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# Electrochemical treatment of papermaking tobacco sheet wastewater on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes

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ABSTRACT

β-$PbO_2$ electrode modified with fluorine resin and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode exhibited excellent performance in electrochemical treatment of papermaking tobacco sheet wastewater. Most of the organic pollutants and suspended solids could be effectively removed from wastewater under optimized conditions and the main recalcitrant components were converted to biodegradable intermediates. The $BOD_5$/COD ratio of wastewater increased from 0.06 to 0.50 (on β-$PbO_2$) or 0.47 (on Ti/$TiO_2$-$RuO_2$-$IrO_2$), indicating that the effluent was more apt to biological treatment. Therefore, electrochemical oxidation could be employed as a promising pretreatment method for wastewater treatment of papermaking tobacco sheet manufacturers.

*Keywords:* β-$PbO_2$ electrode; Electrochemical treatment; Papermaking tobacco sheet; Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode; Wastewater

## 1. Introduction

Papermaking tobacco sheet is a kind of reconstituted tobacco sheet (RTS) made via recomposing and processing using tobacco wastes, such as tobacco stems, leaf scraps, tobacco dust as well as low-grade tobacco leaf [1,2]. RTS can utilize raw leaf materials as far as possible to save cigarette cost. It has been widely utilized by cigarette manufacturers to reduce tar release and nicotine yields and at the same time to minimize cigarette harm [2–6]. Presently, papermaking process is the most widely used RTS producing method [1,2,4,7], and the production procedure of papermaking tobacco sheet is sketched in Fig. 1.

During the extraction and papermaking processes, the alkaloids, solanone and organic acids (oleic acid, palmitic acid, etc.) are transferred from the solid substances (tobacco leaf, stem, and dust) to an aqueous solution and then exist as organic pollutants, resulting in the complicated components of wastewater. According to the statistics of tobacco sheet manufacturing company, approximately 60–80 $m^3$ of wastewater will be generated in papermaking step for yielding one ton of RTS, wherein, nicotine accounts for nearly 95% of the total alkaloid fraction [8], which contributes to the soluble chemical oxygen demand ($COD_s$) of

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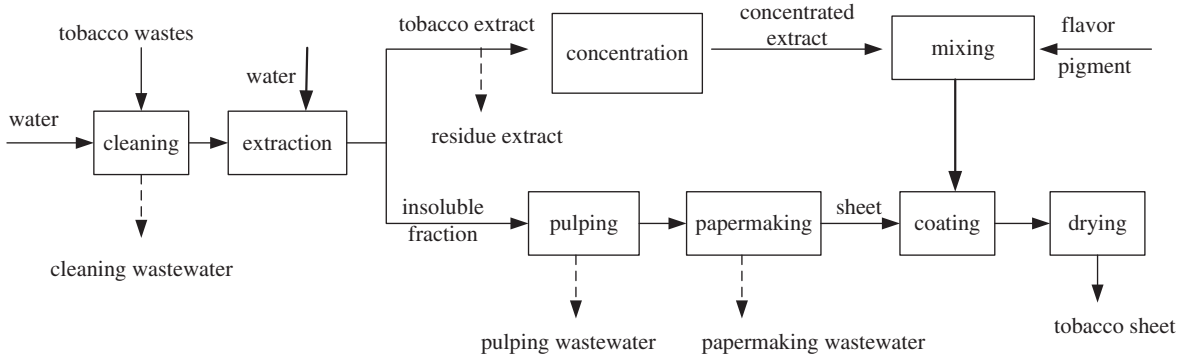



Fig. 1. Production procedure of papermaking tobacco sheet.

wastewater. The conventional biological method in treating papermaking tobacco sheet wastewater often fails to ensure satisfactory performance due to the inhibition of nicotine on the activity of micro-organisms and the existence of suspended solids (SS) in the wastewater [9,10]. Recently, most of the studies concerning tobacco wastewater treatment have been focused on the isolation, inoculation, and culture of nicotine-degrading bacteria [9,11–13]. Additionally, coagulation–flocculation [14], electrocoagulation combined with electrochemical oxidation [15], and Fenton process [16,17] were also attempted to treat tobacco sheet wastewater, among which, Fenton process has the advantages of simple and flexible operation, easy-to-handle chemicals, and no need energy input [18]. Our previous study confirmed that 79.4% of COD and 94.2% of turbidity in papermaking tobacco sheet wastewater could be removed through Fenton process under acidic conditions via the oxidation of hydroxyl radicals ($HO^{\cdot}$) and the coagulation of ferric hydroxide [16]. However, Fenton process is confronted with safety issues in the storage and transportation of hydrogen peroxide ($H_2O_2$), while acidification of wastewater at pH 2.0–4.0 demands high amounts of chemicals [18]. Electrochemical oxidation may be the promising alternative for treating papermaking tobacco sheet wastewater because of its high efficiency and environmental compatibility. During water electrolysis, hydrogen ($H_2$) and oxygen ($O_2$) bubbles released from the cathode and anode, respectively, will be very beneficial for floatation of SS out of wastewater [19,20].

During electrochemical oxidation, the reaction between pollutants and oxidants generated on the surface of electrode depends on the nature of electrode material. Generally, non-active anodes, such as lead dioxide ($PbO_2$) and boron-doped diamond (BDD), favor complete oxidation of organic pollutants to $CO_2$ and $H_2O$. In comparison, active anodes with low oxygen evolution potential, such as graphite, $IrO_2$, $RuO_2$, and mixed metal oxide (MMO), allow only partial oxidation of organic pollutants [21]. But it can make use of indirect oxidation of active chlorines (e.g. HClO and $Cl_2$) when NaCl is employed as supporting electrolyte [22].

In the present study, a β-$PbO_2$ electrode modified with fluorine resin [23] was chosen as the representative of non-active anodes due to its high oxygen evolution potential in acidic media, and the ability of direct and successive generation of $HO^{\cdot}$ by water discharge during electrochemical oxidation (Eqs. (1)–(3)) [24]. For comparison, a Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode was selected as the typical active MMO anode not only due to its dimensional stability, relatively inexpensive and the ability of generating active chlorines *in situ*, but also because it has been commercially applied in the chlorine alkali industry and other electrochemical processes [21]. The electrochemical oxidation performance of papermaking tobacco sheet wastewater on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes was firstly examined and compared under the investigated conditions. Then, the biodegradability and the main components of wastewater prior to and after treatment were also probed under optimized conditions.

$$PbO_2 + H_2O \leftrightarrow Pb*O(OH)_2 \leftrightarrow H_2PbO_3 \quad (1)$$

Crystal layer Hydrated (gel) layer

$$Pb*O(OH)_2 \leftrightarrow Pb*O(OH)^{+}(OH)^{\cdot} + e^{-} \quad (2)$$

$$Pb*O(OH)^{+}(OH)^{\cdot} + H_2O \rightarrow Pb*O(OH)_2\cdots(OH)^{\cdot} + H^{+} \quad (3)$$

## 2. Experimental

### 2.1. Papermaking tobacco sheet wastewater

Wastewater used in this study was obtained from the papermaking step of a tobacco sheet manufacturing company located in Hangzhou, China. It produced averagely 1,600 $m^3$/d of wastewater and the characteristics of wastewater were relatively stable with the change in seasons. The wastewater was stored in a freezer at 4℃ in order to avoid deterioration and the experiments were carried out within 7 d for each batch. The ranges of pH value, conductivity, and initial transmittance value of this wastewater were 6.7–7.0, 2.0–2.5 mS/cm and 0.7–1.0%, respectively. Cellulose, hemicellulose and lignin extensively existed as the SS. Some non-volatile organic acids, alkaloids, tar, and other pollutants darkened the color of wastewater. The other characteristics of papermaking tobacco sheet wastewater are listed in Table 1.

### 2.2. Experimental procedure

Electrochemical oxidation experiments were carried out under galvanostatic conditions in an open, quadrate, undivided Plexiglas reactor (10 × 8 cm, 10 cm of height, 800 mL capacity). A β-$PbO_2$ (28.78 $cm^2$ of area) [23] or Ti/$TiO_2$-$RuO_2$-$IrO_2$ plate (7.5 × 5.5 cm, 2 mm of thickness, 2 × 41.25 $cm^2$ of area) was used as anode and a corresponding size of stainless steel net as cathode. Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode was prepared by a titanium equipment manufacturing company located in Suzhou, China. Before experiment, 650 mL of wastewater was initially added into the reactor. The pH of wastewater was adjusted to a desirable value using NaOH, HCl, or $H_2SO_4$ solutions. NaCl or $Na_2SO_4$ was used as the supporting electrolyte. Then, the anode and cathode were positioned vertically and parallel to each other with an inter-electrode gap of 15 mm. A digital DC power supply (WYL3015, Hangzhou, China) with digital displays was used as the source of electric current for all experiments. The operating parameters included the current density, initial pH, electrolyte type, and dosage. During the experiments, the wastewater was mainly stirred by the $H_2$ gas bubbles generated on the cathode.

Based on the optimization of electrochemical oxidation, the papermaking tobacco sheet wastewater was treated under optimized conditions to investigate the treatment performance, the variation of the main components in wastewater, as well as biodegradability improvement prior to and after oxidation on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes.

All chemicals used in this study were of analytical grade and purchased from Huadong Medicine Group Co. Ltd (Hangzhou, China).

### 2.3. Analytical methods

During experiments, water samples were periodically taken from the sampling port located about 4 cm below the liquid level and then maintained standstill for 30 min. The supernatant solution was taken for COD, SS, turbidity and transmittance value analyses, and three repetitions were performed for each treatment. Samples for the determination of $COD_s$ were firstly filtered with 0.45-μm membrane. $COD_t$ and $COD_s$ were determined in accordance with the method 508 C (closed reflux, colorimetric method) in Standard Methods [25]. The pH was measured using a pH meter (pH3110 SET2, Germany). The transmittance value (in percent) of wastewater or effluent was measured using a visible spectrophotometer (S23A, Shanghai, China) at the wavelength of 630 nm, which was standardized at 100% transmittance with distilled water. The turbidity and conductivity of wastewater were determined using the SGZ-2 digital turbidity meter (Shanghai, China) and YSI Model 30 conductivity meter (USA), respectively. The SS of wastewater was measured using gravimetric method. $BOD_5$ was measured in an OxiTOP system (WTW, Germany) for investigating the biodegradability improvement of wastewater.

Dichloromethane (DCM) was used to extract the main organic components from wastewater prior to and after treatment. The ratio of water sample to DCM was 1:1 (v/v). After extraction, the DCM extract was concentrated with a rotary evaporator (R201BL,

Table 1
Characteristics of papermaking tobacco sheet wastewater

| Parameters | Values |
|---|---|
| Total chemical oxygen demand ($COD_t$, mg/L) | 5,342–6,414 |
| Soluble chemical oxygen demand ($COD_s$, mg/L) | 2,370–2,959 |
| Five-day biochemical oxygen demand ($BOD_5$, mg/L) | 318–386 |
| Turbidity (NTU) | 1,215–1,970 |
| Suspended solids (SS, mg/L) | 1,600–2,145 |

Shanghai, China) to 10 mL and analyzed by gas chromatography–mass spectrometry (GC–MS) using an Agilent 6890N chromatograph coupled to a quadrupole Agilent 5975B inert XL mass selective spectrometer, which is equipped with an HP-Innowax column (Agilent 19091N-233, capillary 30.0 m × 250 μm × 0.5 μm). Helium (99.999%) was used as the carrier gas at a constant flow of 0.7 mL/min. The temperature of injector was 250°C and the injection volume was 2.0 μL in splitless mode. The temperature in column was held at 80°C for 1 min and then increased with 5°C/min to 240°C and maintained for 27 min. The characterization of the obtained spectra was conducted by comparing the mass spectra with those reported in the GC–MS library (NIST).

## 3. Results and discussion

### 3.1. Effect of current density

Fig. 2 presents the effect of current density on the treatment performance of papermaking tobacco sheet wastewater on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes after 30 min of reaction. As demonstrated in Fig. 2(a), the COD removal was not dependent with the current density on both electrodes, whereas, the $COD_s$ removal on β-$PbO_2$ was much more superior with respect to Ti/$TiO_2$-$RuO_2$-$IrO_2$ at the same current density. For instance, at the current density of 60 mA/$cm^2$, 15.5% of $COD_s$ was removed on β-$PbO_2$ electrode, while on Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode, the $COD_s$ removal was only 11.6%. This low $COD_s$ removal may be due to the fact that some organic acids like oleic acid and palmitic acid were difficult to mineralize and the adsorption of fine SS existing in wastewater hindered the rate of mass transfer between HO· and pollutants [21].

However, as shown in Fig. 2(b), a high current density promoted the turbidity removal of wastewater. For example, when the current density increased from 20 to 50 mA/$cm^2$, the turbidity removal increased from 21.5 to 80.8% for Ti/$TiO_2$-$RuO_2$-$IrO_2$, 20.3 to 74.6% for β-$PbO_2$. This could be explained by the fact that more hydrogen ($H_2$) bubbles were generated on the surface of cathode at higher current density, which led to floating more SS out of wastewater. Further increasing the current density to 60 mA/$cm^2$ did not significantly increase the removal of turbidity. Therefore, 50 mA/$cm^2$ of current density was selected for the following experiments.

### 3.2. Effect of supporting electrolyte

Fig. 3 shows the electrochemical treatment performance of papermaking tobacco sheet wastewater

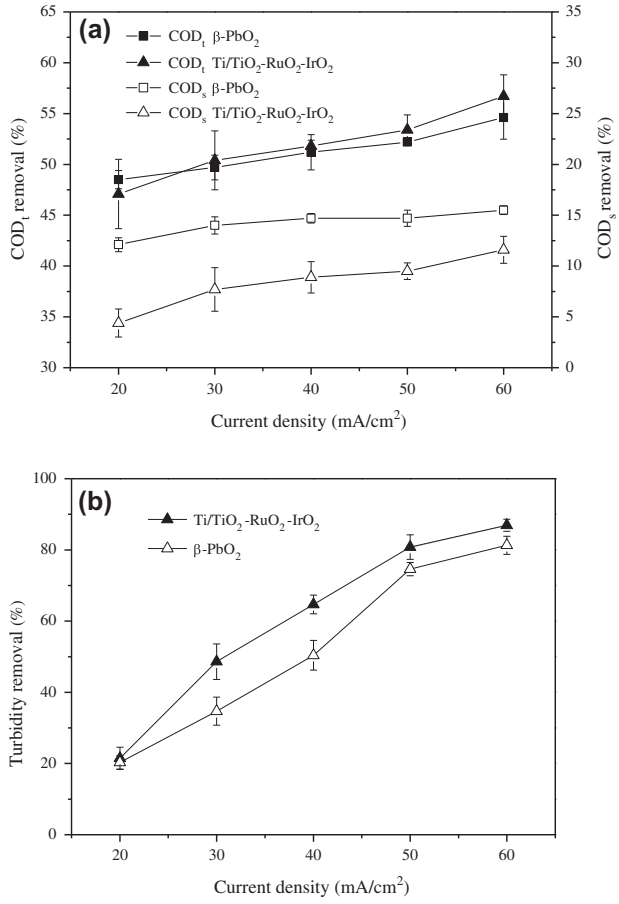



Fig. 2. Effect of current density on COD (a) and turbidity (b) removals on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes. Conditions: NaCl 1.5 g/L, pH 5.0 for β-$PbO_2$, pH 6.8 for Ti/$TiO_2$-$RuO_2$-$IrO_2$.

on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes at 50 mA/$cm^2$ of current density using $Na_2SO_4$ or NaCl as supporting electrolyte. It was observed that on both electrolytes, the treatment performance on β-$PbO_2$ was much better than that obtained on Ti/$TiO_2$-$RuO_2$-$IrO_2$, the maximum transmittance value was 70% for β-$PbO_2$, while only 54.8% for Ti/$TiO_2$-$RuO_2$-$IrO_2$. The greater oxidation ability of β-$PbO_2$ can be explained by the fact that the oxygen evolution potential on β-$PbO_2$ was much higher than on Ti/$TiO_2$-$RuO_2$-$IrO_2$, which prevented the side reactions and greatly improved the current efficiency for HO· formation (Eqs. (1)–(3)). In the case of β-$PbO_2$ electrode, due to the competitive reaction of active chlorines and hydroxyl radical (HO·), and also the relatively lower oxidation of active chlorines [26], the transmittance value of effluent and the removal of COD were only slightly increased when NaCl was used as electrolyte instead of $Na_2SO_4$.

The dosage of electrolyte did not observably affect the treatment performance of wastewater on both

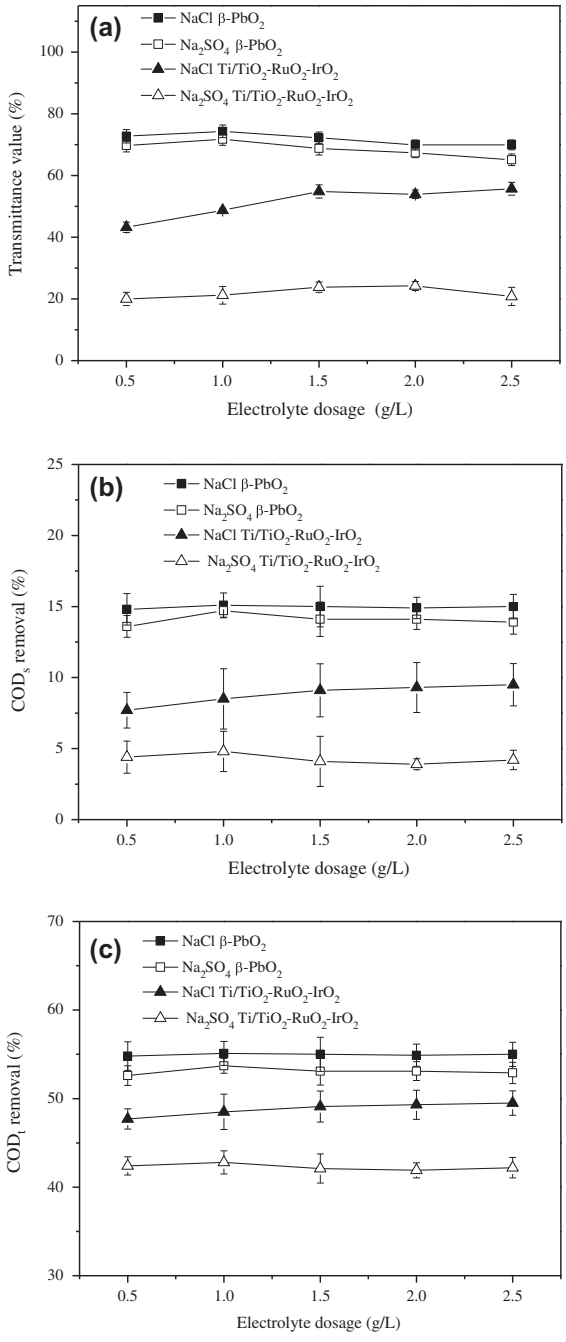



Fig. 3. Effect of supporting electrolyte on transmittance value (a), $COD_s$ (b), and $COD_t$ (c) removals on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes. Conditions: current density 50 mA/$cm^2$, reaction time 30 min, pH 5.0 for β-$PbO_2$, pH 6.8 for Ti/$TiO_2$-$RuO_2$-$IrO_2$.

electrodes. However, the addition of NaCl to wastewater promoted the $COD_s$, $COD_t$ removal, and increased the transmittance value of effluent, especially in the case of Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode. For example, on the Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode, when 1.5 g/L of NaCl was used as electrolyte, the transmittance value (54.8%) was much higher than that (20%) when 1.5 g/L of $Na_2SO_4$ was used as electrolyte. So were the $COD_s$ removal (9.1% vs. 4.1%) and $COD_t$ removal (49.1% vs. 42.1%). This difference could be explained by reactions as shown in Eqs. (4)–(6). When NaCl was used as electrolyte, chlorine/hypochlorite was produced from chloride, which further oxidized the pollutants and then reduced to chloride ion [22]. Although active chlorines enhanced the indirect oxidation of wastewater, it was widely acknowledged that their oxidation power was much lower than that of HO·. Furthermore, the chlorine evolution potential on Ti/$TiO_2$-$RuO_2$-$IrO_2$ was found much lower than that on β-$PbO_2$, which made the generation of active chlorines much easier, and thus promoted the indirect oxidation [26]. However, the treatment performance on Ti/$TiO_2$-$RuO_2$-$IrO_2$ in the presence of NaCl was still less than that obtained on β-$PbO_2$ in the absence of NaCl.

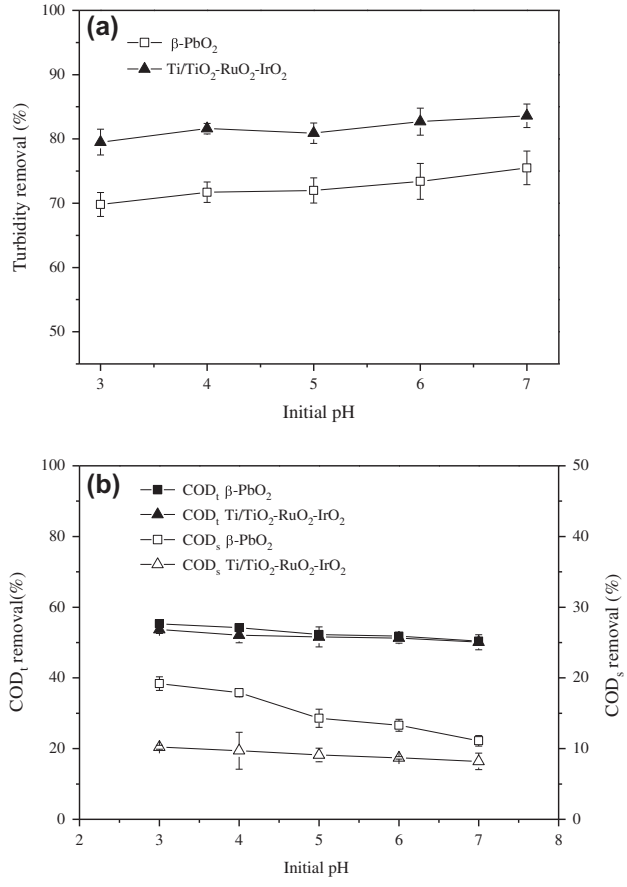



Fig. 4. Effect of initial pH on turbidity (a) and COD (b) removals on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes. Conditions: current density 50 mA/$cm^2$, reaction time 30 min, NaCl 1.5 g/L.

Table 2
Comparison of treatment performance on both electrodes under optimized conditions

| Parameters | Raw wastewater | β-$PbO_2$ | | Ti/$TiO_2$-$RuO_2$-$IrO_2$ | |
|---|---|---|---|---|---|
| | | Effluent | Removal (%) | Effluent | Removal (%) |
| $COD_t$ (mg/L) | 5,798 | 2,580 | 55.5 | 2,829 | 51.2 |
| $COD_s$ (mg/L) | 2,679 | 2,263 | 15.5 | 2,415 | 9.8 |
| Turbidity (NTU) | 1,462 | 363 | 75.2 | 275 | 81.2 |
| SS (mg/L) | 1,978 | 607 | 69.3 | 489 | 75.3 |
| Transmittance value (%) | 0.9 | 71.7 | – | 54.0 | – |
| $BOD_5$ (mg/L) | 350 | 1,280 | – | 1,320 | – |

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (4)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (5)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (6)$$

When β-$PbO_2$ was used as anode, the transmittance value, $COD_s$ removal, and $COD_t$ removal maintained at about 70, 15, and 55%, respectively. Thus, 1.5 g/L of NaCl was appropriate as supporting electrolyte, which would not inhibit the activity of micro-organisms in biological treatment system [27].

### 3.3. Effect of initial pH

Fig. 4 shows the effect of initial pH on the treatment performance of papermaking tobacco sheet wastewater using 1.5 g/L of NaCl as electrolyte at 50 mA/$cm^2$ of current density after 30 min of reaction. As seen in Fig. 4(a), the turbidity removal was not obviously affected by initial pH for both electrodes. According to the determination results of SS, the SS removal of effluent was maintained at 65% under all investigated pH values. This may be due to the fact that most of the SS was removed through the floatation of $H_2$ generated on the cathode. Similarly, the $COD_t$ removal of effluent was maintained at about 50% for both electrodes at different pH values. This indicated that the electrochemical oxidation of papermaking tobacco sheet wastewater performed well on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes in a wide range of pH. It meant that pH adjustment was not required, which could save the operating cost in practical application.

On the Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode, the influence of initial pH on $COD_s$ removal was not obvious. This may be due to the fact that the evolution rate of chlorine/hypochlorite was not dependent on initial pH of wastewater which was in the range of 3.5–8.5 [28,29]. In comparison, on the β-$PbO_2$ electrode, the $COD_s$ removal seemed to be more sensitive to initial pH, which slightly decreased from 19.1% at pH 3.0, and to 11.1% at pH 7.0. This could be explained by the fact that the oxygen evolution potential in acidic media was higher than that obtained in neutral condition, so the equilibrium shifts toward the inhibition of oxygen evolution with the increase in $H^+$ concentration, as shown in Eqs. (7) and (8). Accordingly, acidic condition is beneficial for the electrochemical oxidation of

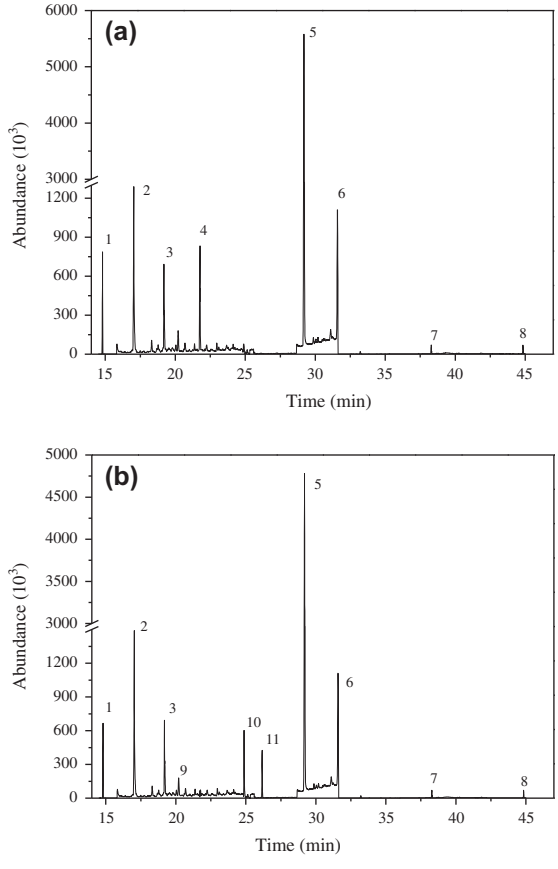



Fig. 5. Gas chromatograms of effluent after 30 min of treatment under optimized conditions. (a) β-$PbO_2$ electrode and (b) Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode.

organic pollutants on β-$PbO_2$ electrode [30]. Therefore, in the subsequent experiment, pH was adjusted to 5.0 in the case of β-$PbO_2$ electrode, while it was maintained at the initial pH value of wastewater for Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode.

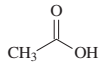
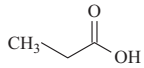
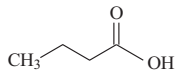
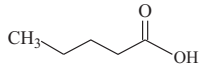
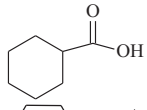
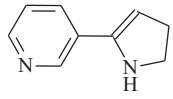
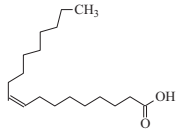
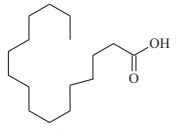
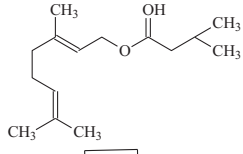
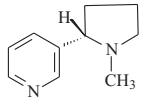
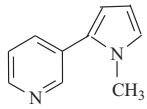
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (7)$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad (8)$$

### 3.4. Electrochemical oxidation of wastewater under optimized conditions

Based on the optimization of electrochemical oxidation, the papermaking tobacco sheet wastewater containing 1.5 g/L of NaCl was treated at 50 mA/$cm^2$ of current density, pH 5.0 for β-$PbO_2$, and pH 6.7 for Ti/$TiO_2$-$RuO_2$-$IrO_2$. After 30 min of reaction, the COD, $BOD_5$, SS, turbidity, and transmittance value of wastewater before and after electrochemical treatment on both electrodes are presented in Table 2.

Table 3
Main components of effluent after 30 min of treatment under optimized conditions

| Peak | Time | Compound | Structure | CAS No. | β-$PbO_2$ | Ti/$TiO_2$-$RuO_2$-$IrO_2$ |
|---|---|---|---|---|---|---|
| 1 | 14.80 | Acetic acid |  | 64-19-7 | √ | √ |
| 2 | 17.03 | Propionic acid |  | 79-09-4 | √ | √ |
| 3 | 19.18 | Butyric acid |  | 107-92-6 | √ | √ |
| 4 | 21.76 | Valeric acid |  | 109-52-4 | √ | × |
| 5 | 29.18 | Hexahyl carbonic acid |  | 98-89-5 | √ | √ |
| 6 | 31.58 | Myosmine |  | 532-12-7 | √ | √ |
| 7 | 38.28 | Oleic acid |  | 112-80-1 | √ | √ |
| 8 | 44.84 | Palmitic acid |  | 57-10-3 | √ | √ |
| 9 | 21.75 | Geranyl isovalerate |  | 109-20-6 | × | √ |
| 10 | 24.87 | Nicotine |  | 54-11-5 | × | √ |
| 11 | 26.13 | β-nicotyrine |  | 487-19-4 | × | √ |

Note: √ and × refers to be detected and undetected, respectively.

As listed in Table 2, Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode performed better on the removal of SS and turbidity than β-$PbO_2$ electrode due to the floatation of $H_2$ and $Cl_2$. Conversely, β-$PbO_2$ exhibited better performance on COD removal under the attack of HO· generated *in situ*, thus improving the transmittance value and biodegradability of the effluent. The $BOD_5$/COD ratio increased from 0.06 to 0.50, while the transmittance value and $BOD_5$/COD ratio of the effluent treated on Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode were 54.0% and 0.47, respectively. Ignoring the difference in transmittance value, the effluents obtained on both electrodes were all suitable to conventional biological treatment.

### 3.5. Variation in the main components of wastewater

It was disclosed that although the COD removal was not satisfactory during electrochemical oxidation process when β-$PbO_2$ or Ti/$TiO_2$-$RuO_2$-$IrO_2$ was used as anode, the color of effluent was transparent and the $BOD_5$/COD ratio of wastewater was significantly increased. In order to examine the variation in the main components of wastewater, the raw wastewater and the effluent treated under optimized conditions were extracted by liquid–liquid extraction using DCM as an extractant and then characterized by GC–MS. Results showed that salanone, nicotine, β-nicotyrine, myosmine, 2-pyrrolidinone, oleic acid, and palmitic acid were the main components of papermaking tobacco sheet wastewater before treatment [31]. During the electrochemical oxidation of wastewater on β-$PbO_2$ electrode, organic acids, pyridine, 1-methyl-2-pyrrolidinone, and 2-pyrrolidinone were detected by GC–MS, indicating that not only the bond between pyridine ring and pyrrolidine ring in nicotine was cleaved under the successive attack of unselective HO·, but also nicotine was changed to myosmine. Afterwards, these intermediates were gradually eliminated and eventually converted to organic acids.

Fig. 5 demonstrates the gas chromatograms of effluent after 30 min of electrochemical oxidation on both electrodes under optimized conditions. The main components in effluent are listed in Table 3.

It could be observed that some dissolved organic compounds in papermaking tobacco sheet wastewater such as nicotine, β-nicotyrine, solanone, and 2-pyrrolidinone were not detected after 30 min of electrochemical oxidation on β-$PbO_2$ electrode, indicating that these components were transformed into smaller molecular organic acids, such as acetic acid, propionic acid, butyric acid, and valeric acid. With the elimination of these recalcitrant and toxic components in wastewater, its inhibition and toxicity to micro-organisms were alleviated, thus the biodegradability of wastewater was enhanced. Although 99.2% of oleic acid and 99.8% of palmitic acid could be removed (according to the change of peak area prior to and after treatment), but the formation of small organic acids, such as acetic acid, propionic acid, and butyric acid, were difficult to further mineralize to $CO_2$ and $H_2O$. This may be the reason why the COD removal, especially $COD_s$ removal, could not be significantly increased as the reaction time prolonged.

As described in Table 3, part of nicotine, β-nicotyrine, and geranyl isovalerate still existed in the effluent after 30 min of treatment on Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode. The possible elucidation might be the lower oxidation power of oxidants generated on the Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode, such as active chlorines. Therefore, the oxidation of organic pollutants on β-$PbO_2$ electrode seemed to be more efficient than that on Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode.

## 4. Conclusions

The electrochemical treatment performance of papermaking tobacco sheet wastewater on β-$PbO_2$ and Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrodes were compared in this study. The influence of current density, initial pH, and electrolyte dosage on the COD removal was not obvious on both electrodes, whereas, higher current density enhanced the removal of turbidity. The presence of NaCl promoted the treatment performance on both electrodes, especially on Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode, due to the co-action of anodic and indirect oxidation, which greatly improved the COD removal and the transmittance value of effluent.

GC–MS analysis results showed that acetic acid, propionic acid, butyric acid, hexahyl carbonic acid, myosmine, oleic acid, and palmitic acid were the common components that existed in the effluent after 30 min of treatment under optimized conditions on both electrodes. Due to the lower oxidation power of Ti/$TiO_2$-$RuO_2$-$IrO_2$ electrode, residue of nicotine, β-nicotyrine, and geranyl isovalerate still existed in the effluent. The $BOD_5$/COD ratio of wastewater increased from 0.06 to 0.50 (on β-$PbO_2$) or 0.47 (on Ti/$TiO_2$-$RuO_2$-$IrO_2$), which is more apt to conventional biological treatment. Therefore, electrochemical oxidation offers an attractive alternative to pre-treat papermaking tobacco sheet wastewater prior to biological treatment and with the advantages such as ease of operation, short reaction time, and no pH adjustment needed.

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