Electrooxidation of tannery wastewater with continuous flow system: Role of electrode materials

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ABSTRACT
Tannery wastewater is known to contain high concentrations of organic compounds, pathogens, and other toxic inorganic elements such as heavy metals, nitrogen, sulfur, etc. Biological methods such as aerobic and anaerobic processes are unsuitable for tannery wastewater treatment due to its high salinity, and electrochemical oxidation offers a promising method to solve this problem. In this study, raw tannery wastewater treatment using DSA® Ti/RuO₂, Ti/IrO₂ and Ti/BDD electrodes with continuous flow systems was examined. Effects of current densities and electrolysis times were investigated, to evaluate the process performance and energy consumption. The results showed that a Ti/BDD electrode is able to reach higher treatment efficiency than Ti/IrO₂ and Ti/RuO₂ electrodes across all parameters, excluding Total Nitrogen. The main mechanism of tannery wastewater oxidation at a Ti/BDD electrode is based on direct oxidation on the electrode surface combined with the generation of oxidants such as •OH and Cl₂ while at DSA® Ti/RuO₂ and Ti/IrO₂ electrodes, the oxidation mechanisms are based on the generation of chlorine. After treatment, the effluents can be discharged to the environment after 6-12 h of electrolysis. Electrooxidation thus offers a promising method for removing the nutrients and non-biodegradable organic compounds in tannery wastewater.

Keywords: Electrooxidation, Tannery wastewater, Ti/BDD, Ti/IrO₂, Ti/RuO₂

1. Introduction

The tanning industry contributes a great deal to Vietnam's current socio-economic development, supplying materials for other industries, and creating stable jobs for thousands of workers [1]. Besides economic development, the environmental issues associated with industrial tanning waste are also a top concern for many enterprises. The specialty of the tanning industry is the use of raw materials such as buffalo, cow, goat, and sheep hides with the production using a large amount of water and a variety of chemicals [2]. Discharged tannery waste contains high concentrations of pollutants, solid wastes, and toxic gases. Tanning wastewater comprises many chemicals, such as dyes, organic solvents, total solids (TS), suspended solids (SS), color, ammonium, oil, high salt content and pathogenic microorganisms [3-10]. The toxic components in the tannery wastewater affect the surrounding environment. Tannery wastewater pollutants have exceeded the Vietnamese discharge standards of industrial wastewater QCVN 40:2011/BTNMT on many occasions. At the moment, most tannery enterprises in Vietnam either do not have adequate sewage treatment systems or discharge wastewaters directly into the general drainage system of the community [1]. The environmental pollution from the tanning industry is thus very serious, and an effective solution is urgently required. High salinity wastewater treatment by a biological method such as an activated sludge process often results in low Chemical Oxygen Demand (COD) removal efficiency, due to the inhibited growth of microorganisms by the inorganic salts if salinity is higher than 1% [11-14]. Removing salts from tannery wastewater is therefore a prerequisite for biological treatment; however, this is not an easy task. Advanced oxidation processes (AOPs) are known for the decomposition of organic compounds by the free hydroxyl radicals (•OH), due to their high oxidation potential and mineralization of almost any organic molecule in wastewater, to produce CO₂ and inorganic ions in the output product [15-17]. Among the AOPs, electrochemical oxidation has been successfully investigated for the removal of toxic organic compounds under the activity of direct and indirect oxidants as •OH radical, H₂O₂, O₃ [18]. In addition, pollutant treatment by electrochemical oxidation has achieved high efficiency when wastewater contains a high chloride concentration, by the gen...
eration of chlorine [19]. Electrochemical wastewater treatment is now of increasingly interest because it has advantages such as simple equipment, high capacity for medium and small scale use, low initial investment, easily automated electrical speed control, reduced chemical reagent, and is an environmentally friendly "green" technology: low generation of secondary chemicals, high selectivity [20]. There are many electrodes which can be used as anode materials for electrochemical water treatment [21]. Among these electrodes, Dimensional Stable Anode (DSA) and Boron Doped Diamond (BDD) have proven the most superior due to their excellent properties in wastewater treatment [22-24]. In this study, primary tannery wastewater with high levels of salinity and organic pollutants was treated by electrochemical methods in the laboratory using commercially available DSA® Ti/RuO2, Ti/IrO2 and Ti/BDD electrodes. The influence of current densities and electrolysis times were assessed according to level of pollutant removal and energy efficiency. The treatment efficiencies were evaluated using COD, Biological Oxygen Demand (BOD5), Total Organic Carbon (TOC), Total Nitrogen (TN), colour. As far as the literature review, this is the first time the treatment of raw tannery wastewater using DSA compared with BDD electrode in the continuous flow system has been reported with multiparameters. This research suggests a platform for proposing appropriate and feasible technology for treating raw tannery wastewater by electrooxidation.

2. Materials and Methods

2.1. Experimental Setup

The experimental setup for the study of tannery wastewater treatment using electrochemical oxidation is shown in Fig. 1. The experiments were performed at room temperature, in a conventional single compartment flow cell with three electrodes, using a computer-controlled potentiostat (PARSTAT 2273A, Princeton Applied Research, USA) and power supply (UDP 1501, Unicorn, South Korea) to maintain a constant current. The applied potential was from 0-3 V vs. Ag/AgCl. Scan rate was 5 mV/s. The change of current vs voltage was recorded as linear sweep voltammetry to monitor the in situ electrochemical process at the electrode surface. The main equipment in the model included: a 7 cm x 6 cm x 6.5 cm input water tank with effective volume of 168 mL; a 3.8 cm x 3.8 cm x 4.5 cm main reaction tank with a volume of 50 mL. The flow of tannery wastewater was controlled by a peristaltic pump with a volumetric flow of 5 mL/min. Ti/RuO2, Ti/IrO2 and Ti/BDD (Permelec De Nora, Japan) were selected as the working electrodes (anode), Pt (Samsung Chemicals, South Korea) as the counter electrode (cathode), and Ag/AgCl (in saturated KCl) as the reference electrode. The size of each electrode was 3 cm x 2 cm, and the distance between anode and cathode was 3 cm. A magnetic agitator was used to control the mass transfer between the wastewater and electrode surface. Tannery wastewater was collected at the Dang Tu Ky leather factory in Binh Tan District, Ho Chi Minh City, Viet Nam. When studying the effect of a changing parameter, the other parameters were held constant. The difference optimum operation parameters were collected in order to achieve high electrochemical degradation efficiency. To evaluate the effects of current density during the electrochemical oxidation of tannery wastewater, the current density was varied between 17 mA/cm² and 80 mA/cm². The mixing speed was set at 400 rpm with a magnetic stirrer. The electrolysis time was set at seven different time periods from 1 h to 12 h. The electrochemical characterizations of the metal oxide electrodes were examined using cyclic voltammetry (CV) measurements. The properties of the input tannery wastewater are shown in Table S1 (in Supporting Information), in which concentration levels can be seen to be much higher than the current Vietnamese Discharge Standard Regulation QCVN 40:2011/BTNMT.

2.2. Wastewater Analysis

All of the experiments were performed at room temperature, and analysis followed the Standard Method for the Examination of Water and Wastewater (APHA, USA) [25]. At regular time intervals, wastewater samples were withdrawn and collected in a beaker for further analysis, pH, and colour were measured using a Metrohm 900 multimeter, Switzerland. COD was measured using a Lovibond RD125 Thermoreactor (England) in Closed Reflux Titrimetric Method. BOD5 were measured using a Lovibond® BD 600, England. A nitrification inhibitor (Formula 2533™, TCMP, 35 g, Hach, USA) was added to the water sample before measurement BOD to hinders the oxidation of ammonia nitrogen, which supplies the nitrogenous BOD, and so ensure the BOD value was not affected by nitrogen bacteria and totally inner. TOC and TN were measured using a TOC Shimadzu 00936, Japan. Total Cl⁻ was measured by using Ion Chromatography (Metrohm IC 883, Switzerland).

2.3. Energy Consumption

Energy consumption during processing was calculated based on the decrease of COD using the following formula [26, 27]:

\[
EC = \frac{tVC}{S_1} \times \frac{1 \times 10^3}{\triangle COD} \times \frac{1 \times 10^6}{L}
\]

Where: \( EC \) is the power consumption (kWh/kgCOD); \( t \) is the time of electrolysis (h); \( V \) is the mean voltage during the electrolysis (V); \( C \) is the current density (A); \( S_1 \) is the volume of electrolyte solution (l) and \( \triangle COD \) is the concentration of COD removed during time \( t \) (mg/L).
3. Results and Discussion

3.1. COD Removal

Fig. 2 shows the COD removal efficiencies of the Ti/RuO₂, Ti/IrO₂, and Ti/BDD electrodes at different current densities and electrolysis times. In general, with all three electrodes, the COD removal efficiencies increased as the current densities increased. As shown in Fig. 2(a) with the Ti/RuO₂ electrode, the COD removal yield of the Ti/RuO₂ electrode at current density 80 mA/cm² after 12 h of treatment was 82%. The corresponding COD of the effluent at that point was 768 mg/L, indicating that tannery wastewater after treatment had not reached the Vietnamese discharge standard QCVN 40:2011/BTNMT. There was no significant difference in COD removal efficiencies between 50 mA/cm² and 80 mA/cm² after 6-12 h of electrolysis (only 3-5%). In particular, after 6 h of electrolysis, the COD removal efficiencies were 55.24%, 70.34% and 70.57% at current densities 16.7 mA/cm², 50 mA/cm² and 80 mA/cm², respectively. The COD removal efficiency of the Ti/RuO₂ electrodes in this study is comparable with the report of Panizza et al. [28] on a Ti/RuO₂ electrode, with removal efficiency of 90% after 12 h of electrolysis at current density of 60 mA/cm² and input COD 2,100 mg/L. Kongjao et al. [29] showed that the COD removal efficiency of Ti/RuO₂ electrodes in tanning effluents with an input concentration of 17,240-17,860 mg/L, gave a high efficiency of 82% at current density 60.5 mA/cm² after 1 h of electrolysis. The main mechanism of pollutant treatment using a Ti/RuO₂ electrode is based on indirect electrolysis, the direct oxidation on the electrode surface is negligible. Since the salinity in tannery was about 5,000 mg/L, COD is eliminated by indirectly electrolyzing chloride ions at Ti/RuO₂ according to the following equations [28]:

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2^{\text{aq}} + 2e^- \quad (2) \]

\[ \text{Cl}_2^{\text{aq}} + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ \quad (3) \]

Organic compound + Cl₂ → oxidation product + 2Cl⁻ (4)

In another aspect, the COD treatment efficiency of Ti/IrO₂ electrodes in tannery wastewater is shown in Fig. 2(b). The results show that COD removal efficiency of Ti/IrO₂ electrode was significantly lower (55.24%) than Ti/RuO₂ electrode.
lower than a Ti/RuO₂ electrode. This is explained by the fact that the pollutant treatment mechanism on the Ti/IrO₂ electrode is similar to the Ti/RuO₂ electrode, which is based on indirect oxidation due to the formation of the chloride compound. However, chlorine evolution efficiency on the Ti/IrO₂ electrode is lower than the Ti/RuO₂ electrode [30]. The COD concentration in effluent after 12 h of electrolysis was 933 mg/L, and had not achieved the Vietnamese discharge standard QCVN 40:2011/BTNMT. In the earlier study of Szpyrkowicz et al. [31], which used a Ti/Pt/Ir electrode on primary tanning effluent, the COD treatment efficiency was 60% after 40 min of electrolysis. However in that study, a positive electrode area was 100 cm² (17 times greater than the electrode in the present study, and was used to treat a 670 mL volume of wastewater). This suggests that the ratio between electrode surface area and volume of treated wastewater has a great influence on process efficiency.

As shown in Fig. 2(c) using a Ti/BDD electrode, the COD removal efficiency of the Ti/BDD electrode was relatively high, corresponding to 88.82% and 98.45% at 50 mA/cm² and 80 mA/cm² after 6 h of electrolysis, respectively. After 6 h of treatment at a current density of 80 mA/cm², COD post-treatment concentration was 64 mg/L, and reached Vietnamese discharge standard QCVN 40:2011/BTNMT. At current density 50 mA/cm² and after 12 h of electrolysis, COD concentration of the effluent was 103 mg/L and also reached the Vietnamese discharge standard QCVN 40:2011/BTNMT. Compared with Ti/RuO₂ and Ti/IrO₂ electrodes, the COD removal efficiency of the Ti/BDD electrode was highest. As shown in Fig. 2(d), with the comparison of three electrodes, at current density 80 mA/cm², and after 6 h of electrolysis, the COD removal efficiency of the Ti/BDD electrode was 98.45%, while at the Ti/RuO₂ electrode efficiency was 70.15% and the Ti/IrO₂ electrode efficiency only 62.01%. The results also suggest that 6 h is the most suitable electrolysis time for all 3 electrodes. The high COD removal efficiency of the Ti/BDD electrode is attributed to the simultaneous oxidation on the electrode surface by direct and indirect oxidation [32]. Direct oxidation on the surface of the Ti/BDD electrodes is accomplished by the first step of releasing water molecules, forming "OH as per Eq. (5). Then, the oxidation of organic compounds is made via the newly formed "OH radical as per Eq. (6) [33, 34].

\[
\text{BDD} + \text{H}_2\text{O} \rightarrow \text{BDD}("\text{OH}) + \text{H}^+ + \text{e}^- \quad (5)
\]

\[
\text{BDD}("\text{OH}) + R \rightarrow \text{BDD} + \text{mCO}_2 + \text{nH}_2\text{O} + \text{H}^+ + \text{e}^- \quad (6)
\]

On the other hand, indirect electrolysis in the presence of chloride ions in wastewater also forms chlorine according to Eq. (4); Cl₂(aq) is then rapidly involved in hydrolysis forming HClO by Eq. (5), which has the effect of decomposing organic compounds as per Eq. (6) [35]. This mechanism is similar to the mechanism of chlorine evolution at Ti/RuO₂ and Ti/IrO₂ electrodes. In addition, HClO can be oxidized on the surface of the BDD electrode to form ClO₂, ClO₃, and this can reduce the chlorine smell during the reaction [32]. The higher the current density applied to Ti/BDD electrode, the higher the COD removal efficiency. This is explained by the fact that increasing the electrical current increases oxidant generation [36]. Beside "OH, chlorine and oxygen evolution as per Eq. (9), H₂O₂ is produced by reaction of "OH radicals as per Eq. (10); O₃ will be formed by reaction of "OH radical and H₂O as per Eq. (11). Then O₃ and H₂O₂ will also participate in organic decomposition to increase process efficiency [37].

\[
\text{BDD}("\text{OH}) \rightarrow \text{BDD} + 1/2\text{O}_2 + \text{H}^+ + \text{e}^- \quad (7)
\]

\[
2\text{BDD}("\text{OH}) \rightarrow 2\text{BDD} + \text{H}_2\text{O}_2 \quad (8)
\]

\[
\text{BDD}("\text{OH}) + 2\text{H}_2\text{O} \rightarrow \text{BDD} + \text{O}_3 + 5\text{H}^+ + 5\text{e}^- \quad (9)
\]

3.2. BOD₅ Removal

Fig. 3 shows the BOD₅ treatment efficiency of Ti/RuO₂, Ti/IrO₂ and Ti/BDD electrodes at different current densities and electrolysis times. Unlike the variation in COD removal efficiency, the biodegradable organic matter in tannery wastewater is easily decomposed by electrochemical oxidation. At all three electrodes, BOD₅ treatment efficiencies ranged from 88% to 99% throughout the process. As shown in Fig. 3(a), with Ti/RuO₂ electrodes, it took up to 12 h of electrolysis at current density 17 mA/cm², while it needed up to 8 h at current density 50 mA/cm² for Ti/IrO₂ electrodes, as shown in Fig. 3(b), to match with Vietnamese discharge standard. After 6 h of electrolysis at current density 17 mA/cm², the output BOD₅ concentration of the Ti/BDD electrode was 47 mg/L, and reached the Vietnamese discharge standard as in Fig. 3(c). The effluent also could be discharged into the environment after 2 h of electrolysis at the current density of 80 mA/cm² for Ti/IrO₂ electrodes, as shown in Fig. 3(d). Increasing the current density had the effect of increasing the removal efficiency of biodegradable organic matter to a similar level as nonbiodegradable compound, as discussed in the previous section.

3.3. Total Nitrogen Removal

Fig. 4 shows the TN removal efficiencies of Ti/RuO₂, Ti/IrO₂ and Ti/BDD electrodes at different current densities and electrolysis times. As shown in Fig. 4(a), the TN treatment efficiency of Ti/RuO₂ electrodes was very high. At a current density of 50 mA/cm², after 2 h of electrolysis, the TN removal efficiency was 90%, and reached the Vietnamese discharge standard after 8 h of electrolysis. It is worth noting that after 1 h of electrolysis at current density 80 mA/cm², the TN treatment efficiency was 93.6%, with output concentration 44.6 mg/L at the Ti/RuO₂ electrode. At later intervals, the TN removal efficiency remained relatively stable and only reached the Vietnamese discharge standard when the electrolysis time was increased to 6 h. This showed that the potential for
nitrogen treatment by electrochemical oxidation at Ti/RuO$_2$ is greater than for other methods, such as physical, chemical and biological treatments which are still problematic. The main mechanism for decomposition of nitrogen compounds of the Ti/RuO$_2$ electrode can be attributed to indirect oxidation by chlorine/hypochlorite generation during electrochemical processes [38]. The HClO produced by chloride ions is involved in the decomposition of nitrogen compounds as per equations 12-14 or direct oxidation of HClO (as per Eq. (15)-(17)) [39-41]. The TN treatment efficiency of the Ti/RuO$_2$ electrode in this study is comparable with the report of Min et al. [42] who found that at a current density 40 mA/cm$^2$, after 30 min of electrolysis, TN removal efficiency was 75%, with an input TN concentration 927 mg/L. However, in that study, the authors used an electrode with a surface area of 279 cm$^2$ and electrolyte volume 1,700 mL. This again demonstrates that the ratio between electrode surface area and volume of wastewater is important, as the larger the area of the electrode, the lower the electrolysis time, leading to a reduction in the amount of electricity consumption and higher performance.

$$\text{HClO} + \text{NH}_4^+ \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{H}^+ \quad (10)$$

$$\text{HClO} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad (11)$$

$$\text{H}_2\text{O} + \text{NHCl}_2 \rightarrow \text{NOH} + 2\text{H}^+ + 2\text{Cl}^- \quad (12)$$

$$\text{NOH} + \text{NHCl}_2 \rightarrow \text{N}_2 + \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (13)$$

$$\frac{2}{3}\text{NH}_4^+ + \text{HClO} \rightarrow \frac{1}{3}\text{N}_2 + \text{H}_2\text{O} + \frac{5}{3}\text{H}^+ + \text{Cl}^- \quad (14)$$

$$\text{NH}_4^+ + 4\text{HOCl} \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 6\text{H}^+ + 4\text{Cl}^- \quad (15)$$

Fig. 4(b) shows the TN removal efficiency of the Ti/IrO$_2$ electrode at different current densities and electrolysis times. After 6 h of electrolysis at a current density of 80 mA/cm$^2$, the TN treatment efficiency at the Ti/IrO$_2$ electrode was approximately 60%. With an increase electrolysis time to 12 h, the TN removal efficiency was 72%, with a post-treatment output concentration 180 mg/L, which did not meet the Vietnamese discharge standard. The study of Szpyrkowicz et al. [31] showed that the TN treatment efficiency of the Ti/Pt-Ir electrode was higher than that of the Ti/IrO$_2$ electrode.

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**Fig. 3.** BOD$_5$ removal efficiency of (a) Ti/RuO$_2$, (b) Ti/IrO$_2$, (c) Ti/BDD electrodes at different current densities and (d) all electrodes at current density 80 mA/cm$^2$. 

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In that study, tannery wastewater treatment using a Ti/Pt-Ir 100 cm² electrode, with an initial TN concentration 370 mg/L and 1 h of electrolysis at a current density of 40 mA/cm² gave an efficiency of 85%. The author explained that the electrochemical process using a Pt-Ir mixture enhanced the chlorine evolution process, producing strong oxidizing radicals such as ClO⁻, Cl₂, \( {^1}OH \), which increased the oxidation efficiency of pollutants. Similar to the decomposition mechanism of nitrogen compounds by indirect oxidation by chlorine evolution reaction but the TN treatment efficiency of Ti/IrO₂ electrode is lower than Ti/RuO₂ electrode. This can be explained by the lower level of chlorine evolution efficiency at Ti/IrO₂ electrodes compared to Ti/RuO₂ electrodes [19].

As shown in Fig. 4(c) with the Ti/BDD electrode, the TN treatment efficiency was lower than with the Ti/RuO₂ electrode but higher than with the Ti/IrO₂ electrode. With a greater current density, the stronger oxidizing radicals generated may increase the efficiency of the process. However at the Ti/BDD electrodes, the maximum TN removal efficiency of 92% was observed after 12 h of electrolysis at a current density of 80 mA/cm², at which the output TN in tannery wastewater 53.5 mg/L had not yet reached the Vietnamese discharge standard. As discussed above, the TN content is largely eliminated by indirect oxidation by chlorine compounds, while the Ti/BDD electrode characteristic produces both direct and indirect processes with lower chlorine evolution than DSA. According to Anglada et al. [43], the ammonium removal process was low during the initial period of electrochemical oxidation processing but then increased in efficiency as the COD concentration decreased. Urtiaga et al. [44] observed the oxidation of COD and ammonium on the surface of the BDD electrode with the ammonium removal rate was lower than the COD value. There was competition between COD and nitrogen decompositions on the surface of BDD electrode. Overall, the COD removal efficiency at a Ti/BDD electrode is higher than at the Ti/RuO₂ electrode.

The evidence for chlorine evolution at Ti/RuO₂ electrode is shown in Fig. S1, with a decrease in Cl⁻ concentration during the reaction. Specifically, Cl⁻ concentrations in tannery wastewater at a Ti/RuO₂ electrode after 6 h of treatment were 3,950, 1,937, 1,400 mg/L, corresponding to current densities of 16.7 mA/cm², 50 mA/cm², 80 mA/cm², respectively. This means that Cl⁻ is involved in the decomposition of organic compounds and nitrogen in the wastewater and that the higher the current density, the stronger...
the chloride decomposition. The electrooxidation does not only decrease the amount of pollutants, but also the salinity contamination in tannery wastewater.

3.4. TOC Removal

Fig. 5 shows the TOC removal efficiencies of Ti/RuO$_2$, Ti/IrO$_2$ and Ti/BDD electrodes at different current densities and electrolysis times. By increasing the current density and electrolysis time, the TOC removal efficiencies were increased. As shown in Fig. 5(a), the TOC removal efficiency of the Ti/RuO$_2$ electrodes was below 40%, and slightly lower at a current density of 17 mA/cm$^2$ and 50 mA/cm$^2$. The TOC removal efficiency of the Ti/IrO$_2$ electrode was lower than the Ti/RuO$_2$ electrode, with maximum 30% at current density 80 mA/cm$^2$ after 12 h of electrolysis as shown in Fig. 5(b). This result agrees with the report of Costa et al. [45], who also found that TOC treatment efficiency at Ti/Ir$_{0.01}$Sn$_{0.99}$O$_2$ electrode on tannery wastewater was below 30% with input current density 20 mA/cm$^2$ after 5 h of electrolysis. At current density 80 mA/cm$^2$ after 12 h of electrolysis, the TOC removal efficiency at the Ti/BDD electrode was nearly 70%. Ti/BDD electrodes showed superior TOC removal efficiency compared with Ti/RuO$_2$ and Ti/IrO$_2$ electrodes. This can be attributed to the generation of •OH at Ti/BDD electrodes, which has the main role in the mineral of organic compound. Whereas the decomposition mechanism at Ti/RuO$_2$ and Ti/IrO$_2$ electrodes is based on chlorine evolution, which is a weaker oxidation agent compare with •OH.

3.5. Colour Removal

Fig. 6 shows the colour removal efficiencies of Ti/BDD, Ti/RuO$_2$ and Ti/IrO$_2$ electrodes at different current densities and electrolysis times. As shown in Fig. 6, colour removal efficiencies varied with current densities and electrolysis times. The color removal efficiencies of tannery wastewater at all 3 electrodes were high, from initial period of 1-2 h of electrolysis, yielding higher than 90% at current densities of 16.7 mA/cm$^2$, 50 mA/cm$^2$ and 80 mA/cm$^2$. However, there was a tendency for decreased performance at a longer electrolysis times. For example, at the Ti/RuO$_2$ electrode, as shown in Fig. 6(a), after 12 h of electrolysis at current densities 16.7 mA/cm$^2$, 50 mA/cm$^2$, 80 mA/cm$^2$, the remaining color efficiencies were 73%; 78%; 87%, respectively. However after 6 h of elec-

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Fig. 5. TOC removal efficiency of (a) Ti/RuO$_2$, (b) Ti/IrO$_2$, (c) Ti/BDD electrodes at different current densities and (d) all electrodes at current density 80 mA/cm$^2$. 

Fig. 6. Colour removal efficiency of Ti/BDD, Ti/RuO$_2$ and Ti/IrO$_2$ electrodes at different current densities and electrolysis times.
trolysis, the smaller the current density, the higher the colour removal efficiency. This may be due to the fact that over a long period of electrolysis, by-products are created which further discolor in the output wastewater.

3.6. Electrochemical Measurement

Fig. 7 shows the experimental results of cyclic voltammogram monitoring of the electrochemical oxidation of tannery wastewater at Ti/RuO₂ and Ti/IrO₂ and Ti/BDD electrodes. There were significant differences in typical cyclic voltammogram of DSA Ti/RuO₂ and Ti/IrO₂ electrodes, compared with Ti/BDD electrode. With Ti/RuO₂ and Ti/IrO₂ electrodes, the onset potential at 1.3 V vs. Ag/AgCl can be attributed to the oxidation peak of Cl⁻ to Cl₂, due to the high salinity concentration in the tannery wastewater. These peaks also overlap with the oxygen evolution peaks, since the onset potentials of oxygen evolution and chlorine evolution are very close. There are quite similar about the oxidants evolution mechanism at Ti/RuO₂ and Ti/IrO₂ electrodes since it belong with DSA group. The current density at the Ti/RuO₂ electrode was higher than at the Ti/IrO₂ electrode, suggesting that the chlorine evolution efficiency was higher. In another aspect, the Ti/BDD electrode had an onset potential of oxygen evolution reaction at
2.6 V vs. Ag/AgCl. There was one oxidation peak at 2.2 V vs. Ag/AgCl which could be attributed to the oxidation peak of tannic acid at the surface of the Ti/BBD electrode [46]. This is clearly seen in Fig. 7, there is a difference about oxidant generation mechanisms at 3 electrodes. The mechanism of electrochemical oxidation at DSA Ti/RuO2 and Ti/IrO2 electrodes is based on indirect chlorine evolution. And the direct oxidation on the electrode surface is negligible. While at Ti/BDD anode, the mechanism is mainly the direct oxidation of tannic acid on the electrode surface. Ti/BDD electrode is not so strong in the chlorine evolution reaction compared with Ti/RuO2 and Ti/IrO2 electrodes.

3.7. Energy Consumption

Fig. 8 shows the respective energy consumption of electrochemical tannery wastewater treatment using Ti/RuO2, Ti/IrO2, and Ti/BDD electrodes. As can be seen, the energy consumption increases with the increase of current density with all 3 electrodes. The Ti/BDD electrode showed the lowest energy consumption, while the Ti/RuO2 electrode was a little bit higher, and the highest energy consumption being at the Ti/IrO2 electrode (Fig. 8(d)). This result shows that Ti/BDD and Ti/RuO2 electrodes are more suitable for tannery wastewater treatment, since they have the lowest energy consumption and the highest pollutant removal performances. Overall, Ti/BDD is the best electrode for industrial tannery wastewater treatment.

4. Conclusions

In this study, DSA® Ti/RuO2, Ti/IrO2 and Ti/BDD electrodes were used to treat raw tannery wastewater treatment in a flow system. The results show that current density and electrolysis times strongly affect pollutant treatments. Increasing the current density and electrolysis time leads to increases in treatment efficiency, in all regards except colour. The Ti/BDD electrodes demonstrated the best levels of COD, BOD5 and TOC removal efficiency and energy consumption while Ti/RuO2 is better at nitrogen removal. The main pollutant mechanism in tannery wastewater treatment at a Ti/BDD electrode is based on direct oxidation on the electrode surface combined with the generation of oxidants such as ”OH and Cl2, while the main oxidation mechanism at DSA® Ti/RuO2 and Ti/IrO2 electrodes is by the generation of chlorine. Electrochemical oxidation using DSA® Ti/RuO2, Ti/IrO2 and
Ti/BDD electrodes can be used to treat tannery wastewater to achieve the Vietnamese discharge standard for effluents after 6-12 h of electrolysis in a flow system.

Acknowledgments

This work is supported by the funding from Vietnamese Ministry of Education and Training (MOET) under the grant B2016-VGU-02 (2016-2018).

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