Deep Treatment of Ammonia Nitrogen Tannery Wastewater by an Electro-Fenton System

by
Hui Chen,[1,2] Li-Wei Chen,[1,2] Shu-Qing Li,[3] Yao Hu,[1,2] Zhi-Hua Shan,[1,2] Rui Dai[1,2*] and Jie Yi[3]
[1]*College of Biomass Science and Engineering, Sichuan University,*
Chengdu 610065, China
[2]*National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University,*
Chengdu, 610065, China
[3]*College of Material and Textile Engineering, Jiaxing University,*
Jiaxing, 314001, China

Abstract

The effect of an Electro-Fenton system on the deep treatment of ammonia nitrogen (NH_3-N) and corresponding removal rate was investigated in this article. By using simulated ammonia nitrogen wastewater, it included a Cl^- concentration of 3000 mg/L, SO_4^{2-} concentration of 100 mg/L according to conventional leather wastewater conditions. Furthermore, Cl^- and SO_4^{2-} can be used as supporting electrolyte. After pretreatment, the ammonia nitrogen concentration kept about 100 mg/L. The optimal treatment conditions of Electro-Fenton system were obtained throughout single factors experiments. The current density was 150 A/m^2, the reaction time was 30 min, the plate spacing distance was 40 mm, and the reaction temperature was adjusted to 40°C. After flocculation treatment of leather wastewater, the ammonia nitrogen concentration was 142.11 mg/L, and the tanning wastewater was further treated with an Electro-Fenton system. The final ammonia nitrogen concentration was 11.23 mg/L, which meets the first-level wastewater discharge standard. The removal rate was 92.10%, which indicated that the Electro-Fenton system is one kind of clean, feasible and sustainable treatment method for the deep treatment of ammonia nitrogen in tannery wastewater.

Introduction

In the leather industry, after anaerobic, aerobic, and flocculation treatment, the ammonia nitrogen concentration is between 15 mg/L and 100 mg/L. The standard discharge concentration limit of ammonia nitrogen in industrial wastewater is 15 mg/L. It is difficult to reduce the ammonia nitrogen concentration further with chemical systems. Therefore, in order to solve high costs, undesirable emissions,a solution for the deep treatment of ammonia nitrogen in leather industrial wastewater is desired.

Ammonia nitrogen (NH_3-N) refers to nitrogen of water in the form of free ammonia (NH_3) and ammonium ions (NH_4+).[1] The discharge of ammonia nitrogen in wastewater can cause water eutrophication. Inorganic ammonium salt is used in the deliming and bating process of leather-making, which can lead to high ammonia nitrogen concentrations in leather-making wastewater.[2] Moreover, from the perspective of cost and application effectiveness, there is no complete replacement for inorganic ammonium salt deliming agents. Furthermore, during the process of leather pretreatment, the removal of useless collagen fibers can also cause a large amount of collagen protein to be hydrolyzed in the wastewater. With the ammoniation of the protein in the wastewater, the concentration of ammonia nitrogen also increases rapidly. Therefore, it is necessary to remove the ammonia nitrogen when considering the removal of organic pollutants.

The basic principle of ammonia nitrogen removal is to transform the organic nitrogen and ammonia nitrogen to nitrogenous nitrogen, which will escape in the form of nitrogen. Then, the concentration of ammonia nitrogen in water can reach national emission standards. At present, there are two kinds of ammonia nitrogen removal technologies for leather wastewater treatment. One method is physicochemical treatment, and the other is biological nitrogen removal.[3,4] Physicochemical treatment techniques include point-break chlorination.[5] This method has the advantages of less equipment, less investment, fast reaction speed and high-efficiency denitrification. However, due to its strict operation requirements and high operation cost, this process produces harmful gases. Air stripping technology has been used to address nitroaniline wastewater.[6] When the pH exceeded 11, the ammonia nitrogen in the wastewater decreased from 3150 mg/L to 187 mg/L, and the removal rate was 93%. This method displayed the advantages of a simple process, stability, high practicability and low investment cost. However, the energy consumption is still large, and there is secondary

*Corresponding author email address: dairui@scu.edu.cn
Manuscript received May 27, 2019, accepted for publication July 31, 2019

pollution. Chemical precipitation methods[7,8] have achieved a removal rate of ammonia nitrogen of 80%~90% at mole ratio of Mg^{2+} : NH_4-N: PO_4^{3-} of 1:1:1 and pH of 9.0.[9] If the residual concentrations of NH_4^+-N and PO_4^{3-} are relatively high, the contents of N and P can be further reduced by biological treatment after chemical precipitation treatment. This method is easy to perform and can save energy and improve efficiency with a fast reaction speed. However, large quantities of precipitation agents are needed, which carries a high cost. The removal of ammonium ions from simulated wastewater containing organic compounds by the ion-exchange method has been studied.[10] The ion-exchange method is suitable for the treatment of low-concentration wastewater, but the adsorbent requires frequent regeneration when treating high-concentration organic wastewater. The dilute ammonia liquid is not easy to recover, the waste liquid generated in the regeneration process may also cause secondary pollution, and the treatment process should be subjected to protection measures. Membrane absorption used emulsion liquid membrane method to remove wastewater with an ammonia nitrogen content of more than 1000 mg/L, with a first-stage removal rate of more than 97%.[11] The removal of ammonia nitrogen from wastewater is primarily influenced by the membrane surface area. The larger the area the better the removal rate. While membranes with a large surface area have smaller particles and are prone to emulsification, the separation of oil and water is difficult. In the presence of oleophilic organics, the liquid membrane organic phase is difficult to regenerate, so future research should focus on how to prevent emulsification and reduce secondary pollution in wastewater. Wet air oxidation,[12] based on a M/CeO_2 catalyst, a temperature of 200°C and an oxygen partial pressure of 20 bar, has achieved a removal rate of over 95% for an NH_3-N mass concentration of 700 mg/L. Wastewater has been treated by the electroosmosis method with a mass concentration of ammonia nitrogen ranging from 3000 to 3200 mg/L, and the removal rate of ammonia nitrogen was over 85%.[13] This method is not limited by pH value and temperature, is easy to operate and can recover ammonia. Ros *et al*. made use of an A_2/O process to treat leather wastewater. The removal rate of ammonia nitrogen reached 96.3% and the sludge yield was very low.[9] This process is a biological nitrogen removal technology. Electrochemical methods are a combination of electrooxidation and chemical oxidation and are a kind of advanced oxidation technology for the degradation of organic pollutants in water bodies. At present, such methods are environmentally friendly and energy-saving green treatment for the removal of ammonia nitrogen in wastewater. Electrochemical treatment mainly proceeds through direct oxidation at the anode and the indirect oxidation in solution.[14] The direct oxidation at the anode generates hydroxyl radicals (•OH) that can degrade organic matter through anode electrolysis, and the reaction can be expressed as follows[15]:

Anode: $2H_2O \rightarrow 2{\bullet}OH + 2H^+ + 2e^-$

$$2NH_3 + 6{\bullet}OH \rightarrow N_2 + 6H_2O$$

The Electro-Fenton method is an electrochemical method to remove ammonia nitrogen from wastewater. The principle is that H_2O_2 (which can be produced by electrolysis or directly added) reacts with Fe^{2+} to form a Fenton agent:[16]

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + {\bullet}OH$$

Hydroxyl radical (•OH) can oxidize and degrade organic pollutants and has an obvious effect on the removal of ammonia nitrogen and nitrite nitrogen; this process is rapid and stable.[17] Fenton system has been extensively studied and used in the treatment of textile and dye industrial wastewater, but there are few studies on the direct use of the Electro-Fenton oxidation method to remove ammonia nitrogen from leather wastewater. Due to cost problems, flocculation with polyferric chloride has been widely adopted by tanneries.[18,19] After treatment by this method, the terminal wastewater contains a high concentration of Fe(III). In this paper, after tanning wastewater was treated with a polyferric flocculant, the Electro-Fenton method was used to further reduce the ammonia nitrogen concentration. The effectiveness of ammonia nitrogen treatment in tanning wastewater was investigated by simulating leather wastewater. The optimal parameters of the Electro-Fenton method were obtained to treat real leather wastewater; the results are intended to provide a feasible green environmental protection method for the removal of leather wastewater in the future.

Experimental

Materials

Tanning wastewater was collected from Xuzhou Hongfeng Polymer Materials Co., LTD. from pigskin garment leather processing. Wastewater samples were collected in polyethylene bottles, the pH was adjusted to below 2 by adding sulfuric acid, and the samples were stores at 2-5°C. According to the optimized conditions for the Electro-Fenton treatment of simulated leather wastewater, the actual tanning wastewater was treated to determine the effect of ammonia nitrogen treatment. $(NH_4)_2SO_4$, H_2O_2, $FeSO_4{\cdot}7H_2O$, Na_2SO_4, NaCl and other conventional reagents were all analytical pure and purchased from Kelong Chemical Reagent Factory in Chengdu. Ammonium sulfate, magnesium borate, methyl red, methylene blue, polyferric sulfate and hydrochloric acid were obtained from Chongqing Beibei Chemical Reagent Factory. All reagents were analytically pure.

Treatment of Simulated Ammonia Nitrogen Wastewater by Electro-Fenton

A homemade electrolytic cell with a size of 1.0 m×0.5 m×0.5 m was used. Graphite was used as the anode and cathode electrodes, with a size of 0.45 m×0.45 m. Air was pumped into the cathode surface to produce H_2O_2, which is a necessary reagent for the Fenton system. The experiment was carried out in a diaphragm-free electrolyzer (Figure 1). The experimental conditions included 3000 mg/L Cl^-, 100 mg/L SO_4^{2-}, and 100 mg/L ammonia nitrogen. Above parameters have been testified throughout previous experiments in our lab. The current density was 150 A/m^2, the plate spacing distance was 40 mm, the reaction temperature was 30°C, and the initial pH was 9.0. The total volume of the solution was 50 mL. The ammonia nitrogen concentration in the simulated wastewater was determined at varied times (5, 10, 20, 30, 45, and 60 min).

According to the above experiments, the optimal treatment time was obtained. All other experimental conditions were kept the same. The ammonia nitrogen concentration was investigated at electrode plate spacing distances of 40, 60, 85, 95 and 140 mm, respectively.

According to the above experiments, the optimal processing time and the best electrolyzer plate spacing distance were determined. All other experimental conditions were kept the same. The ammonia nitrogen concentration was researched by varying the reaction temperature at 20, 25, 30, 35 and 40°C.

Finally, the optimal treatment conditions were determined in terms of treatment time, electrode plate spacing distance and reaction temperature.

Tanning Wastewater Treatment

Ammonia nitrogen in leather wastewater mainly comes from leather wastewater in the deliming and bating stages.

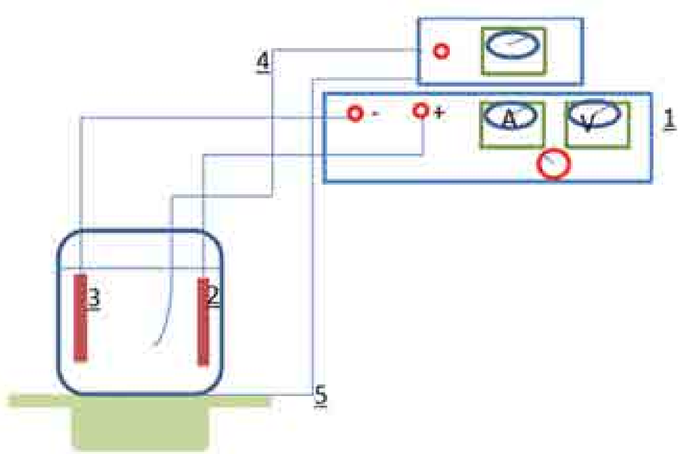

Figure 1. Experimental apparatus for electrolysis without membrane (1:direct current; 2:positive electrode; 3:negative electrode; 4:temperature controller; 5:heater).

Figure 2. The simplified flow chart of waste water treatment.

The collected wastewater was treated with a polyferric flocculant (190 mg/L) and then treated with the optimal conditions of the Electro-Fenton system. The specific treatment flow chart is shown in Figure 2. The conditions of Electro-Fenton treatment were obtained according to the treatment of simulated ammonia nitrogen wastewater by the electro –Fenton process. In the actual tanning wastewater process, there is a large amount of Cl^- and $SO4^{2-}$, so these two electrolytes were not added in the electrochemical treatment of the actual tanning wastewater.

Measurement of Ammonia Nitrogen Concentration

For the tannery wastewater, a modified distillation-acid titration method was used to determine ammonia nitrogen because of the high ammonia nitrogen concentration.[20] The main principle of distillation-acid titration was as follows. The pH of the wastewater sample was adjusted in the range of 6.0 ~ 7.4. Magnesium oxide was added, making the wastewater slightly alkaline. Finally, ammonia was released by the distillation process. The ammonia was absorbed by boric acid solution in a bottle, and the ammonia in the distillate was titrated with acid standard solution with methyl red and methylene blue as indicators. The reaction process can be described as follows:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$
$$NH_3 + HBO_3 \rightarrow NH_4BO_3$$
$$NH_4BO_3 + HCl \rightarrow NH_4Cl + HBO_3$$

A modified method for the microdetermination of nitrogen was used for the determination of the ammonia nitrogen content (Figure 3). The value can be calculated according to the following formula:

$$X = \frac{(V_1 - V_0) \times C \times 14}{10 / 1000} \quad (1)$$

where,

X: Ammonia nitrogen content in the water sample, mg/;

V_1: Volume of standard solution of hydrochloric acid (0.05 mol/L) consumed in the sample titration, mL;

V: Volume of standard solution of hydrochloric acid was 0.05 mol/L in blank test, Ml;

C: Molar concentration of the standard solution of hydrochloric acid, mol/L.

COD_{Cr} Measurement of Tanning Wastewater

A Rapid potassium dichromate method was used to determine the CODCr of water samples.[21] A colorimetric method for the determination of total chromium in wastewater was developed.[22] The turbidity of the water sample was determined by a colorimetric method with a 722 spectrophotometer.[23]

Energy Consumption during of Electro-Fenton Treatment

During the removal process of ammonia nitrogen, the current, voltage and treatment time were proportional to the treatment volume and ammonia nitrogen concentration before and after treatment. The calculation formula was as follows:

$$E = \frac{UIt}{(C_0 - C)\,V}$$

where,

E: power consumption, Wh/mg ammonia nitrogen;
U: voltage, V;
I: electric current, A;
t: time, h;
V: wastewater volume, L;
C_0: ammonia nitrogen concentration before treatment, mg/L
C: ammonia nitrogen concentration after treatment, mg/L.

Figure 3. The modified distillation-acid titration distiller.

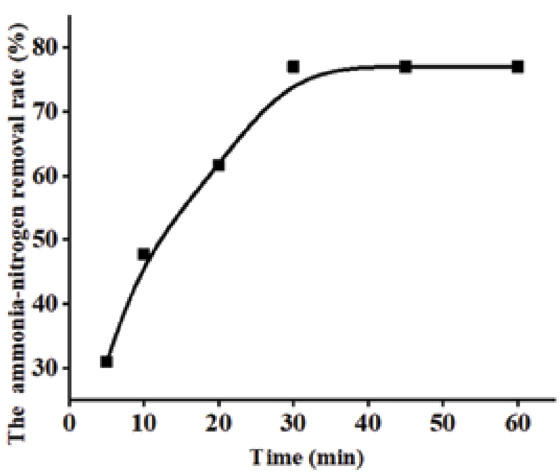

Figure 4. The influence of reaction time on the ammonia-nitrogen removal rate.

Results and Discussion

Treatment of Simulated Ammonia Nitrogen Wastewater by Electro-fenton

The effect of reaction time on the removal rate of ammonia nitrogen in simulate wastewater was investigated, and the test results were shown in Figure 4.

As seen from Figure 4, the first 30 min, in the ammonia nitrogen removal rate had a nearly linear rising trend with increasing reaction time. After 30 min, the ammonia nitrogen removal rate in the solution remained essentially unchanged and the reaction reached an equilibrium state. After reaction for 30 min, the ammonia nitrogen content decreased from 100 mg/L to 11.51 mg/L, and the removal rate was 76.98%; the content was lower than 15 mg/L, which is the comprehensive first-level standard for sewage discharge.

During the reaction, the electrode voltage and solution pH of the electrolyzer changed with time, as shown in Figure 5 and Figure 6, respectively.

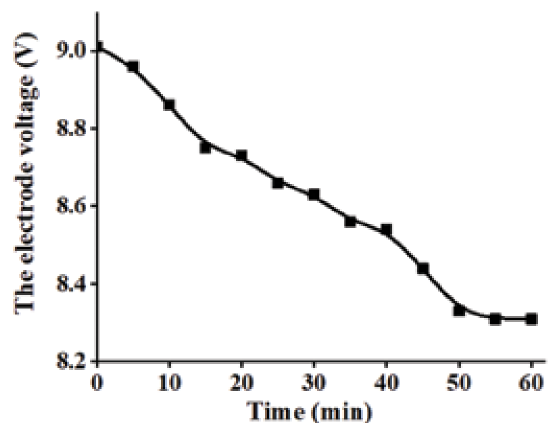

Figure 5. The electrode voltage varies with reaction time.

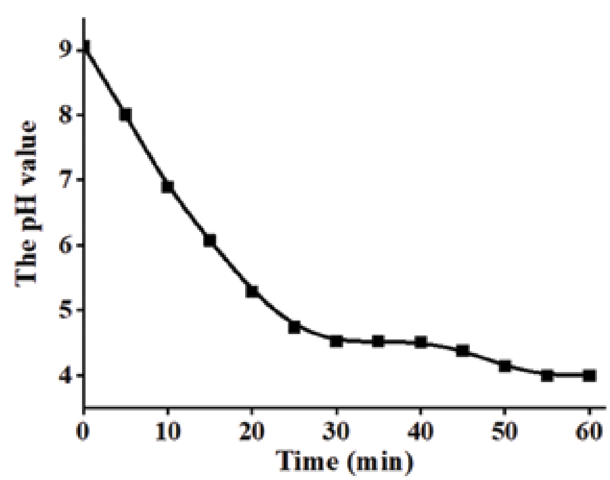

Figure 6. The pH value varies with reaction time.

It can be seen from Figure 5 that under the condition of constant current density, with increased reaction time, the electrode voltage of the electrolyzer decreased steadily, indicating that the effective electrolyte content in the solution increased and the conductivity of the solution improved.

In Figure 6, the solution pH in the first 30 min exhibited a linear downward trend that was essentially unchanged after 30 min, which indicated that the electrochemical oxidation speed remained fast before 30 min; additionally, Cl_2 was generated from Cl^- so the amount of HClO also showed a sharply increasing trend. Therefore, the ability to oxidize ammonium sulfate also increased, as also indicated in Figure 4. The change trend of ammonia nitrogen content with time was consistent. The removal rate appeared to reach the maximum value at a reaction time of 30 min.

Figure 7 showed the influence of the electrode plate spacing distance of the electrolytic cell on the removal rate of ammonia nitrogen in wastewater. With increasing plate spacing distance, the residual ammonia nitrogen content in the wastewater increased, and the removal rate of ammonia nitrogen in the wastewater decreased. When the plate spacing distance was between 40 mm and 60 mm, it had little effect on the ammonia nitrogen content. When the plate spacing distance was more than 60 mm, the residual ammonia nitrogen content in the wastewater increased significantly, and the removal rate decreased significantly. The main reason was that with increased plate spacing distance, the oxidation potential decreased under constant current density. Therefore, the oxidation of Cl^- and the direct electrochemical oxidation of ammonia nitrogen was weakened. Furthermore, with increased plate spacing distance, the likelihood of contact between oxidant and ammonia nitrogen compounds was likely weakened with the larger space, which has a detrimental treatment effect.

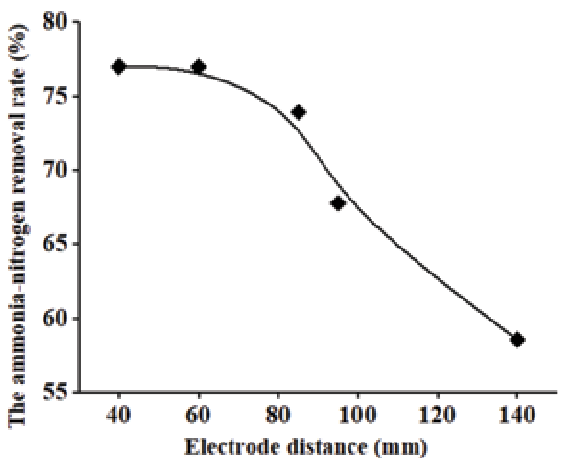

Figure 7. The influence of electrode distance on the ammonia-nitrogen removal rate.

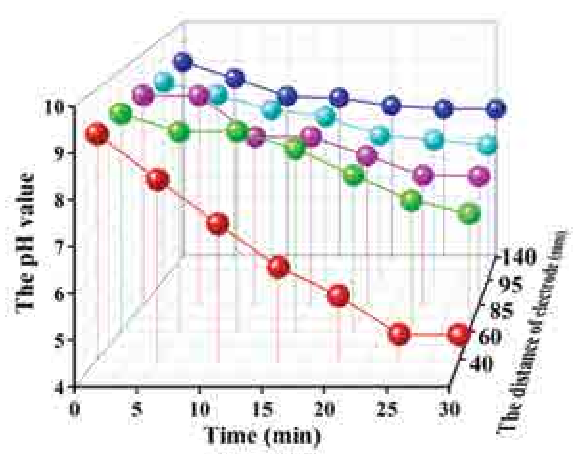

Figure 9. The relation of pH value and electrode distance.

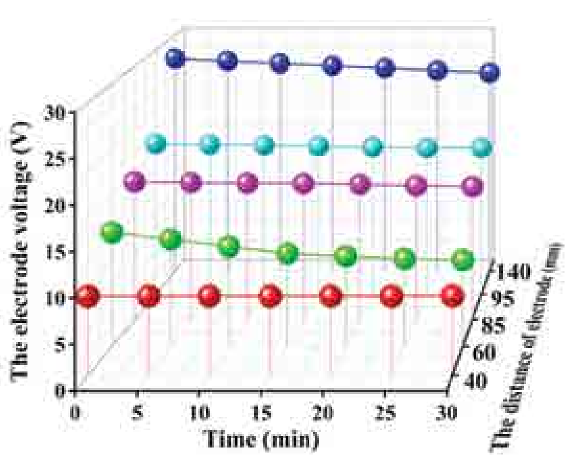

Figure 8. The relation of electrode voltage and electrode distance.

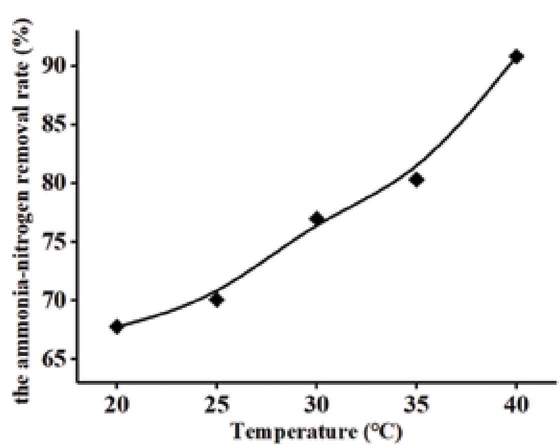

Figure 10. The influence of temperature on the ammonia-nitrogen removal rate.

The relationship between the electrode voltage, solution pH and electrode plate spacing of the electrolyzer during the reaction process with different electrode plate spacing distances was shown in Figure 8 and Figure 9.

It can be seen from Figure 8 that when the current density was constant, with an increased electrode plate spacing distance of the electrolytic cell, the electrode plate voltage clearly increased and then basically remained constant. An increase in electrode voltage will lead to an increase in energy consumption. Figure 7 showed that the removal rate of ammonia nitrogen also decreased. Therefore, an electrolytic cell with a small electrode spacing distance (40 mm) was selected for the follow-up experiment.

As shown in Figure 9, when the electrode plate spacing distance of the electrolytic cell was 40 mm, the pH of the solution showed a significant decreasing trend during the reaction and declined from 9.0 to 4.5. When the distance between plates was 60, 85, 95 and 140 mm, the change trend of pH was essentially the same, and the pH decreased slowly. The pH dropped from 9.0 to 6.5, 7.0 and 7.5, respectively, and the pH at the end point was approximately neutral. As also shown in Figure 8, the removal rate of ammonia nitrogen was the highest when the plate spacing was 40 and 60 mm and the terminal pH was in the acidic range, thus proving that the oxidation effect was the strongest under acidic conditions.

Figure 10 showed the effect of reaction temperature on the removal rate of ammonia nitrogen. With increasing reaction temperature, the residual ammonia nitrogen content in the solution clearly decreased. As the temperature increased, the reaction rate increased, and the oxidation capacity improved. Moreover, as the temperature increased, the nitrogen solubility decreased, so the residual ammonia nitrogen content in the solution decreased significantly. When the temperature was 25°C, the ammonia nitrogen content fell from 100 mg/L to 14.97 mg/L, meeting the wastewater discharge standard, so

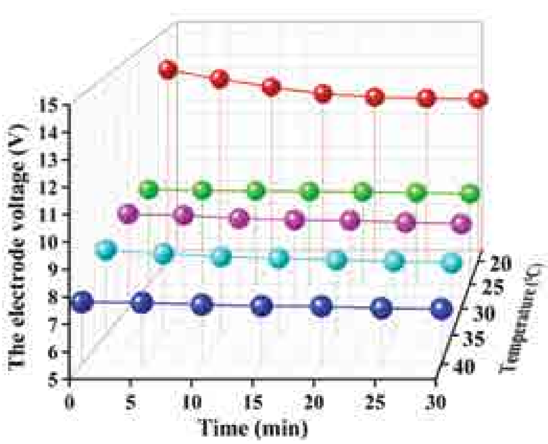

Figure 11. The relation between electrode voltage and temperature.

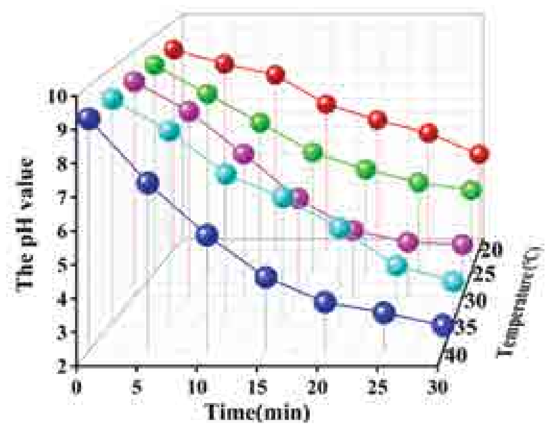

Figure 12. The relation between pH value and temperature.

Table I
The treatment effect of tannery wastewater.

Item	Before flocculation	After flocculation	Removal rate/%	After Electric-Fenton treatment	Removal rate
COD_{Cr}/(mg/L)	495	99	80	87	12.12
Total Chromium/(mg/L)	2.223	0.23	89.77	0.22	4.35
Turbidity	88	7	92.04	5	28.57
NH3-N/(mg/L)	243	142.11	41.52	11.23	92.10

Table II
The voltage varies with time.

Time/min	0	5	10	15	20	25	30
Voltage/V	9.0	8.9	8.7	8.7	8.5	8.4	8.2

temperatures in summer and autumn will enable the electrochemical treatment of ammonia nitrogen wastewater to reach the expected treatment effect. The energy consumption and the cost of dealing with waste water can be controlled.

The relationships between the electrode voltage, solution pH and temperature of the electrolyzer at different reaction temperatures during the reaction process were shown in Figure 11 and Figure 12.

It can be seen from Figure 11 that under constant current density, the reaction temperature increased, and the electrode voltage decreased and remained essentially constant. With increased temperature, the heat mass transfer rate and conductivity of the solution were strengthened and the voltage appeared to decrease.

As seen from Figure 12, the pH of the solution presented a steady decreasing trend as the reaction progressed, but with increased the reaction temperature, the final pH of the solution decreased gradually. According to Figure 11, the higher the temperature was, the lower the ammonia nitrogen content in the solution was. Therefore, the lower the final pH of the solution was, the stronger the oxidation capacity was, and the lower the ammonia nitrogen content was, the higher the ammonia nitrogen removal rate was.

The best conditions determined for efficient ammonia nitrogen removal in laboratory included a of Cl^- concentration of 3000 mg/L, SO_4^{2-} 100 concentration of mg/L, ammonia nitrogen concentration of 100 mg/L, current density of 150 A/m^2, and reaction time of 30 min. The plate spacing distance was 40 mm, and the reaction temperature was 30°C. Under these reaction conditions, the ammonia nitrogen content of the ammonium sulfate solution decreased from 100 mg/L to a minimum of 4.6 mg/L, far exceeding the first-level standard for sewage discharge.

Ammonia Nitrogen Removal from Tannery Wastewater by Electro-Fenton

The Electro-Fenton treatment results of tannery wastewater are shown in Table I .As shown in Table I, after flocculation treatment, the total chromium removal rate of wastewater treated with polyferric sulfate was 89.77%, and the concentration was 0.23 mg/L. The turbidity removal rate was 92.04%, and the turbidity after treatment was 5, meeting the international first-class discharge standards requiements. However, the treatment effect of ammonia nitrogen was poor, and the removal rate was only 41.52%. When the wastewater was deeply treated by the Electro-Fenton oxidation method, the removal rate of ammonia nitrogen was 92.10%, and the final concentration was 11.23 mg/L, which meets the national first-level discharge standard. In the simulated leather wastewater experiment mentioned above, the concentration of ammonia nitrogen was 100 mg/L, and the removal rate was 95.4%, indicating that the lower the concentration of ammonia nitrogen is, the better the effect of deep treatment. It is further proven that the Electro-Fenton method is suitable for the deep treatment of leather wastewater, and can produce a wastewater ammonia nitrogen content that meets the discharge requirements.

Energy Consumption by the Electro-Fenton System

When the current was constant, the voltage changed over time, as shown in Table II.

According to the data in Table II, the voltage was integrated from 0 to 30 min to obtain Ut= 259 v.min. From the calculation formula of energy consumption, the total E was 0.047 kw.h/mg.

Conclusions

After the flocculation treatment of tannery wastewater, the treatment conditions of the Electro-Fenton oxidation system included a current density of 150 A/m^2, a reaction time of 30 min, a plate spacing distance of 40 mm, and a reaction temperature of 30°C. The tanning wastewater with an ammonia nitrogen content of 142.1 mg/L was treated further, and the removal rate of ammonia nitrogen reached 92.10%. The final ammonia nitrogen content of the wastewater was 11.23 mg/L at last, which meets the national first-level emission standard. The energy consumption was 0.047 kw.h/mg, which indicated the Electro-Fenton is a sustainable and eco-friendly ammonia nitrogen treatment method for tannery wastewater.

Acknowledement

This work was supported by Natural Science Foundation of China (51703100) , Sichuan Science, Technology Program(2019YFG0269), Chengdu Science and Technology Project(2017-RK00-00330-ZF), Jiaxing Technology Innovation Team - Cleaner Production of Leather Processing and Fabric Dyeing & Finishing (2014) and Educational Commission of Zhejiang Province of China Grant No. Y201840368.

References

1. Zeng, Y. H., Wang, Y. N., Song, Y., *et al.*; A cleaner deliming process using sodium gluconate for reduction in nitrogen pollution in leather manufacture. *JALCA* **113**, 19-25, 2018.
2. Zhou, J. F., Wang, Y. N., Zhang, W. H., *et al.*; Nutrient balance in aerobic biological treatment of tannery wastewater. *JALCA* 109, 154-160, 2014.
3. Wang, Y. N., Zeng, Y. H., Chai, X. W., *et al.*; Ammonia nitrogen in tannery wastewater: distribution, origin and prevention. *JALCA* **107**, 40-50, 2012.
4. Jochimsen, J. C., Schenk, H., Jekel, M. R. *et al.*; Combined oxidative and biological treatment for separated streams of tannery wastewater. *Water science and technology* **36**, 209-216, 1997.
5. Nagabalaji, V., Sivasankari, G., Srinivasan, S. V., *et al.*; Nutrient removal from synthetic and secondary treated sewage and tannery wastewater through phycoremediation. *Environ. Technol.* **40**, 784-792, 2019.
6. Gao, M. H., Gao, N.Y., Zhou C., *et al.*; Chlorination method of raw water from Huangpu river with medium-high concentration of ammonia nitrogen. *Journal of Central South University (Science and Technology)* **45**, 1354-1360, 2014.
7. Wang Z., Ji Y.Z.,; Application of physico-chemical and biochemical composite process under high salt and high ammonia-nitrogen content organic sewage treatment. *Jiangsu Environment Science and Technology* **13**, 10-13, 2000.
8. Feng, X. D., Wang, W., Dong, L. M., *et al.*; Technics of treating wastewater containing high concentration ammonical nitrogen. *Journal of Beijing technology and business university (Natural Science Edition)* **22**, 5-8, 2004.
9. Tunay, O., Kabdasli, I., Orhon, D., *et al.*; Ammonia Removal by magnesium ammonium phosphate precipitation in industrial wastewaters. *Wat. Sci. Tech.* **36**, 225-228, 1997.
10. Jorgensen, T. C., Weatherley, L. R.; Ammonia removal from wastewater by ion-exchange in the presence of organic contaminants. *Wat. Res.* **37**, 1723-1728, 2003.
11. Li, K. B., Jin, S. D.; Decontaminating ammoniacal nitrogen from waste water by emulsion liquid membrane. *Membrane Science and Technology* **16**, 40-45, 1996.
12. Keav, S., Barbier, J. Jr., Duprez, D.; Deactivation and regeneration of wet air oxidation catalysts. *Catal. Sci. Technol.* **1,** 342-353, 2011.
13. Shu, J. C., Liu, R. L., Liu, Z. H., *et al.*; Electrokinetic remediation of manganese and ammonia nitrogen from electrolytic manganese residue. *Environ. Sci. Pollut. R.* **22**, 16004-16013, 2015.
14. Sundarapandiyan, S., Guntamadugu, B. R., Bhaskar, C., *et al.*; Removal of organic materials from tannery wastewater containing ammonia for reuse using electro-oxidation. *Environ. Eng. Manag. J.* **17**, 2157-2164, 2018.
15. Zhang, L., Su, F., Wang N., *et al.*; Biodegradability enhancement of hydrolyzed polyacrylamide wastewater by a combined Fenton-SBR treatment process. *Bioresource Technol.* **278**, 99-107, 2019.
16. Adesogan, A.T., Arriola, K.G., Jiang, Y., *et al.*; Symposium review: Technologies for improving fiber utilization. *J. Dairy Sci.* **102**, 1-30, 2019.
17. Szpyrkowicz, L., Naumczyk, L., Zilio-Grandi, F.; Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes. *Wat. Res.* **29**, 517-524, 1995.
18. Wang, W., Ding Z. N., Xu P. Y., *et al.*; Tannery wastewater treatment by different inorganic macromolecule flocculants. *China Leather* **37**, 24-27, 2008.
19. Ovenden, C., Xiao, H.; Flocculation behaviour and mechanisms of cationic inorganic microparticle/polymer systems. *Colloid. Surface. A.* **197**, 225-234, 2002.
20. National environmental monitoring agency; Methods for monitoring and analyzing water and wastewater. Environmental Science Press, Beijing, China, 2002.
21. Wang, K., Li X., Cai J., *et al.*; Removal Effect for Ammonia-nitrogen and COD in Coking Wastewater by Using Six Kinds of Aquatic Plants. *Science & Technology Review* **30**, 76-81, 2012.
22. Kocurek, P., Kolomaznik, K., Barinova, M., *et al.*; Total control of chromium in tanneries-thermal decomposition of filtration cake from enzymatic hydrolysis of chrome shavings. *Waste Manage. Res.* **35**, 444-449, 2017.
23. Sodhi, V., Bansal, A., Jha, M. K.; Excess sludge disruption and pollutant removal from tannery effluent by upgraded activated sludge system. Bioresource Technol. 263, 613-624, 2018.