1.2 to +2.4 V,
which implied that the direct electrochemical oxidation of organics occurred at the BDD electrode. However, this process would result in electrode fouling, which was confirmed by the decrease of current at potential $+2.2 \text{ V}$ as the increase of scan cycle (Canízares et al., 2003; Iniesta et al., 2001; Zhu et al., 2007). Fig. 7 showed the SEM images of BDD electrode before (a) and after (b) advanced treatment of coking wastewater. It can be observed that the surface morphology of BDD electrode had no significant changes, which demonstrated that no electrode fouling occurred during the electrochemically advanced treatment of coking wastewater. It implied that direct electrochemical oxidation was negligible in the bulk electrolysis, which was in agreement with our previous studies (Zhu et al., 2007, 2008).

In the presence of sulfates, peroxodisulfates can be formed at BDD electrodes (Reaction (9)). Peroxodisulfates can decompose to form hydrogen peroxide and other oxidants (Canízares et al., 2005; Zhu et al., 2008). Therefore, some contaminations might be degraded by these electrogenerated oxidants during electrochemically advanced treatment of coking wastewater. In order to determine the role of these electrogenerated oxidants, electrochemical oxidation of coking wastewater using $0.2 \text{ M Na}_3\text{PO}_4$ as supporting electrolyte was performed, because no electrogenerated oxidants were detected in $0.2 \text{ M Na}_3\text{PO}_4$ solution (Zhu et al., 2008). Fig. 8 showed the evolution of TOC as a function of electrolysis time in supporting media containing $0.2 \text{ M Na}_2\text{SO}_4$ and $0.2 \text{ M Na}_3\text{PO}_4$. The TOC removal rate only decreased by 10–15% when $\text{Na}_3\text{PO}_4$ was used as supporting electrolyte instead of $\text{Na}_2\text{SO}_4$. This result indicated that the electrogenerated oxidants ($\text{S}_2\text{O}_8^{2-}$, $\text{H}_2\text{O}_2$, and other oxidants) played a relative important role in electrochemically advanced treatment of coking wastewater.

$$2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2\text{e}^- \quad (9)$$

Coking wastewater contains chloride, which can be oxidized to active chlorine ($\text{Cl}_2$, $\text{HClO}$, and $\text{ClO}^-$) by Reactions (6)–(8) (Panizza and Cerisola, 2004). As a result, a part of pollutants might be degraded by indirect electrochemical oxidation mediated by electrogenerated active chlorine during electrochemically advanced treatment of coking wastewater. However, the concentration of chloride ion in coking wastewater was only $52 \text{ mg L}^{-1}$, which was much lower than that in landfill leachate ($1600–3230 \text{ mg L}^{-1}$) (Cossu et al., 1998) and tannery wastewater ($1500–28,000 \text{ mg L}^{-1}$) (Szpyrkowicz et al., 2005). When $400 \text{ mg L}^{-1}$ KCl was added into electrolyte, no apparent improvement of TOC removal rate was observed (Fig. 9). This result demonstrated that the role of active chlorine was limited in electrochemically advanced treatment of coking wastewater.

Therefore, it can be concluded that organic pollutants in BDD anode cell were mainly degraded by reaction with...
hydroxyl radicals during electrochemically advanced treatment of coking wastewater. Electrogenerated oxidants (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}, H\textsubscript{2}O\textsubscript{2}, and other oxidants) played a relative important role. Direct electrochemical oxidation and indirect electrochemical oxidation mediated by active chlorine could be negligible.

4. Conclusions

The electrochemical oxidation using BDD anode was very promising for advanced treatment of coking wastewater. In the investigated conditions, complete mineralization of organic pollutants and removal of NH\textsubscript{3}-N was almost achieved. Compared to the SnO\textsubscript{2} and PbO\textsubscript{2} anodes cells, the TOC and NH\textsubscript{3}-N removal rates in BDD anode cell were much greater, and the energy consumption could be reduce about 40%. The excellent performance of BDD anode cell was attributed that organic pollutants were mainly degraded by reaction with free hydroxyl radicals during electrochemically advanced treatment of coking wastewater. In addition, electrogenerated oxidants (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}, H\textsubscript{2}O\textsubscript{2}, and other oxidants) played a relative important role, while direct electrochemical oxidation and indirect electrochemical oxidation mediated by active chlorine could be negligible.

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