

Tannery Wastewater Treatment After Biological Pretreatment by Using Electrochemical Oxidation

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Abstract

Tanning industry is receiving a lot of attention due to its pollution levels and discharge legislations toward the environment. Tanerry wastewater treatment by using electrochemical oxidation with $SnO₂/Ti$ and $PbO₂/Ti$ anodes. The tannery wastewater was pretreated using biological method with aerotank process. $SnO₂/Ti$ and $PbO₂/Ti$ anodes effectively treated COD and total nitrogen over 85% after 90 min of electrolysis. The treatment efficiency in tannery wastewater of $SnO₂/Ti$ anode is greater than $PbO₂/Ti$ anode.

Keywords

Tannery wastewater • Aerotank • Electrochemical oxidation • $SnO₂/ti$ • $PbO₂/ti$

1 Introduction

Tanning is an industry that pollutes the environment, including solids, liquids, and gaseous media. Unwanted organic substances such as hair, fat, and meat in the original materials (fresh skin, salted skin) are removed with the excess chemicals with inorganic and organic waste to the wastewater (Dinh et al. [2013](#page-2-0)). The decomposition of organic matter in the original material creates a foul smell characteristic in the production area and the surrounding area. Evaporation and boiler emissions also contribute negatively

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to the state of the environment. The pollutants in tannery wastewater require a combination of treatments such as mechanical, physical, chemical like fenton, and biological methods. However, due to economic and technical constraints, the majority of pollutants after treatment at the factories are still high, the basic pollution parameters such as $BOD₅$, COD, NH₃, and color do not still not meet the effluent discharge standards. Recently, the electrochemical oxidation has been extensively studied for the application of many types of wastewater treatment. Electrochemicals open up new avenues for the treatment of harmful organic pollutants, which can oxidize toxic organic pollutants with phenolic microorganisms into organic substances that can be completely oxidized to $CO₂$ and water. This technology consists of the direct and/or indirect oxidation of organic matter contained in wastewater in a suitable anode or in a solution of an electrochemical device. However, in the process of electrolysis, the side reactions that make up oxygen can occur and reduce the oxidation efficiency. The electrochemical treatment of industrial wastewater is increasingly in concern because it has its own advantages such as simple equipment, high capacity for medium and small scale, low initial investment, electrical speed control and easy automation, requires very little or no chemicals in the process, environmental friendly, and high selectivity.

2 Materials and Methods

All the experiments were performed at room temperature and analysis followed the Standard Method for the examination of Water and Wastewater (USA). At regular time intervals, wastewater samples were withdrawn and collected in beaker for further analysis. pH, color, and conductivity were measured by using Metrohm 900 multimeter, Switzerland. Chemical oxygen demand (COD) was measured by using Lovibond RD125 Thermoreactor Closed Reflux Titrimetric Method, England. Total Nitrogen (TN) was measured by using TOC Shimadzu 00936, Japan.

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Total Chromium in the wastewater was analyzed by using an atomic absorption spectrometer (Analytic Jena Contraa 300, Germany). Total NO_3^- , NH_4^+ , and Cl^- were measured by using ion chromatography (Metrohm IC 883, Switzerland).

3 Results and Discussion

3.1 Effect of pH

The result of treatment of pollutants in tanning effluents with $SnO₂/Ti$ and $PbO₂/Ti$ anodes corresponding to difference pH is presented in Fig. 1. As shown in Fig. 2a, the color treatment efficiency of the $SnO₂/Ti$ electrode was quite high, up to

60.7% at pH 8, equivalent to a drop of color to 186 Pt–Co. Increasing or decreasing pH of the wastewater compared to pH 8 resulted in a reduction of treatment efficiency. The color treatment efficiency in the base medium is higher than the acidic environment. The COD removal efficiency of $SnO₂/Ti$ anode when changing the pH of the wastewater gave similar results to the color treatment, which is due to the colorant compounds in the wastewater treatment is mainly the organic residue remaining after biological pretreatment (e.g., tannic acid). When chemically oxidized organic compound into easily digestible secondary products, like either $CO₂$ or $H₂O$, is followed by a reduction in COD and color. The COD and TN treatment efficiencies when using $SnO₂/Ti$ electrode gave the best at pH 8 with 51.8 and 55.2%, equivalent to 149 and

Fig. 1 Effect of pH on tannery wastewater treatment efficiency of $SnO₂/Ti$ (a) and $PbO₂/Ti$ (b) anodes. Experimental condition: current density 33.3 mA/cm² , agitation rate 200 rpm and electrolysis time 60 min

Fig. 2 Effect of current density on the treatment efficiency of SnO₂/Ti and PbO₂/Ti anodes. Experimental condition: pH 8, electrolysis time 60 min, agitation rate 200 rpm

77.4 mg/L, respectively. Similar to the color processing efficiency, total COD and nitrogen removal efficiency were lowest at pH 3 with 37.7 and 24.6%. The pH values significantly influence on the effluent treatment efficiency of the SnO₂/Ti electrode. The color, COD, and TN removal efficiencies are best in neutral medium (pH 7), which results in higher processing efficiency in the acid or base mediums. This result agreed with the study of Xiuping Zhu et al. (2009) reported the $N-NH_3$ treatment by changing pH that neutral $N-NH₃$ was more effective than in acidic environments. This is explained by the fact that nitrogen in tannery wastewater after biological pretreatment mainly exists in the N–NH3 form and is readily decomposed in the base medium according to the following reaction:

$$
2NH_4^+ + 6OH^- \rightarrow N_2 + 6H_2O + 2H^+ + 6e -
$$

As another aspect showed in Fig. [2b](#page-1-0), the color treatment efficiency of the $PbO₂/Ti$ electrode was highest at pH 7 with 56.3%, corresponding a reduction to 196 Pt–Co. Effectively, color treatment in acidic environments showed better performance than in the base environment. The lowest color treatment efficiency was achieved at pH 11 when the treatment efficiency was only 31.6%, equivalent to the color reduction to 299 Pt–Co. Similarly with the color efficiency, COD and TN efficiencies also were best achieved at pH 7 with a COD removal efficiency 47.1%, equivalent to a reduction to 165 mg/L, the TN removal efficiency was 52.81% equivalent to the reduction to 78.2 mg/L. COD removal efficiency was low at pH 3 and pH 11 with 31.6 and 31.8%, respectively. Meanwhile, the TN treatment efficiency was lowest at pH 3, reaching only 35.67%. After treatment, the pH of the wastewater was reduced.

3.2 Effect of Current Density

Figure [2](#page-1-0) shows the experimental result of tannery wastewater treatment using electrochemical oxidation at $SnO₂/Ti$ and $PbO₂/Ti$ anodes with different current densities. The current densities significantly affect tannery wastewater after biological pretreatment with $SnO₂/Ti$ anode. Increasing the current density increases the treatment efficiency of pollu-tants in wastewater. As shown in Fig. [2](#page-1-0)a with $SnO₂/Ti$ anode, the color treatment efficiency rapidly increased as the current density increased from 16.7 to 100 mA/cm^2 then decreased at 133.3 mA/cm². In particular, at current density 16.7 mA/cm² , the treatment efficiency was 41.6%, equivalent to the reduction of 279 Pt–Co. When increasing the current density to 33.3, 66.6, and 100 mA/cm², the color

treatment efficiency achieved 59, 82.4, and 87%, respectively. At the current density 133.3 mA/cm^2 , the color treatment efficiency reduced to 78.7%, equivalent to 102 Pt– Co. The trend of decreasing COD and total Nitrogen is quite similar to color, however at a smaller scale. This indicates the stable and comprehensive treatment of $SnO₂/Ti$ anode after biological pretreatment of tannery wastewater.

4 Conclusion

In this study, $SnO₂/Ti$ and $PbO₂/Ti$ anodes can thoroughly treat the pollutants in the tannery wastewater after activated sludge pretreatment. $SnO₂/Ti$ and $PbO₂/Ti$ anodes effectively treated COD and total nitrogen to up to 85% after 90 min of electrolysis at a current density of 66.7 mA/cm². From the above results, it was found that the pH of the wastewater directly affected the efficiency of the treatment. $SnO₂/Ti$ electrode gave higher efficiency in wastewater with neutral pH to base, while $PbO₂/Ti$ electrode offered higher processing efficiency in acidic to neutral wastewater. The current density and the rate of agitation affected the treatment efficiency of the two electrodes, while the duration of the treatment is inversely proportional to the depletion of pollutants in the effluent. $SnO₂/Ti$ anode has higher treatment efficiency, lower energy consumption, and lower cost compared to $PbO₂/Ti$ anode in tannery wastewater treatment; however, its stability is not quite good. The combination of biological pretreatment and electrochemical oxidation can treat the tannery wastewater to achieve the Vietnamese discharge standard for effluents.

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