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A novel combined electrochemical-biological method for non-biodegradable pollutants degradation

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ABSTRACT

A novel combined electrochemical-biological method for non-biodegradable pollutants degradation using a new Ti/SnO_2–Sb–Mn electrode as the anode was studied. The electrode characterization showed a good formation of SnO_2–Sb–Mn film and compact structure of electrode. The experiments of orangeII electrochemical conversion demonstrated that the Ti/SnO_2–Sb–Mn electrode could increase the bio-degradability of the simulated orangeII wastewater effectively due to converting the orangeII into small molecule organics. Finally, the residual solution could be degraded by aerobic biological treatment.

Keywords: Electrochemical oxidation; Ti/SnO_2–Sb–Mn electrode; Combined electrochemical-biological method; Wastewater treatment

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1. Introduction

Nowadays, the electrochemical oxidation and combined methods have attracted a great deal of attention for non-biodegradable wastewater treatment, because they are environmentally-friendly and do not add extra chemicals into the system [1–8]. The "electrochemical combustion" and "electrochemical conversion" are the two main applications for the electrochemical oxidation [5]. The electrochemical combustion method can completely mineralize the organics to CO_2 and H_2O, which has been investigated extensively. It is suitable for the treatment of organic wastewater with low concentration, but unacceptable for the treatment of organic wastewater with high concentration due to its high energy consumption. Chen and co-workers reported that the energy consumption for dyes wastewater electrochemical combustion was about 8.9–17.9 kWh m^{-3} with over 90% chemical oxygen demand (COD) removal obtained on the BDD electrodes [9]. It is much higher than that for the conventional biological treatment, which was only about 0.3–0.5 kWh m^{-3} for the biodegradable pollutants removal. On the other hand, little attention was paid to the electrochemical conversion, which could transform the non-biodegradable pollutants into bio-compatible organics. Compared with the electrochemical combustion, the electrochemical conversion involves less transferred electrons. For example, electrochemical combustion of 1 mol phenol into CO_2 and H_2O needs 28 mol electrons; while electrochemical conversion of 1 mol phenol into acetic acid only needs 4 mol electrons. Since the energy consumption depends on the transferred electrons, the electrochemical conversion can greatly reduce the energy consumption.

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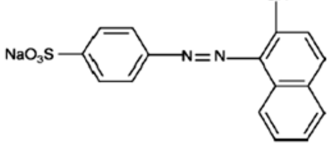
Considering the virtue of the electrochemical conversion and biological treatment, we combined the two methods to degrade the non-biodegradable pollutants. It could be easily convinced that the combined electrochemical-biological method would have a good performance on pollutants degradation and require lower energy consumption.

It is well known that the electrochemical combustion or conversion of pollutants is determined by the anodes [3–5]. In general, the anodic oxygen-transfer reactions mainly occur on the sites of dopants for a semiconducting oxide mixture with high overpotential for oxygen evolution [10–12]. Therefore, the electrochemical properties of electrodes should be determined primarily by the properties of dopants. Comninellis reported that the high valence metal oxides were favored for electrochemical conversion [5,13]. The Mn element has wide range of valences. In addition, MnO_2 have good catalytic activity for volatile organic compounds oxidation [14–16]. The Ti/SnO_2–Sb–Mn electrode was therefore fabricated for electrochemical conversion. The objective of this paper is to demonstrate the good performance of the combined electrochemical-biological method for pollutants treatment using Ti/SnO_2–Sb–Mn as the anode. The orangeII, a typical toxic and non-biodegradable azo dye, was selected as a model pollutant.

2. Experimental

The orangeII (purity 98%, Huadong Medicine, Zhejiang, China) was used as it was, and its characteristics are given in Table 1. Ti plates (20 mm × 24 mm × 1.6 mm) were used as substrates. Before deposition, the substrates were sandblasted first, then etched in boiling 37% hydrochloric acid for two minutes, and finally cleaned ultrasonically in deionized water for ten minutes. After pretreatment, the SnO_2–Sb–Mn films were deposited on the Ti substrates using ultrasonic spray pyrolysis (USP) with the precursor that was prepared by dissolving $SnCl_4{\cdot}5H_2O$, $MnCl_2{\cdot}4H_2O$, and $SbCl_3$ into dilute hydrochloric acid solution. The concentration of $SnCl_4{\cdot}5H_2O$ was 0.5 M and the molar ratio of Sn:Sb:Mn was 89:3:6. The USP deposition parameters were: substrate temperature 600°C, atomizing rate 0.17 mL min^{-1}, N_2 flow rate 5 L min^{-1}, deposition time 0.5 h. The total oxide coating loading was about 20 g m^{-2}. More details about the USP deposition procedures can be found elsewhere [17].

Table 1
The orangeII characteristics

Structure	Formula	Molar mass
	$C_{16}H_{11}N_2NaO_4S$	350

Coating morphology and microstructure were examined by field emission scanning electron microscopy (FE-SEM: Sirion-100, FEI, the Netherlands) and X-ray diffraction (XRD: D/max-rA, Rigaka, Japan). The pH values were measured using a pH meter (420A, Orion, USA). COD was measured using a COD reactor and a direct reading spectrophotometer (DR/2500, Hach, USA). Biology oxygen demand (BOD_5) was measured according to the Chinese National Standard Method (GB7488-87). The products were analyzed by the GC-MS (Trace2000GC, THECMO QUEST CO, England).

The electrochemical reactor had dimensions of 100 mm in height and 80 mm in diameter, and was operated in batch. A magnetic stirrer was used to enhance mass transport. Temperature was controlled at 30°C with a water bath. More details about the electrochemical reactor can be found elsewhere [18]. The initial concentration of orangeII was 600 mg L^{-1}. The initial pH was adjusted to 11.2 by NaOH electrolyte. The aerobic bioreactor had dimensions of 350 mm in height and 65 mm in diameter, and was also operated in batch. Temperature was controlled at 30°C using an air conditioner. The activated sludge was domesticated, and the mixed liquor suspended solids was about 6 g L^{-1}.

3. Results and discussion

3.1. Electrode characterization

Fig. 1 presents a typical FESEM image of a Ti/SnO_2–Sb–Mn electrode. It was found that the Ti substrate was completely covered by the SnO_2–Sb–Mn film. Moreover, no cracks were observed on the film. The average size of the SnO_2–Sb–Mn grains was about 1 μm, only half of the SnO_2–Sb grains [18]. This may be attributed to the formation of heterogeneous nuclei, MnO_2.

Fig. 2 shows the XRD of the SnO_2–Sb–Mn film coated on a Ti substrate. It was found that the film was polycrystalline with tetrahedral structure of SnO_2 [19]. In addition, only a single set of peaks with their positions deviating slightly from the pure SnO_2 was found, indicating the formation of a solid solution of SnO_2–Sb–Mn.

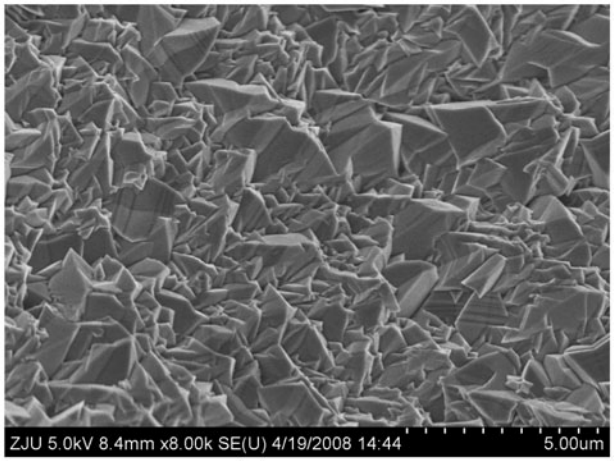


Fig. 1. FESEM image of Ti/SnO_2–Sb–Mn electrode prepared by USP.

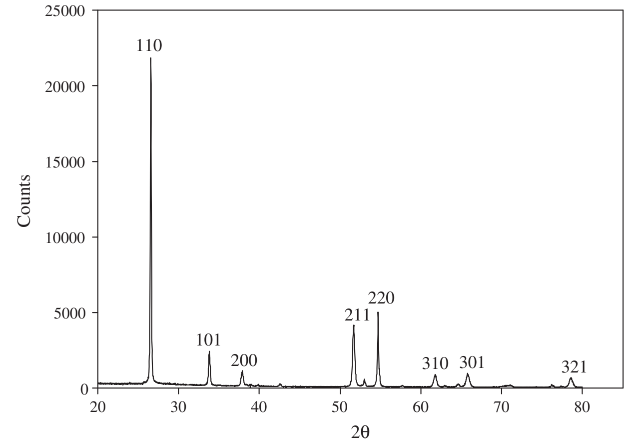


Fig. 2. XRD pattern of Ti/SnO_2–Sb–Mn electrode prepared by USP.

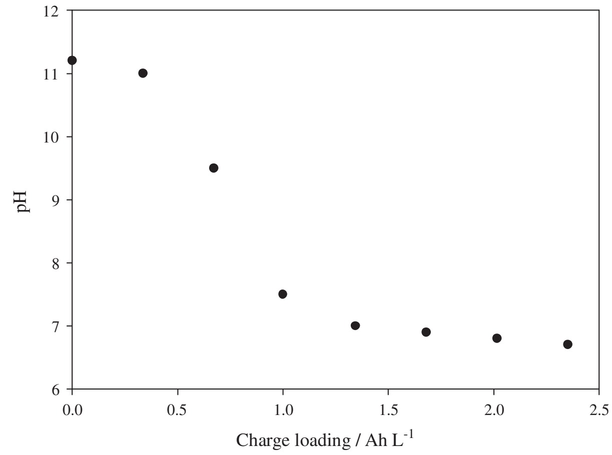


Fig. 3. The variation of pH depending on the charge loading. (Initial orangeII concentration = 600 mgL^{-1}, current density = 100 Am^{-2}, reaction temperature = 30℃, and pH = 11.2).

3.2. Electrochemical conversions

Fig. 3 shows the variation of pH depending on the charge loading. It was clearly found the pH decreased quickly with the charge loading initially. This was caused by lots of organic acidic intermediates produced during the electrochemical conversion, which counteracted with the OH^-. However, the pH decreased slowly beyond charge loading of 1.5 Ah L^{-1}. This was because the weak organic acids accumulated and many of them were further converted into smaller molecule organics.

Fig. 4 shows the removal efficiency of colority on the charge loading. The removal efficiency of colority increased fast with the charge loading, and reached

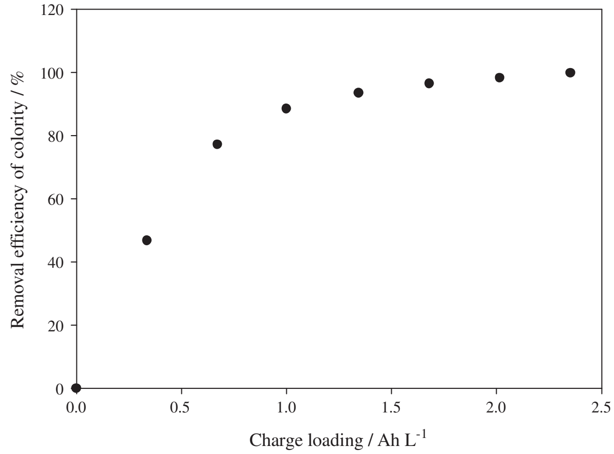


Fig. 4. The removal efficiency of colority on the charge loading. (Initial orangeII concentration = 600 mgL^{-1}, current density = 100 Am^{-2}, reaction temperature = 30℃, and pH = 11.2).

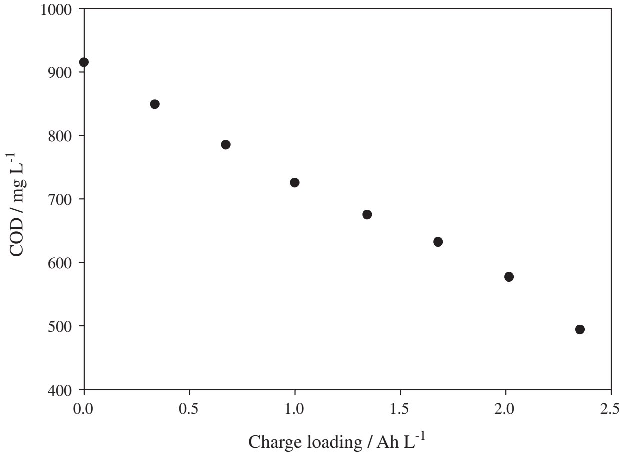


Fig. 5. The COD variation with the charge loading. (Initial orangeII concentration = 600 mgL^{-1}, current density = 100 Am^{-2}, reaction temperature = 30℃, and pH = 11.2).

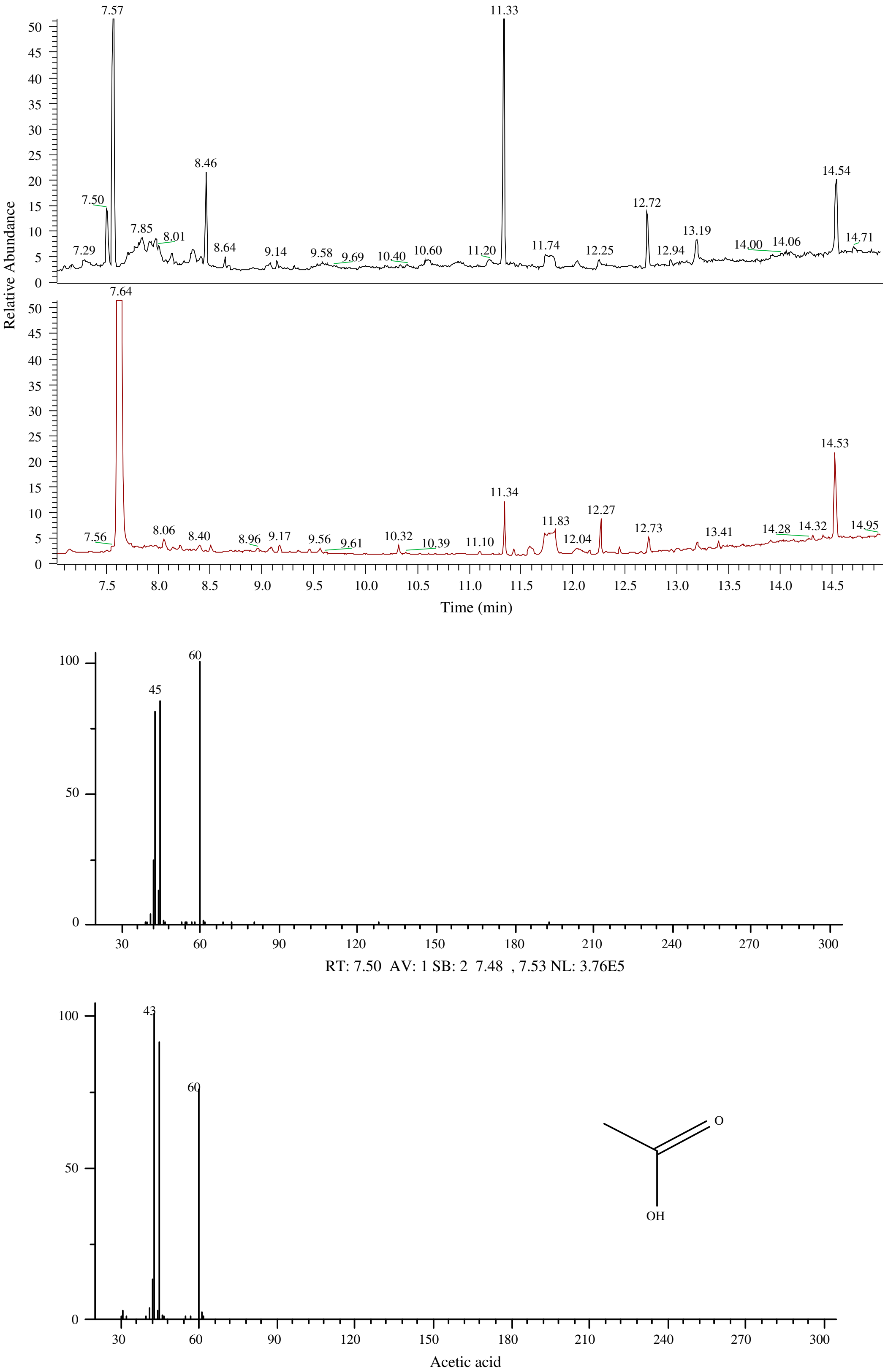
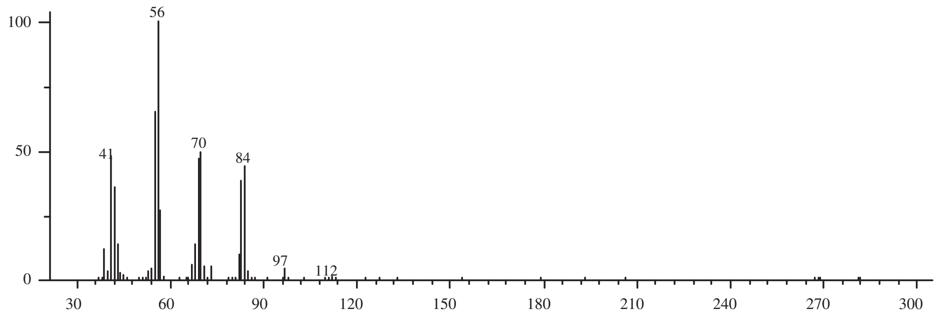
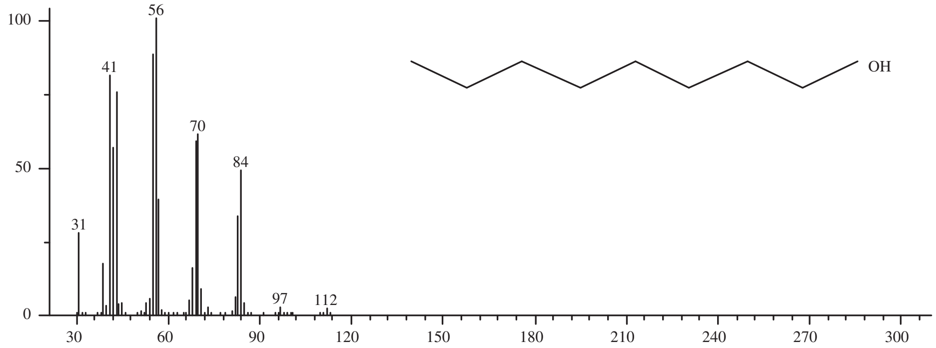


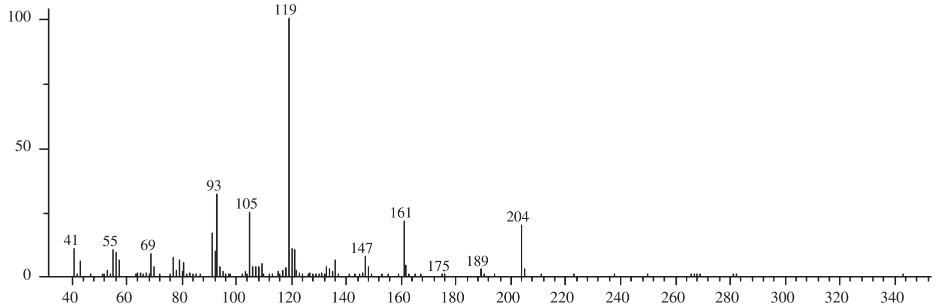
Fig. 6. The test results of the products by GC-MS. (acetic acid at retention time of 7.5 min, octanol at retention time of 8.46 min, 1H-3a, 7-methanoazulene,2,3,4,7,8,8a-hexahydro-3,6,8,8-tetramethyl at retention time of 8.64 min).



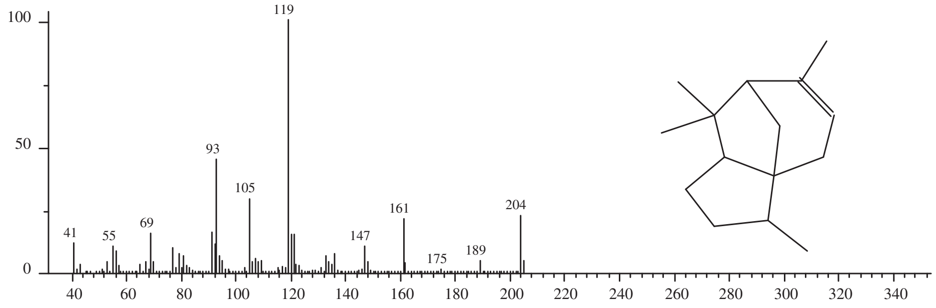
RT: 8.46 AV: 1 SB: 2 8.45 , 8.48 NL: 3.22E5



Octanol



RT:8.64 AV: 1SB:28.60, 8.66 NL : 5.60 E4



1H-3a,7-Methanoazulene, 2,3,4,7,8,8a-hexahydro-3,6,8,8-tetramethyl

Fig. 6. (*Continued*).

99.8% at a charge loading of 2.35 Ah L^{-1}. However, the rate of removal efficiency became slow beyond charge loading of 1.5 Ah L^{-1}. This was understandable. The colority is highly dependent on the concentration of orangeII. It is generally believed that mass transport, adsorption, and reaction on the anode are the main steps for the electrochemical conversion of orangeII [4]. On the initial stage of electrochemical conversion, the rate of mass transfer and adsorption were fast due to the high concentration of orangeII.

The rate of orangeII oxidation was therefore determined by the reaction on the anode as the charge loading was below 1.5 Ah L^{-1}. Then, the concentration of orangeII decreased quickly. The mass transfer rate of orangeII from the bulk solution to the anode became the rate determining step of orangeII oxidation beyond the charge loading of 1.5 Ah L^{-1}. Since the rate of orangeII removal decreased due to the mass transfer control, the rate of removal efficiency of colority decreased.

Fig. 5 shows the COD variation with the charge loading. It was found the COD decreased with the charge loading. At a charge loading of 2.35 Ah L^{-1}, COD was reduced from initial 915 to 494 mg L^{-1}, with only 46% of total COD removed. Although the orangeII were not mineralized during the electrochemical conversion, the degradability of the solution was changed. The comparison of degradability of the model pollutants depending on the electrochemical conversion is shown on Table 2. The BOD_5/COD ratio increased from 0.01 initially to 0.25 due to an increase in BOD_5 value from 5.3 to 123.5 mg L^{-1} by electrochemical conversion. Therefore, the degradability of the solution was increased greatly by the electrochemical conversion. Although the limit of biodegradability (0.4) was not achieved, a biological treatment could be promisingly considered. It should be noted that the limit of biodegradability (0.4) is just a reference for biodegradation. Yahiaoui and co-workers have reported that the basic yellow 28 dye could be well degraded by the activated sludge with BOD_5/COD of 0.3 after pretreatment [8]. Moreover, the residual solution treated by the activated sludge could meet the national discharge standard. Actually it is easy to improve the BOD_5/COD value using Ti/SnO_2–Sb–Mn electrode with sufficient charge loading. The charge loading adopted in this experiment is for the sake of saving energy.

3.3. Why did the bio-degradability increase?

In order to investigate the reason why the biodegradability of the wastewater was enhanced by electrochemical conversion, the electrochemical conversion products were analyzed by the GC-MS. Fig. 6 shows the results of GC-MS. There were clearly three main peaks at retention time of 7.50, 8.46, and 8.64 min, and the structure of the organics was therefore analyzed, respectively. No orangeII was detected, indicating that the orangeII was entirely converted into the small molecule organics, which caused the high removal efficiency of colority (99.8%). Major constituents of the conversion products were small molecule organics such as acetic acid and octanol. The accumulated acetic acid caused a decrease in the pH value, which was consistent with the results of Fig. 3. It is well known that the acetic acid and octanol could be biodegraded easily, resulting in higher biodegradability of wastewater, and a more favorable condition for further treatment biologically.

Table 2
The biodegradability test of orangeII solution and orangeII solution under electrochemical pretreatment

OrangeII	COD mg L^{-1}	BOD_5 mg L^{-1}	BOD_5/COD
Before pretreatment	915	5.3	0.01
After pretreatment	494	123.5	0.25

3.4. Biological treatment

The residual solution was degraded by aerobic biological treatment. The COD variation with the reaction time is shown in Fig. 7. It was found the residual COD decreased with the reaction time. Moreover, there is a large COD decrease within 2 h. This is not a new finding, but a common phenomenon. Many researchers have observed the big decrease during the first stage of culture. This was caused by the quick bio-sorption of intermediates compounds formed on the activated sludge and degradation by activated sludge [6,8,20]. At reaction time of 10 h, the COD of solution pretreated was reduced from 502 to 80 mg L^{-1}, which could meet the national discharge standard. Whereas the residual COD of orangeII solution without electrochemical pretreatment remained almost constant within

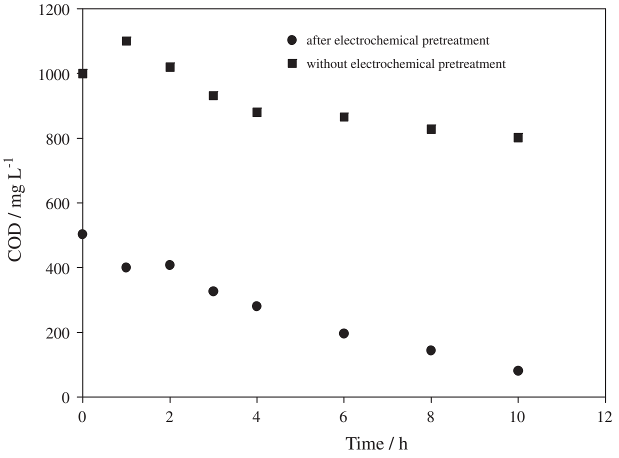


Fig. 7. The time-courses of COD values on the electrochemical pretreated solution (◆) and non-treated solution (■).

10 h by the activated sludge. A slight increase in COD value during the first 2 h was observed in Fig. 7. This may be caused by the organics released by the dead micro-organisms, which have been poisoned by the orangeII. It confirmed that the orangeII was refractory and could not be degraded by biological treatment. After 10 h, the residual COD was still about $802\,\mathrm{mg\,L^{-1}}$. The result of comparison indicated that the electrochemical conversion could greatly enhance the degradability of orangeII solution. Moreover, the energy consumption for orangeII degradation by the combined electrochemical-biological method was about $6\,\mathrm{kWh\,m^{-3}}$, which was much lower than that for orangeII electrochemical combustion [9].

4. Conclusion

A novel combined electrochemical-biological method for non-biodegradable pollutants degradation using Ti/SnO_2–Sb–Mn electrode prepared as the anode was firstly proposed and tested. The physicochemical characterization revealed the compact structure of the electrode and good formation of SnO_2–Sb–Mn solid solution. The orangeII degradation experiment demonstrated the good performance and lower energy consumption of the novel combined electrochemical-biological method.

References

[1] E. Brillas, E. Mur, R. Sauleda, L. Sanchez, J. Peral, X. Domenech, J. Casado, Aniline mineralization by AOP's: Anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes, J. Appl. Catal. B: Environ. 16 (1998) 31–42.

[2] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[3] G.H. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

[4] C.A. Martinez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: Direct and indirect processes, Chem. Soc. Rev. 35 (2006) 1324–1340.

[5] Ch. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, Electrochim. Acta 39 (1994) 1857–1862.

[6] I. Yahiaoui, F. Aissani-Benissad, F. Fourcade, A. Amrane, Removal of tetracycline hydrochloride from water based on direct anodic oxidation (Pb/PbO_2 electrode) coupled to activated sludge culture, Chem. Eng. J. 221 (2013) 418–425.

[7] I. Yahiaoui, F. Aissani-Benissad, F. Fourcade, A. Amrane, Response surface methodology for the optimization of the electrochemical degradation of phenol on Pb/PbO_2 electrode, Environ. Prog. Sustain. Eng. 31(4) (2012) 515–523.

[8] I. Yahiaoui, F. Aissani-Benissad, F. Fourcade, A. Amrane, Combination of an electrochemical pre-treatment with a biological oxidation for the mineralization of nonbiodegradable organic dyes: Basic yellow 28 dye, Environ. Prog. Sustain. doi: 10.1002/ep.11774.

[9] X.M. Chen, G.H. Chen, P.L. Yue, Anodic oxidation of dyes on Ti/BDD electrodes, Chem. Eng. Sci. 58 (2003) 995–1001.

[10] D. He, S. Mho, Electrocatalytic reactions of phenolic compounds at ferric ion co-doped SnO_2:Sb^{5+} electrodes, J. Electroanal. Chem. 568 (2004) 19–27.

[11] I.H. Yeo, D.C. Johnson, Electrocatalysis of anodic oxygen-transfer reactions, J. Electrochem. Soc. 134 (1991) 1973–1977.

[12] J. Feng, D.C. Johnson, Electrocatalysis of anodic oxygen-transfer reaction: Titanium substrates for pure and doped lead dioxide films, J. Electrochem. Soc. 138 (1991) 3329–3337.

[13] Ch. Comninellis, A. De Battisti, Electrocatalysis in anodic oxidation of organics with simultaneous oxygen evolution, J. Chim. Phys. 93 (1996) 673–679.

[14] C. Lahousse, A. Bernier, P. Grange, B. Delmon, P. Papaefthimiou, T. Ioannides, X. Verykiosy, Evaluation of γ-MnO_2 as a VOC removal catalyst: Comparison with a noble metal catalyst, J. Catal. 178 (1998) 214–225.

[15] S.J. Lee, A. Gavriilidis, Q.A. Pankhurst, A. Kyek, F.E. Wagner, P.C.L. Wong, K.L. Yeung, Effect of drying conditions of Au–Mn co-precipitates for low-temperature CO oxidation, J. Catal. 200 (2001) 298–308.

[16] F.T. Chen, S.C. Yu, X.P. Dong, S.S. Zhang, High-efficient treatment of wastewater contained the carcinogen naphthylamine by electrochemical oxidation with gamma-Al_2O_3 supported MnO_2 and Sb-doped SnO_2 catalyst, J. Hazard. Mater. 227 (2012) 474–479.

[17] P.D. Yao, Q.N. Jin, X.M. Chen, Y.Q. Xing, D.H. Wang, Ti/SnO_2-Sb electrodes for pollutant degradation prepared using ultrasonic spray pyrolysis, Electrochem. Solid St. 11 (2008) J37–J39.

[18] X.M. Chen, F.R. Gao, G.H. Chen, Comparison of Ti/BDD and Ti/SnO_2–Sb_2O_5 electrodes for pollutant oxidation, J. Appl. Electrochem. 35 (2005) 185–191.

[19] Powder Diffraction File Alphabetic PDF-2 Data Base, File 41–1445, International Center of Diffraction Data, Newtown Square, PA, 1994.

[20] J.M. Zhao, Y.M. Li, C.J. Zhang, Q.L. Zheng, Q. Zhou, Sorption and degradation of bisphenol A by aerobic activated sludge, J. Hazard. Mater. 155 (2008) 305–311.