Electrochemical degradation of atrazine on Pt anode with cathodic electro-generation of H$_2$O$_2$

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Abstract. This study investigated the degradation of atrazine by anodic oxidation with cathodic electro-generation of H$_2$O$_2$ (AO—H$_2$O$_2$). A series of trials were conducted in an undivided cylindrical glass cell using Pt anode and graphite cathode, air was compressed into working solution at atmospheric pressure. The oxidation experiments were carried out to assess the influence of primary parameters (current intensity, air feeding flow rate, cathode—to—anode area ratio and initial organic concentration) on atrazine removal. During all trials performed, the concentration of atrazine declined significantly, and in the best operating parameters found (current intensity 80 mA, air feeding flow rate 0.9 L min$^{-1}$, cathode—to—anode area ratio 12), 72% of atrazine removal was obtained within 120 min oxidation time. CV tests exhibited that the intensity of anodic peak was strengthened when the working solution is O$_2$—saturated, implying that O$_2$ might play an important role in the anodic oxidation of atrazine.

1. Introduction

In recent decades, novel methods have grown up to develop the electrochemical advanced oxidation processes (EAOPs) on the basis of electro—generation of H$_2$O$_2$, including anodic oxidation with electrogenerated H$_2$O$_2$(AO—H$_2$O$_2$), electro—Fenton (EF) and photoelectro—Fenton (PEF) [1-3]. The most essential part of these EAOPs is the electro—generation of H$_2$O$_2$ via two—electron reduction of dissolved oxygen in water (as described in Eq. (1)) at carbonaceous cathodes, including stable carbon or graphite felt [4-5], poly porous carbon sponge [6], carbon nanotubes with large specific surface area [7-8] and carbon—polytetrafluoroethylene (PTFE) gas diffusion devices [9-10].
During the AO—H₂O₂ process, organic pollutants can be oxidized by (i) direct electron transfer with the anode surface (M), (ii) oxidized by hydroxyl radical M(•OH) originated from anodic oxidation of H₂O molecular (as described in Eq. (2)), and (iii) oxidized by H₂O₂ and its anodic oxidation intermediates, such as adsorbed hydroperoxyl radical M(HO₂•) generated at the anode surface (as described in Eq. (3)) [11]:

\[ M + H_2O = M(HO\bullet) + H^+ + e^- \]  
\[ M + H_2O_2 = M(HO_2\bullet) + H^+ + e^- \]  
\[ O_2 + 2H^+ + 2e^- = H_2O_2 \]  

Chlorinated triazines, the most important herbicides, were widely used for weed control in agriculture, forestry and animal husbandry for the past few decades. Atrazine, one of the major herbicide of the chlorinated triazines, is used so much all over the world to control weed in farmland during the last decades [12]. Furthermore, atrazine is slightly soluble in water (33 mg L⁻¹ at 22 °C) with comparatively low adsorption in clay. Atrazine migrates easily towards the underground and surface waters, possessing potential danger to the aquatic ecosystem and public health due to its chlorinated metabolites [13-15]. The adverse impact of atrazine on ecosystems rouses great efforts for the development of efficient and environmentally friendly technologies for degradation of herbicides in water.

The objective of this work is to elucidate the oxidation behaviours of atrazine by anodic oxidation with electrogenerated H₂O₂. A series of trials was carried out to assess the effect of the primary variables on atrazine removal.

2. Material and methods

2.1. Materials

Atrazine, purchased from TCI (Japan) was used as received (98% purity). Methanol, HPLC grade used as chromatographic analysis, was purchased from Tianjin Shield Company. Sulfuric acid (H₂SO₄, 98%) and sodium sulfate (Na₂SO₄) were of analytical grade and used without purification. Ultrapure water, resistivity >18 MΩ cm at 25 °C, derived from Millipore Milli—Q system (Billerica, MA, USA) was used to prepare all the electrolytes. The initial pH of electrolyte was adjusted to 6.7 used sulfuric acid.

2.2. Electrolysis system and analytic methods

Anodic oxidation experiments was conducted in a home—made polymethyl methacrylate reactor with 200 ml capacity. Anodic oxidation trials were performed under galvanostatic condition used a CHI 660 electrochemical workstation. The anode was a Pt plate (20 mm×50 mm) and the cathode was a piece of graphite (60 mm×120 mm). The high performance liquid chromatography system (HPLC, Waters, USA) equipped with a Waters 1525 binary HPLC pump, a reverse—phase T3 column (5 µm particle size and 250 mm×4.6 mm, Waters) and a Waters 2487 absorbance detector was used to detect the concentration of atrazine. A mixture with flow rate of 1 mL min⁻¹ (methanol and water, 8/2, V/V) was used as mobile phase. Water samples were extracted and filtered through 0.2 mm filter at settled time for HPLC analysis.

3. Results and discussion

3.1. Effect of current on the oxidation of atrazine

During the anodic oxidation process, the applied current of oxidation process is a dominating parameter. Applied current determines the electron transfer, the yield of electro-generated reactive oxidants on the anode surface and in solutions. Furthermore, in AO—H₂O₂ system, current intensity determines the anodic oxidation efficiency and the formation speed of H₂O₂.

So as to research the impact of current intensity on atrazine removal in AO—H₂O₂ system, the electrolysis trials at current intensity ranged from 40 to 100 mA were conducted. Fig.1 clearly exhibits
the oxidation efficiency of atrazine under different current density used Pt anode. The impact of current density on atrazine oxidation in AO—H₂O₂ system was obvious. The removal efficiency of atrazine was increased with the increasing current from 40 to 80 mA. However, atrazine removal efficiencies at current of 80 and 100 mA were almost the same after 2 h oxidation. This tendency is because of these parasitic reactions occurred on the anode surface among the entire electrolysis process. Account for these, the optimal current would be 80 mA.

3.2. Effect of air rates on the oxidation of atrazine
The air rate, determines the formation of H₂O₂, is an important parameter in AO—H₂O₂ system. So as to research the impact of air rates on the atrazine removal, the electrolysis trials at air rates ranged from 0 to 1.2 L min⁻¹ were conducted. Fig. 2 shows the oxidation efficiencies of atrazine at different air rates. Generally, the air rates influence the anodic oxidation rate of atrazine. The atrazine removal efficiencies at air rates of 0.9 and 1.2 L min⁻¹ were almost the same after 2 h oxidation. Account for these, the optimal current would be 0.9 L min⁻¹.

3.3. Effect of atrazine concentration on the oxidation of atrazine
So as to research the impact of initial concentrations on the atrazine removal, the electrolysis trials with atrazine concentrations ranged from 5 to 20 mg L⁻¹ were conducted. Fig. 3 shows the oxidation efficiencies of atrazine under different initial concentration. Generally, the increase of atrazine
concentration led to decay of atrazine removal efficiency. This phenomenon could be deciphered by the sluggish oxidation of more quantity of atrazine molecules with similar amount of hydroxyl radicals.

![Graph showing the effect of atrazine concentration on the oxidation efficiency of atrazine.](image)

Fig. 3. Effect of atrazine concentration on the oxidation efficiency of atrazine (initial pH value: 6.7).

3.4. *Effect of oxygen on the anodic oxidation*

Pt anode shows favorable oxidation power in many anodic oxidation processes. Conventional anodic oxidation of organics is generally conducted in the absence of oxygen. And in our paper, it is meaningful to observe that oxygen can effectively promote atrazine oxidation at Pt anode. Anodic peaks were found in all CV figure obtained in nitrogen and oxygen saturated working solutions. The anodic peak is strengthened when the working solution is saturated with oxygen as shown in Fig. 4, indicating that oxygen might play an important role in the anodic oxidation of atrazine.

![Graph showing the effect of oxygen on the voltage—current curves.](image)

Fig. 4. Effect of oxygen on the voltage—current curves.

4. **Conclusion**

Atrazine oxidation in the presence of Pt anode was conducted under different experimental conditions in AO—H₂O₂ system. Experimental results show that AO—H₂O₂ oxidation system appeared to be an efficient method to reduce atrazine in aqueous solution at appropriate operating conditions. CV tests demonstrated that dissolved oxygen in solution would enhance the anodic oxidation ability with Pt anode.

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