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Study of the treatment of tannery wastewater after biological pretreatment by using electrochemical oxidation on BDD/Ti anode

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ABSTRACT

In the last two decades, electrochemical oxidation has been extensively studied for the treatment of wastewater. This technology consists of the direct and/or indirect oxidation of organic matter in wastewater at the anode or in the solution of an electrochemical device. In this study, a laboratory-scale experimental model was performed to evaluate the effect of tannery wastewater treatment on electrochemical oxidation with boron-doped diamond (BDD)/Ti anode and cathode Pt/Ti. Before the electrochemical oxidation, the tannery wastewater was pretreated by using a biological method with activated sludge. The effects of current density, pH of the solution, stirring rate, and reaction time on the treatment efficiency were studied. The results show that BDD/Ti anode treated effectively chemical oxygen demand and total nitrogen over 85% after 90 min of electrolysis at the current density of 66.7 mA/cm^2. BDD/Ti anode gave higher efficiency with neutral pH and base. The current density and agitation rate affect the treatment efficiency, whereas the treatment time is inversely proportional to the depletion of pollutants in the effluent. The combination of biological pretreatment and electrochemical oxidation helps effluents meet the Vietnamese discharge standard after 30–60 min of electrolysis.

Keywords: Tannery wastewater; Activated sludge; Electrochemical oxidation; BDD/Ti

1. Introduction

In the past 20 years, the tanning industry in Vietnam has experienced rapid growth. In 2002, production reached 30 million square feet. In 2012, production exceeded 200 million square feet. This output is forecast to increase rapidly as Vietnam is facing more favorable opportunities than ever through a series of Free Trade Agreements such as free trade between Vietnam and the European Union and Vietnam with the Russian Federation of Tariffs (Belarus–Kazakhstan). These are the markets of Vietnam's huge footwear production [1]. Tanning is the process by which raw skin is transformed into leather with optimal properties such as high temperature resistance, no rot in contact with water and other environments, and resistance to destructive effects of microorganisms and the atmosphere. Leather raw materials used in the leather tanning industry are animal skins such as those of buffalo, cow, pig, sheep, goat, and horse as well as rare animal skins such as deer, tiger, crocodile, python, snake, etc. [2]. Besides the great economic contribution made by leather industry in general and tanning industry in particular, the environmental pollution from this industry is a very big issue. Tanning is an industry that pollutes the environment in all three forms: solid, liquid, and gaseous. Unwanted organic substances, such as hair, fat, meat, etc., in the original materials (fresh skin, salted skin) are removed with the excess chemicals in use (inorganic and organic, especially chromium (III)). The decomposition of organic matter in the

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original material creates a foul smell, characteristic of the production and the surrounding area [3]. Thorough treatment of pollutants in tannery wastewater requires a combination of treatments such as mechanical, physical, chemical methods like Fenton, and biological methods [4–7]. However, due to the economic and technical constraints, the majority of pollutants even after treatment at the factories are still high, and the basic pollution parameters such as BOD_5, chemical oxygen demand (COD), NH_3, color, etc. still do not meet the effluent discharge standards [8–10].

In the last two decades, electrochemical oxidation has been extensively studied for application in wastewater treatment [11–15]. This technology consists of the direct and/or indirect oxidation of organic matter contained in wastewater in the anode or in the solution of an electrochemical device. Under the effects of electricity, toxic and biodegradable wastes will be oxidized into less toxic intermediates and biodegradable or oxidizable to CO_2 and H_2O. The method of electrochemical treatment of industrial wastewater is of increasing concern because it has advantages such as simple equipment, high capacity for medium and small-scale use, low initial investment, electrical speed control and easy to automate, requires very few or no chemicals, and environmental friendly "green" technology: low generation of secondary chemicals and high selectivity [16,17]. There are many electrodes which can be used as anode materials for electrochemical water treatment [18]. Among these electrodes, boron-doped diamond (BDD) has proven the most superior due to its excellent properties in treating wastewater by the generation of strong oxidants ^{o}OH, Cl_2, H_2O_2, and O_3 [19–24]. The treatment of tannery wastewater using electrochemical oxidation has been reported in some previous studies [25–28]. However, it is quite difficult to treat tannery wastewater well if electrochemical oxidation is alone applied due to the high concentration of pollutants [29–33]. In this study, the treatment ability of tannery wastewater after biological pretreatment with activated sludge process was tested by electrochemical oxidation with BDD/Ti anode. The effects of current density, pH of the solution, stirring rate, and reaction time were studied to the treatment efficiency. To the best of our knowledge, this is the first time the treatment of tannery wastewater after biological pretreatment by using BDD electrodes has been reported. This research suggests a platform for proposing appropriate and feasible technology for treating the tannery wastewater after biological pretreatment by electrochemical oxidation with BDD/Ti anode.

2. Materials and methods

2.1. Experimental setup

The experimental setup for the study of tannery wastewater treatment is shown in Fig. 1. The experiments were performed at room temperature in a conventional single compartment cell with two electrodes using a computer-controlled potentiostat (PARSTAT2273A, Princeton Applied Research, USA) and power supply (UDP 1501, Unicorn, South Korea) to control constant current. The volume of electrolyte in the cell batch system was 150 ml. BDD/Ti (Permelec De Nora, Japan) was used as the working

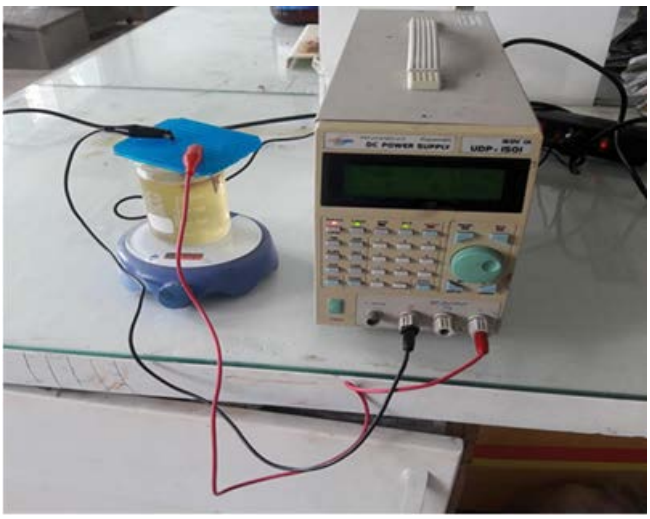

Fig. 1. The experimental setup.

electrode (anode), Pt (Samsung Chemicals, South Korea) as the counter electrode (cathode), and Ag/AgCl (in saturated KCl) as the reference electrode [11–13]. The size of each electrode was 3 × 2 × 0.5 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 after the aerotank basin in the current wastewater treatment plant at the Dang Tu Ky leather factory (Binh Tan District, Ho Chi Minh City, Vietnam). The primary treatment was done by chemical coagulation and the continuous to secondary pretreatment by aerotank process (activated sludge). To determine the effect of pH when treating tannery wastewater by using BDD/Ti electrode, the pH of the solutions were adjusted from 3.0 to 11.0 with 20% NaOH or 20% H_2SO_4. To evaluate the effects of current density during the electrochemical oxidation of tannery wastewater by BDD/Ti electrode, the current density was changed from 16.7 to 133.3 mA/cm^2. The mixing speed in this study was changed from 100 to 600 rpm with a magnetic stirrer. The electrolysis time was set at seven different time periods: 10, 20, 30, 45, 60, 75, and 90 min. The electrochemical characterizations of the metal oxide electrodes were examined using cyclic voltammetry (CV) measurements [11–13]. Properties of tannery wastewater after biological pretreatment (aerotank process) are shown in Table 1, in which the contamination level is much higher than the current Vietnamese Discharge Standard Regulation QCVN 40:2011/BTNMT.

2.2. Wastewater analysis

All experiments were performed at room temperature, and the analyses were conducted following the standard method for the examination of water and wastewater (USA) [34–36]. At regular time intervals, wastewater samples were withdrawn and collected in beaker for further analyses. pH, color, and conductivity were measured using a Metrohm 900 multimeter, Switzerland. COD was measured using a Lovibond RD125 Thermoreactor (England) in Closed Reflux

Table 1
Properties of input tannery wastewater

Parameter	Raw tannery wastewater	After activated sludge treatment	Vietnamese Discharge Standard (QCVN 40:2011/BTNMT)
pH	6.5	7.7	5.5–9
Color, P_t/C_0	2,042	508	150
COD, mg/L	2,530	332	150
Total nitrogen, mg/L	576.1	206.7	40
N-NH_4^+, mg/L	321.8	186.7	–
N-NO_3, mg/L	57.3	14.7	–
TDS, mg/L	822	167	100
Total crom, mg/L	57.4	0.41	1
Conductivity, μs/cm	33,269	19,987	–
Cl^-, mg/L	5,017	4,862	1,000

Titrimetric Method. Total nitrogen was measured using a TOC Shimadzu 00936, Japan. Total chromium in the treated wastewater was analyzed using an atomic absorption spectrometer (Analytic Jena Contraa 300). Total NO_3^-, NH_4^+, and Cl^- were measured by using Ion Chromatography (Metrohm IC 883, Switzerland).

2.3. Determination of the treatment efficiency and electrochemical process

The treatment efficiency of pollutants in wastewater was determined to assess the ability of different pollutants to be treated on electrode, thereby determining the treatment capacity and the effect of some operation condition [37]. The treatment efficiency of pollutants is determined by the following formula [38]:

$$\text{Efficiency of treatment} = \frac{\text{ON}t - \text{ON}s}{\text{ON}t} \times 100(\%) \quad (1)$$

where ON*t*: concentration of pollutants in wastewater before treatment; ONs: concentration of pollutants in wastewater after treatment.

The factors influencing the efficiency of the electrolysis process are time of electrolysis (*t*), pH of the medium, current density (*i*), rate of agitation (*v*), and nature of anode material. When studying the effect of a parameter, just change this parameter and the other remaining parameters remain fixed. Different operation parameter will be applied in order to achieve high degradation efficiency of the electrochemical process. The oxidation efficiency is determined by the following equation:

$$H(\%) = \frac{\Delta\text{COD} \times V_{\text{dd}} \times F}{8 \times i \times S \times \Delta T} \times 100 \quad (2)$$

where ΔCOD is the variation of the COD, V_{dd} is the volume of electrolyte solution (l), *S* is the surface area of the electrode (cm^2), *I* is the current density (A/cm^2), *F* is Faraday constant (96,487 C/mol), Δ*T* is electrolysis time (s), 8 is mass equivalent to oxygen.

2.4. Energy consumption calculation

Power consumption when adjusting the operation voltage was calculated as follows [39,40]:

$$P = U \times I \quad (3)$$

where *U*: voltages (V); *I*: current intensity (A).

The energy consumption required to handle COD variability is as follows:

$$G = \frac{P \times t}{V\left(\text{COD}_0 - \text{COD}_t\right)} \quad (4)$$

where *G*: energy consumption; *P*: minimum power (W); *t*: processing time (h); *V*: volume of treatment (L); COD_0 and COD_t: COD before and after treatment (mg/L)

COD efficiency on energy required:

$$Y = \frac{\text{COD}_0 \times V \times \%\text{COD}}{100 \times P \times t} \quad (5)$$

where *P*: minimum power (W); *t*: processing time (h); *V*: volume of treatment (L); % COD: effective % COD treatment of the electrode [38].

3. Results and discussion

3.1. Effect of pH

The results of pollutant treatment in tanning effluents, with BDD/Ti anodes, corresponding to different pH, is presented in Fig. 2. After treatment, the color removal efficiency of the BDD/Ti electrode was higher at pH 8, equivalent to 56.3%. Increasing or decreasing the pH of the solution compared with pH 8 resulted in a reduction of treatment efficiency. In particular, when increasing pH from 8 to 9, the color treatment efficiency decreased from 56.3% to 47.9% and to 39.1% at pH 11. However, in alkaline medium (pH 9 and pH 11), the treatment efficiency was superior to that in acidic environments; at pH 5, color removal efficiency was 41% and reduced to 35.5% at pH 3. The COD removal efficiency of BDD/Ti electrode, when changing the pH of the

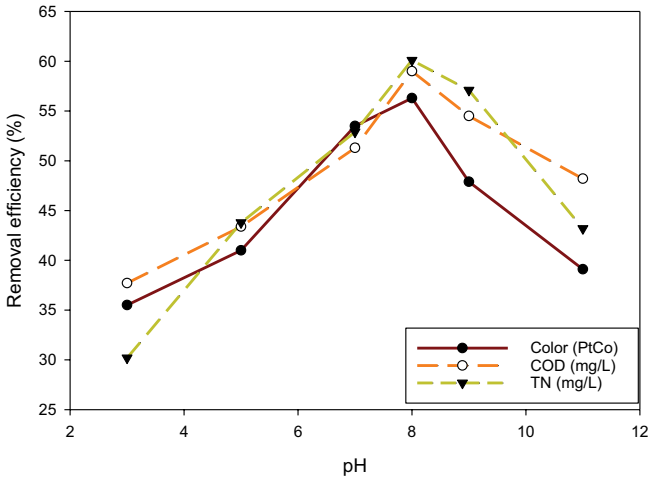

Fig. 2. Effect of pH on tannery wastewater treatment efficiency.
Notes: Experimental condition: current density 33.3 mA/cm², agitation rate 200 rpm and electrolysis time 60 min.

solution, provided similar results to the color treatment, due to the colorant compounds in the wastewater treatment being mainly the organic residue remaining after biological treatment (like tannic acid). When organic chemical is oxidized into easily digestible secondary products, either CO_2 or H_2O, followed by a reduction in COD and color of the wastewaters. The highest COD removal efficiency was achieved at pH 8 with 58.3%. Comparison of COD removal efficiency between different pH levels of 7, 8, and 9 showed no significant difference; at pH 7, the COD removal efficiency was 52.2% and at pH 9 it reached 54.5%. COD removal efficiency in an alkaline environment was higher than in an acidic environment.

The total nitrogen removal efficiency increased with increasing pH from 3 to 8, then decreased at pH 9 and pH 11. At pH 8, the highest total nitrogen treatment efficiency was 60.1%, while at pH 9, the total nitrogen removal efficiency was higher than that at pH 5, indicating that total nitrogen treatment efficiency in the base medium was better. This is explained by the fact that nitrogen in tannery wastewater after biological pretreatment mainly exists in the N-NH_3 form and is readily decomposed in the base medium according to the following reaction [10]:

$$2NH_4^+ + 6OH^- \rightarrow N_2 + 6H_2O + 2H^+ + 6e^- \quad \text{(Reaction 1)}$$

The pH value significantly affects the tannery treatment of the BDD/Ti anode. Color values and COD gave the best results in neutral medium (at pH 7, 8) while total nitrogen yielded higher efficiency in alkaline medium (at pH 8, 9). In acidic field, treatment efficiency of the pollutants of BDD/Ti anode gave the lowest efficiency. In the study of Xiuping Zhu et al. [41], the N–NH_3 treatment of BDD electrode by changing the pH value also showed that neutral N–NH_3 is more effective than in acidic environments. In the present study, at pH 7.7 and pH 9.9, the N–NH_3 treatment efficiency was 85% and 78%, respectively, after 10 h, at current density of 20 mA/cm² and at temperature of 30°C. The pH value tends to decrease compared with the original, which may be due to the direct oxidation of organic compounds on the electrode surface of BDD/Ti according to the following reaction equation (reactions 2–4) which produced H^+ ions that reduced the pH of the solution:

$$BDD + H_2O \rightarrow BDD(^{\circ}OH) + H^+ + e^- \quad \text{(Reaction 2)}$$

$$R + xBDD(^{\circ}OH) \rightarrow xBDD + Sp + yH^+ + e^- \quad \text{(Reaction 3)}$$

$$BDD(^{\circ}OH)hp \rightarrow BDD + \frac{1}{2}O_2 + H^+ + e^- \quad \text{(Reaction 4)}$$

Another reason for the depletion of the pH in the reaction solution is that acidic recyclate intermediates such as Cl_2, HClO, and OCl^- are produced by the electrolysis of Cl^- [41]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \text{(Reaction 5)}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad \text{(Reaction 6)}$$

$$HClO \rightarrow H^+ + ClO^- \quad \text{(Reaction 7)}$$

Considering the effect of color, COD, and total nitrogen on the treatment, the attenuation of the acidic pH may affect the corrosion rate of the electrode. So pH 8 was selected for further experiments.

3.2. Effect of current density

Fig. 3 shows the experimental result of tannery wastewater treatment by using electrochemical oxidation at BDD/Ti anode, with different current densities. Increasing the current density will increase the treatment efficiency of pollutants in wastewater. COD and total nitrogen treatment yields increased, when current density increases from 16.7 to 133.3 mA/cm², with an average 20% after each step. The treatment efficiency of pollutants started to increase slowly when increasing the current density from 100 to 133.3 mA/cm², equivalent to 5%.The trend of decreasing COD, color, and total nitrogen is quite similar, indicating the

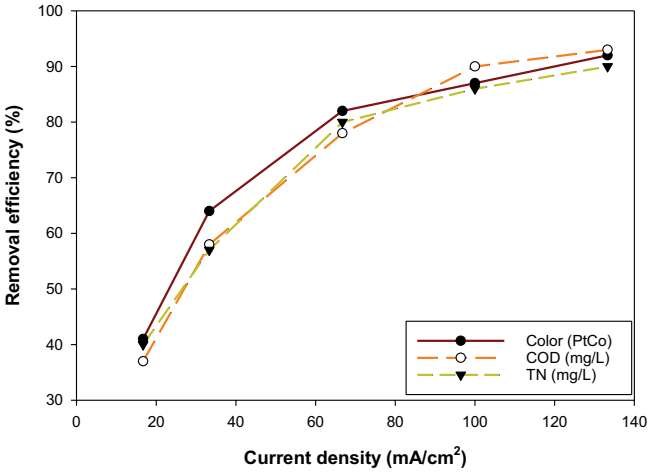

Fig. 3. Effect of current density on the treatment efficiency.
Notes: Experimental condition: pH 8, time of electrolysis 60 min, agitation rate 200 rpm.

stable and comprehensive treatment of BDD/Ti electrode, after biological treatment of tannery wastewater.

Color treatment efficiency was the lowest at current density of 16.7 mA/cm^2, when color values decreased 41.9%. This is explained by the fact that a low current density will reduce the production of OH^o radicals and secondary oxidants such as O_3, HClO, H_2O_2, resulting in reduced treatment efficiency. The color removal efficiency increases clearly at the current density of 66.7 mA/cm^2 with 80.8%. The value of color did not decrease significantly when increasing the current density from 100 to 133.3 mA/cm^2 with reduction only 32 Pt Co. The COD removal efficiency of the BDD/Ti electrode increased as the current density increased. At current density of 16.7 mA/cm^2, the COD value decrease was equivalent to 36.5% treatment efficiency, which was lower than that of color treatment of 41.9%. When the current density was increased to 133.3 mA/cm^2, COD removal efficiency was 93%. The results showed that it was possible to completely eliminate COD in subsequent experiments when changing the rate of incubation and electrolysis time. The total nitrogen removal efficiency after 60 min at the current density of 16.7 mA/cm^2 was 38.3%. When increasing the current density to 33.3 mA/cm^2, the treatment efficiency increased to 58.9% and increased to 80% at 66.7 mA/cm^2. The treatment efficiency then increased slowly, similar to the treatment efficiency of COD and color when increasing the current density from 100 to 133.3 mA/cm^2. This is because when the current density increases, the direct oxidation of the electrode becomes stronger, more oxidants are generated, and the intermediate oxidation products are more likely to oxidize the organic matter into CO_2 and H_2O faster. However, the change value of pollutants varies more slowly as the current density increases from 100 to 133.3 mA/cm^2, which is explained as follows [4]: If the oxidation of organic matter is chemical oxidation, the initial surface of the anode will react:

$$MO_x + H_2O + e \rightarrow MO_x(OH^o) + H^+ \quad \text{(Reaction 8)}$$

M here is BDD anodes. OH^o is a strong oxidizer that can oxidize organic matter directly into wastewater into CO_2:

$$MO_x(OH^o)_{ad} + R + e \rightarrow CO_2 + H^+ + MO_x \quad \text{(Reaction 9)}$$

R is the organic compound in the solution. However, at high current density, the $MO_x(O^o)MO_x$–O converts MO_x–O into an electrolyte that contains an oxygen atom.

$$MO_x(OH^o)_{ad} + e \rightarrow MO_x\text{–}O + H^+ \quad \text{(Reaction 10)}$$

These atomic oxides are chemically adsorbed to the activated oxide layer of the coating and have the ability to oxidize organic matter adsorbed on the electrode surface by reaction:

$$MO_x\,(\text{–}O)_{ad} + R \rightarrow MO_x + RO^o \quad \text{(Reaction 11)}$$

However, the ability of the $MO_x(\text{–}O)_{ad}$ to oxidize organic compounds is lower than that of $MO_x(OH^o)_{ad}$, which reduces the oxidation efficiency of the electrode. Another unwanted parallelism may occur with the $MO_x(\text{–}O)_{ad}$ compound, which continues to be converted to MO_x and is not involved in the oxidation of organic compounds.

$$MO_x(\text{–}O)_{ad} \rightarrow MO_x + \frac{1}{2}O_2^- \quad \text{(Reaction 12)}$$

On the other hand, when high current density occurs, competing oxidation of water produces oxygen that obstructs the oxidation of organic compounds that produce CO_2 and H_2O. Therefore, selection of suitable current density for each electrode is very important in wastewater treatment by electrochemical oxidation.

In order to ensure the treatment efficiency and to avoid the use of unsuitable electrical currents, energy wastage may occur, or may affect electrode lifetime, determining the efficiency of the oxidation process. The oxidation efficiency is calculated in terms of COD loss, current density, and reaction time, as shown in Fig. 4. At current density of 16.7 mA/cm^2, the highest oxidation efficiency was 76.4%, and this decreased as the current density increased to 133.3 mA/cm^2. The corresponding efficiency decreased to 24.1%. This shows that as the process of decomposition decreases, the concentration of pollution slows down, while the current density continues to increase, reducing the efficiency of the process. However, it depends on the purpose of the process to choose the balance between treatment efficiency and performance of the process. Based on the effect of BDD/Ti on tannery treatment with the current density value to choose the suitable operation condition. In order to achieve the minimum pollution values of Vietnamese discharge standard QCVN 40:2011/BTNMT, the applied current density should be ≥66.7 mA/cm^2. The difference in electrochemical oxidation efficiency between 66.7 and 100 mA/cm^2 is 8.9% and for 133.3 mA/cm^2 is 16.1% relatively large. Thus, 66.7 mA/cm^2 was chosen as the preferred current density of the model for subsequent experiments.

3.3. Effect of agitation speed

The electrochemical oxidation of organic matter and pollutants in wastewater occurs on the surface of the anode. After a period of time, a membrane of the secondary pollutants would have formed around the electrode, which affects the

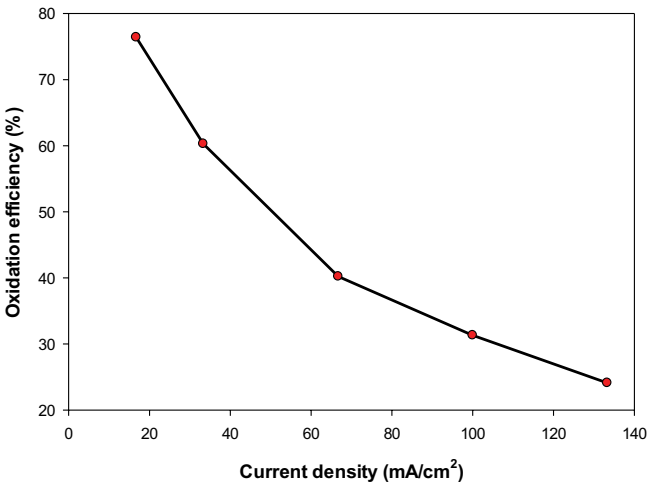

Fig. 4. Effect of current density on oxidation efficiency.
Notes: Experimental condition: pH 8, electrolysis time 60 min, agitation rate 200 rpm.

electrode's treatment ability. In order to limit this problem, the study conducted an assessment of the effects of agitation rate on BDD/Ti tannery wastewater treatment. Fig. 5 shows the experimental results of tannery wastewater treatment using electrochemical oxidation at BDD/Ti anode at differing agitation speeds. It is apparent from Fig. 5 that there were no significant changes in color treatment efficiency due to changing agitation rates. The highest increase in treatment efficiency was achieved by changing the agitation rate from 100 to 200 rpm, equivalent to an increase in efficiency from 68.8% to 80.8%. In subsequent experiments, further agitation speed increase was not necessary, as the color treatment efficiency increased only 3% on average for each increase of 100 rpm.

Notably, when the speed of the agitator was increased to 600 rpm, the efficiency of the color treatment started to decrease, and the treatment efficiency was only 80.2%.

COD conversion efficiency also results in the same effect as color removal. However, there was no noticeable increase in processing efficiency between the stirring speed from 100 to 200 rpm when the difference in treatment efficiency is 5%, equivalent to a difference of 16 mg/L COD. On the other hand, the COD treatment efficiency decreases as the stirrer speeds up to 500 and 600 rpm. The highest total nitrogen removal efficiency at 400 rpm was 85.15%, equivalent to 28.4 mg/L, compared with just over 2.2 mg/L, an agitation rate of 300 rpm. Similarly, the COD treatment efficiency increased when the agitation speed was increased to 500 and 600 rpm. Mixing wastewater in electrochemical oxidation using BDD/Ti electrode is necessary to enhance the treatment efficiency of the process due to the increasing mass transfer. However, the level of effect of agitation rate on the treatment efficiency is relatively low compared with other influencing factors examined, such as pH and current density. The difference in treatment efficiency at stirring speeds of 200 and 300 rpm was not large. To ensure the post-processing value of contaminants in wastewater satisfies the required agitation speed of 300 rpm, is selected to run the model at the rear processing time change conditions.

3.4. Effect of electrolysis time

Electrolysis time is another factor that was studied in order to guide and propose a technological chain, as well as calculate the energy consumption of the whole process, to ensure the balance between economic and treatment efficiency. Fig. 6 show the pollutant treatment efficiency with different electrolysis time. At 10 min, the color treatment efficiency was 26.6% and continued to rise as the time increased from 10 to 45 min and then tended to increase slowly. At 45 min, the color treatment efficiency was 78.1%, equivalent to a reduction to 106 mg/L. At a maximum treatment time of 90 min, the color treatment efficiency was 91.1%. This result shows that the BDD/Ti electrode can thoroughly treat the coloration in the tanning wastewater as it increases the treatment time. COD removal efficiency also increased with time. However, COD removal efficiency was slower than that in the first period. In the first 10 min, COD removal efficiency was only 22.4%, and then COD removal efficiency increased slowly as treatment time increased from 20 to 30 min with 32.8% and 45.2%, respectively. The treatment efficiency increased sharply to 75.3% when the treatment time was 45 min. This suggests a need for 45 min of treatment time to remove the persistent organic matter of this study. Similar to the effect of color and COD treatment, total nitrogen treatment yields increased as processing time increased with a relatively stable growth average rate of about 15% after each increment of time from 10 to 45 min. The total nitrogen treatment efficiency began to increase slowly after 45 min of treatment, only increasing 5% after every 15 min of treatment. At 90 min, the total nitrogen value decreased to 7.4 mg/L, equivalent to 96.1% treatment efficiency.

3.5. Electrochemical measurement

Fig. 7 shows the experimental result of cyclic voltammogram of the electrochemical oxidation of tannery wastewater with different scan rates. Since the tannery wastewater was pretreated by an activated sludge process to reduce large

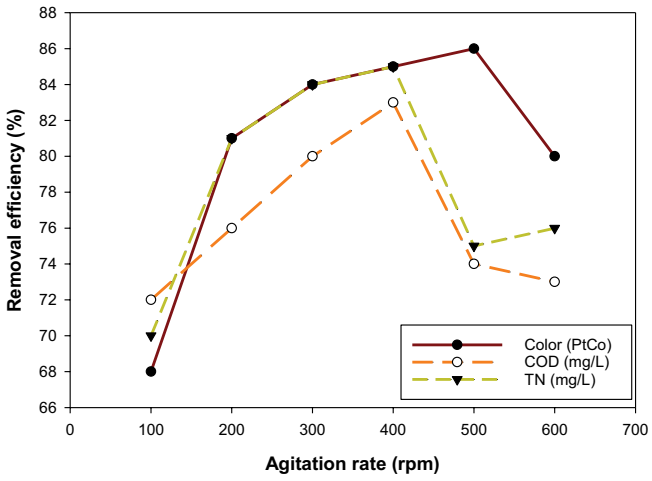

Fig. 5. Effect of agitation speed on tannery treatment efficiency at BDD/Ti anode.
Notes: Experimental condition: current density 66.7 mA/cm², electrolysis time 60 min, pH 8.

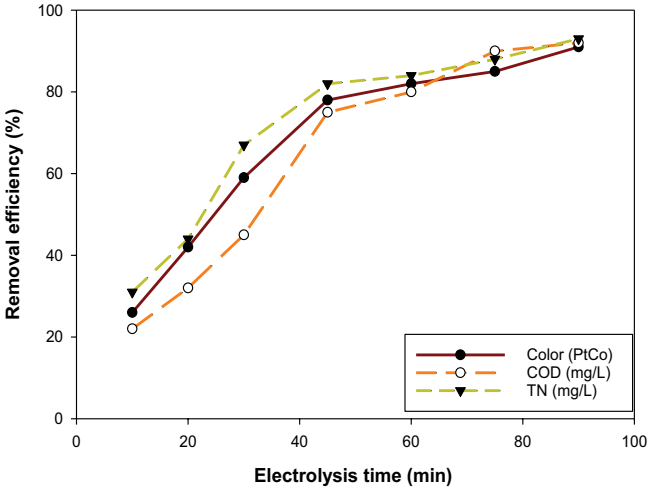

Fig. 6. Effect of current density on the tannery treatment efficiency.
Notes: Experimental condition: current density 66.7 mA/cm², agitation speed 300 rpm, pH 8.

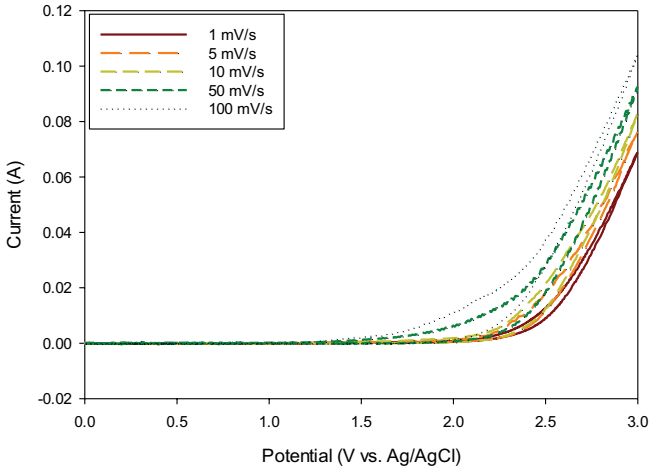

Fig. 7. Cyclic voltammogram of the tannery wastewater treatment by BDD/Ti anode.
Notes: scan rate 1–100 mV/s.

amounts of contaminants, its voltammogram is quite smooth. When the scan rate increased, the current value also increased and the oxidant generation also grew stronger. The first onset potential at 1.3 V vs. Ag/AgCl can be attributed to the oxidation peak of Cl^- to Cl_2 due to the high salt concentration in the tannery wastewater. The oxygen evolution reaction starts at the onset potential of 2.3 V vs. Ag/AgCl. There was one oxidation peak at 1.4 V vs. Ag/AgCl that can be attributed to the oxidation peaks of tannic acid [26].

3.6. Energy and cost calculation

Based on Eqs. (4) and (5), the energy needed to treat COD is 335.8 J/mg and COD efficiency required on energy is 12.97 g COD/kWh. At the moment, the price of electricity in Viet Nam about VND (Vietnamese currency) 1,800/kWh, then to reduce 12.97 g of organic matter in wastewater to VND 1,800 for 1 m^3 of COD effluent. A total of 18 kWh for the price of 1,800 VND/kWh needs 32,400 VND, equivalent of 1.5 USD.

4. Conclusion

In this study, BDD/Ti electrode could thoroughly treat the pollutants in the tannery wastewater after biological pretreatment. From the above results, it was found that the pH of the wastewater directly affected the efficiency of the treatment, with a neutral to base giving a higher treatment efficiency than an acidic medium. By increasing the current density and treatment time, the processing efficiency will increase. However, it is important to look at the economics of these two parameters. The results also show that agitation was necessary; however, the rate of agitation had a little effect on the treatment efficiency compared with other influencing factors in this study. The cyclic voqltammograms clearly show the oxidation peaks of chlorine, oxygen evolution, and tannic acid. The combination of biological pretreatment and electrochemical oxidation can thus be used to treat tannery wastewater to achieve the Vietnamese Discharge Standard for effluent.

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