Electrochemical degradation of chemical wastewater by anodic oxidation process

Kai Zhu1*, Huayu Zhu2**, Shangti Feng3, Jianying Fu3, Debao Guo3, Qing Sun4, Lihua Huang1 and Xiaodong Hao1

1College of resources and environment, Linyi University, Linyi, Shandong Province, 276000, China
2School of chemistry & chemical engineering, Linyi University, Linyi, Shandong Province, 276000, China
3Shandong linyi sunny wealth chemicals Co., Ltd, Linyi, Shandong Province, 276000, China
4Municipal engineering design institute, Linyi architectural design & research institute Co., Ltd, Linyi, Shandong Province, 276000, China

*Corresponding author’s e-mail: zhukai@lyu.edu.cn
**Corresponding author’s e-mail: zhuhuayu@lyu.edu.cn

Abstract. The wastewaters produced in chemical production contain large numbers of persistent organic pollutants, posing potential adverse impacts to aquatic ecosystem and human health. In this work, the electrochemical degradation of organic pollutants in chemical wastewater belonging to Sunny wealth chemicals (Linyi, Shandong Province) was conducted using anodic oxidation process. Three commercially available anodes (Pt, boron-doped diamond (BDD) and Ti-Ru-Sn ternary oxide (Ti/RuO2-SnO2)) were chosen to investigate the effect of several primary operating parameters, such as electrolyte composition, electrolyte concentration and applied current density. Total organic carbon (TOC) was detected as reference parameters to assess the performance of anodic oxidation. The experimental results show that BDD anode exhibited excellent oxidation capacity for degradation of organics in chemical wastewater, achieving over 30% removal efficiency in all cases within 4 h. TOC removal efficiency of 52% was obtained with BDD anode in 4 h of reaction time at applied current density 30 mA cm\(^{-2}\), NaCl concentration 0.05 mol L\(^{-1}\); nevertheless, less than 45 % of removal was achieved with Pt and Ti/RuO2-SnO2 anode under the same conditions.

1. Introduction

Many chemical industries, including plastics, dyestuffs, pesticides and textile, are characterized by the enormous use of water, generating large volumes of wastewater [1]. Biorecalcitrant organic pollutants, such as phenols, chlorophenols, dyes and pesticides, presented in high concentrations industrial wastewaters cause potential harm to aquatic organism and human health [2-5]. Hence, there is imperative need for the development of some effective technologies to thoroughly remove persistent organic pollutants (POPs) from chemical wastewaters [6].

Anodic oxidation, one of the most efficient and environmentally electrochemical advanced oxidation processes (EAOPs), is the most generally used technologies for the cleaning treatment of
During anodic oxidation process, persistent organic pollutants can be oxidized through two modes, direct oxidation by electron transfer from organic to anode and indirect oxidation by electrogenerated reactive species and their basic conjugates, including hydroxyl radicals, active chorine, persulfate and ozone [8-10]. The oxidation effect mainly relies on the anode material employed and some key operational parameters, such as electrolyte composition, electrolyte concentration and applied current density.

A diverse range of anode materials has been tested for anodic oxidation of chemical wastewaters [11-14]. Candida-Onfray et al. [15] obtained excellent removal effect of organic pollutants from winery wastewater in real effluents from the wine industry using AO technology with BDD anode. During anodic oxidation process without any support electrolyte, COD removal efficiency of 63.6% was obtained, whereas nearly complete mineralization was reached after adding 50 mM sodium sulfate and sodium chloride. Caliari et al. [16] investigated the anodic oxidation of high organic load in real tannery effluent under galvanostatic mode. Three anode materials were employed including Ti/Pt/PbO2, Ti/Pt/SnO2-Sb2O4 and BDD. The removal efficiencies of the anodes were assessed by evaluating removal rate of chemical oxygen demand (COD), total carbon (TC) and dissolved organic carbon (DOC). Although all three used anodes showed good removal effect in organic load, BDD anode exhibited the best performance in the removal of COD and TC.

In this paper the oxidation of real chemical wastewater was conducted by AO using three commercially available anodes (Pt, BDD and Ti/RuO2-SnO2). A series of batch experiments were conducted to investigate the behaviour of the chosen anodes the effect of several primary operating parameters.

2. Material and methods

2.1. Materials
The supporting electrolyte, including sodium sulfate, sodium chloride, and sodium nitrate, were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. Platinum plate and Ti/RuO2-SnO2 used as anode material was supplied by General Research Institute for Nonferrous Metals (Beijing, China) and Baoji Longsheng Non-ferrous Metal Co., Ltd, respectively. BDD electrode was purchased from CONDIAS®. The chemical wastewater oxidized in this work was taken from Sunny wealth chemicals (Linyi, Shandong Province). The major characteristics of the raw chemical wastewater are presented in Table 1.

| Parameter   | Value |
|-------------|-------|
| Colour      | Brown |
| pH          | 6.4   |
| TOC (mg/L)  | 132   |

2.2. Electrolysis system and analytic methods
Anodic oxidation of chemical wastewater was performed in a home-made reactor with 200ml capacity. During treatment process, chemical wastewater was under vigorous stirring at room temperature (25±2 °C). All oxidation reactions were carried out under galvanostatic mode with a CHI 660 electrochemical workstation as power supply. The anode was a Pt, Ti/RuO2-SnO2 or BDD plate (20*50 mm) and a piece of graphite with the same geometric area was employed as cathode. The working area of both anode and cathode was 8 cm². Samples, filtered through 0.2 mm filter, were taken during oxidation process at certain time intervals for analysis. The determination of TOC was carried out by a TOC analyser (Shimadzu, Japan).
3. Results and discussion

3.1. Effect of Electrolyte Composition

The oxidation effect of chemical wastewater during the AO process rely heavily on the composition of electrolyte. The effect of three common electrolytes (NaCl, Na₂SO₄, NaNO₃) on the oxidation of organics in chemical wastewater were investigated in the use of Pt, Ti/RuO₂-SnO₂ and BDD anode. The electrolysis experiments with different electrolytes were conducted with chemical wastewater added 0.01 mol L⁻¹ electrolyte.

Figure 1. Effect of electrolyte on TOC removal with Pt (a) Ti/RuO₂-SnO₂ (b) and BDD (c).

Fig. 1 clearly exhibits the removal efficiency of TOC with different electrolytes employed Pt (Fig. 1a), Ti/RuO₂-SnO₂ (Fig. 1b) and BDD (Fig. 1c) under the condition of constant applied current density of 20 mA cm⁻². The impact of electrolyte composition on the TOC removal was distinct in the presence of Pt, Ti/RuO₂-SnO₂ and BDD anodes. High TOC removal efficiency was obtained in case NaCl was used as background electrolyte. On the contrary, TOC removal was poor in the presence of NaNO₃ and Na₂SO₄. This phenomenon may be caused by the mediated oxidation of electrogenerated active chlorine species [17]. Furthermore, BDD anode is a common electrode material with nature for the electro-generation of active chlorine during anodic oxidation [18]. During the anodic oxidation process, active chlorine species can be continuously supplied to chemical wastewater from the direct oxidation of chloride ions distributed near the suitable anode surface via Eq. (1)-(3). Hence, oxidation of organics existed in chemical wastewater can be achieved by means of reactive oxygen species on the anode surface and electrogenerated oxidants (active chlorine species) in the bulk used NaCl as electrolyte.

\[
\begin{align*}
    Cl^- & \rightarrow Cl_2 + 2e^- \\
    Cl_2 + H_2O & \rightarrow HClO + Cl^- + H^+ \\
    HClO & \leftrightarrow ClO^- + H^+
\end{align*}
\]

Among the three anode materials used, BDD anode was more effective than Pt and Ti/RuO₂-SnO₂. As it can be seen, the TOC removal of 37%, 39% and 47% was achieved used BDD anode in the presence of NaNO₃, Na₂SO₄ and NaCl, respectively. However, the TOC removal of 32%, 35% and 38% was achieved with Pt anode in the presence of NaNO₃, Na₂SO₄ and NaCl, respectively. And the TOC removal of 34%, 37% and 41% was obtained under the same oxidation conditions with Ti/RuO₂-SnO₂.
anode in the presence of NaNO₃, Na₂SO₄ and NaCl, respectively. Pioneer works reported that anode material with high oxygen over-potential possesses high oxidation ability during anodic oxidation process [19]. BDD anode has higher oxygen over-potential than Pt and Ti/RuO₂-SnO₂, since BDD is evidently more effective in oxidation of organics than Pt and Ti/RuO₂-SnO₂.

3.2. Effect of electrolyte concentration

Now that the best treatment effects were obtained in the presence of Pt, Ti/RuO₂-SnO₂ and BDD anode when NaCl was used as background electrolyte, subsequent experiments were conducted under various NaCl concentrations within the scope of 0.01 to 0.1 mol L⁻¹.

Figure 2. Effect of NaCl concentration on TOC removal with Pt (a) Ti/RuO₂-SnO₂ (b) and BDD (c).

Fig. 2 exhibits the TOC removal with different NaCl concentrations in aqueous solutions used Pt (Fig. 2a), Ti/RuO₂-SnO₂ (Fig. 2b) and BDD (Fig. 2c) anode under applied current density of 20 mA cm⁻². As described in Fig. 2a and Fig. 2b, the TOC removals were improved accompanied with the increasing of NaCl concentration from 0.01 to 0.1 mol L⁻¹ in the presence of Pt and Ti/RuO₂-SnO₂ anode. This phenomena proved that higher chloride concentration facilitates the electro-generation of active chlorine species during anodic oxidation process. The TOC removal was promoted through increasing the NaCl concentration from 0.01 to 0.05 mol L⁻¹ in the presence of BDD anode. However, further increase of NaCl concentration to 0.1 mol L⁻¹ had less effect on organics oxidation, as shown in Fig. 2c. The oxidation efficiencies of Pt and Ti/RuO₂-SnO₂ anode are obviously lower than BDD anode at NaCl concentration ranging from 0.01 to 0.1 mol L⁻¹.

3.3. Effect of applied current density

The most important factor that affects the efficiency and expense of anodic oxidation process is the applied current density. Hence, the effect of applied current density on the oxidation of organics in chemical wastewater was studied in the presence of Pt, Ti/RuO₂-SnO₂ and BDD anode in working solutions of 0.05 mol L⁻¹ NaCl.

The effects of applied current density on the oxidation of organics were shown in Fig. 3. The increase of applied current density from 10 to 40 mA cm⁻² had obvious influence on atrazine oxidation with Pt anode. Higher applied current density leads to larger production of reactive oxygen species
adsorbed on the anode surface and active chlorine species free in solution bulk during anodic oxidation process. Therefore, the oxidation efficiency of organics increased accompanied with the increase of applied current density.

Fig. 3c exhibits the influence of applied current density on the TOC removal efficiency in the presence of BDD anode. The removal efficiency was unobvious with applied current density of 30 and 40 mA cm\(^{-2}\). This is mainly due to parasitic reactions that occurred on the anode surface during the overall anodic oxidation process with high applied current density.

![Figure 3](image)

Figure 3. Effect of current density on TOC removal with Pt (a) Ti/RuO\(_2\)-SnO\(_2\) (b) and BDD (c).

4. Conclusion
Systematic researches on the anodic oxidation of chemical wastewater in the presence of Pt, Ti/RuO\(_2\)-SnO\(_2\) and BDD anode were conducted under different experimental conditions. Experimental results show that NaCl was the most advantageous supporting electrolyte for the anodic oxidation of chemical wastewater, achieving 38\%, 41\% and 47\% TOC removal efficiency within 4 h under the conditions of NaCl 0.01 mol L\(^{-1}\), current density of 20 mA cm\(^{-2}\), used Pt, Ti/RuO\(_2\)-SnO\(_2\) and BDD anode, respectively. In addition, TOC removal increased from 46\% to 49\% through increased the NaCl concentration from 0.01 to 0.05 mol L\(^{-1}\) in the presence of BDD anode. Among the three anode materials, BDD anode possessed the most excellent oxidation capacity for degradation of organics in chemical wastewater. This paper proved that anodic oxidation process could be employed for the effectively removal of organics in real chemical wastewater at appropriate operating conditions.

Acknowledgments
This work was supported by Ministry of Industry and Information Technology of People's Republic of China (High-efficiency catalyst and antioxidant green process breakthrough system integration project).

References
[1] Shen, L., Wang, W., Li, T., Cui, Y., Wang, B., Yu, G., Wang, X., Wei, D., Xiao, J., Deng, S. (2019) Powdered activated coke for COD removal in the advanced treatment of
mixed chemical wastewaters and regeneration by Fenton oxidation. Chem. Eng. J., 371: 631-638.

[2] Kong, Z., Li, L., Xue, Y., Yang, M., Li, Y. (2019) Challenges and prospects for the anaerobic treatment of chemical-industrial organic wastewater: A review. J. Clean. Prod., 231: 913-927.

[3] Tran, N. H., Reinhard, M., Khan, E., Chen, H., Nguyen, V. T., Li, Y., Goh, S. G., Nguyen, Q. B., Saiedi, N., Gin, K. Y. (2019) Emerging contaminants in wastewater, stormwater runoff, and surface water: Application as chemical markers for diffuse sources. Sci. Total. Environ., 676: 252-267.

[4] Tran, N. H., Hoang, L., Nghiem, L. D., Nguyen, N. M. H., Ngo, H. H., Guo, W., Trinh, Q. T., Mai, N. H., Chen, H., Nguyen, D. D., Ta, T. T., Gin, K. Y. (2019) Occurrence and risk assessment of multiple classes of antibiotics in urban canals and lakes in Hanoi, Vietnam. Sci. Total. Environ.

[5] Elgallal, M., Fletcher, L., Evans, B. (2016) Assessment of potential risks associated with chemicals in wastewater used for irrigation in arid and semi-arid zones: A review. Agr. Water. Manage., 177: 419-431.

[6] Zhou, Z., Ruan, D., Jiang, L., Yang, Y., Ge, H., Wang, L. (2019) Comparison on treatment strategy for chemical cleaning wastewater: Pollutants removal, process design and techno-economic analysis. J. Environ. Manage., 235: 161-168.

[7] Moreira, F. C., Boaventura, R. A. R., Brillas, E., Vilar, V. J. P. (2017) Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. Applied Catalysis B: Environmental., 202: 217-261.

[8] Martínez-Huitle, C. A., Panizza, M. (2018) Electrochemical oxidation of organic pollutants for wastewater treatment. Current Opinion in Electrochemistry., 11: 62-71.

[9] de Moura, D. C., de Araújo, C. K. C., Zanta, C. L. P. S., Salazar, R., Martínez-Huitle, C. A. (2014) Active chlorine species electrogenerated on Ti/Ru0.3Ti0.7O2 surface: Electrochemical behavior, concentration determination and their application. J. Electroanal. Chem., 731: 145-152.

[10] Da Silva, A. J. C., Dos Santos, E. V., de Oliveira Morais, C. C., Martínez-Huitle, C. A., Castro, S. S. L. (2013) Electrochemical treatment of fresh, brine and saline produced water generated by petrochemical industry using Ti/IrO2–Ta2O5 and BDD in flow reactor. Chem. Eng. J., 233: 47-55.

[11] Klidi, N., Clematis, D., Delucchi, M., Gadri, A., Ammar, S., Panizza, M. (2018) Applicability of electrochemical methods to paper mill wastewater for reuse. Anodic oxidation with BDD and TiRuSnO2 anodes. J. Electroanal. Chem., 815: 16-23.

[12] Zhang, X., Shao, D., Lyu, W., Tan, G., Ren, H. (2019) Utilizing discarded SiC heating rod to fabricate SiC/Sb-SnO2 anode for electrochemical oxidation of wastewater. Chem. Eng. J., 361: 862-873.

[13] Zhu, K., Qi, H., Sun, X., Sun, Z. (2019) Anodic oxidation of diuron using Co3O4/graphite composite electrode at low applied current. Electrochim Acta., 299: 853-862.

[14] Sui, X., Duan, X., Xu, F., Chang, L. (2019) Fabrication of three-dimensional networked PbO2 anode for electrochemical oxidation of organic pollutants in aqueous solution. J. Taiwan Inst. Chem. E., 100: 74-84.

[15] Candia-Onfray, C., Espinoza, N., Sabino Da Silva, E. B., Toledo-Neira, C., Espinoza, L. C., Santander, R., Garcia, V., Salazar, R. (2018) Treatment of winery wastewater by anodic oxidation using BDD electrode. Chemosphere., 206: 709-717.

[16] Caliari, P. C., Pacheco, M. J., Ciriaci, L., Lopes, A. (2019) Tannery wastewater: Organic load and sulfide removal dynamics by electrochemical oxidation at different anode materials. Environmental Technology & Innovation., 14: 100345.
[17] Zambrano, J., Min, B. (2019) Comparison on efficiency of electrochemical phenol oxidation in two different supporting electrolytes (NaCl and Na2SO4) using Pt/Ti electrode. Environmental Technology & Innovation., 15: 100382.

[18] Bensalah, N., Dbira, S., Bedoui, A. (2016) The contribution of mediated oxidation mechanisms in the electrolytic degradation of cyanuric acid using diamond anodes. J. Environ. Sci-China., 45: 115-123.

[19] Jeong, J., Kim, C., Yoon, J. (2009) The effect of electrode material on the generation of oxidants and microbial inactivation in the electrochemical disinfection processes. Water Res., 43: 895-901.