Study on the Characteristics of Nitrogen Transformation in Effluents from Cattlehide Leather-making Process

Ding Shao-lan ⃰ ***, Li Ling, Zhao Meng-jun***

College of Resource and Environment, Shaanxi University of Science and Technology，Xi`an, 710021，Shaanxi, P.R. China

Abstract: The effect of activated sludge on effluents from each section during cattlehide leather-making process was tested, and the results showed that the pH increased slightly after the treatment by microorganisms, staying at 7-8; Samples from wet finishing got highest ammonium removal rate of 78.24% and the ammonium concentration of wastewater from liming increased. As to the organic nitrogen, wastewater sample from liming got the highest removal rate of 38.97%. The majority of ammonium was from liming and deliminig, while organic nitrogen was mainly from liming. The nitrogen transformation was mainly due to the microbial metabolism and nitrification, according to the experiment.

Key words: Leather-making, cattlehide, ammonium, organic nitrogen, COD

1 Introduction

Ammonium in water bodies, especially in those slow-flowing lakes or bays, would easily cause crazy multiplication of algae and other microorganisms, resulting in eutrophication. It would not only add difficulty to water treatment, but also produce abnormal flavor in drinking water, and consume dissolved oxygen (DO), thus lead to death of fishes, and even dry up or ruin a whole lake. In water disinfection and industrial circulating water sterilization, ammonium increases the use of chlorine. Of certain metals, particularly copper, it is corrosive. When the wastewater was recycled, the ammonia could promote microbial breeding in the water-carrying pipe and facilities, forming biofouling, plugging pipes, and affect the heat transformation.

As a complicated organic wastewater with high concentration, the tannery effluent change frequently in quality and quantity, and is treated by activated sludge system more often. Practical operations show that the traditional activated sludge system could decrease COD effectively; meanwhile, it would increase the ammonium in the effluent. From the point of view of leather-making process, the ammonium pollution is mainly produced from two points, on the one hand, the traditional liming tech with lots of scrap skin and hairs discharged, all the scraps would decompose, adding to ammonium; on the other hand, the ammonium salt, including ammonium sulfate, ammonium chloride, used during deliming and dyeing processes, and the insufficient use of the salt would also release into wastewater, elevating the ammonium concentration. With the adjustment of national policies, the discharge standard of water pollutants for leather and fur making industry (manuscript) has been proposed, in which the ammonium discharge concentration limit for present companies is 65 mg/L, and for the new-built companies is 35 mg/L. Over the years, most researches for tannery wastewater were focused on COD, chromium, sulfur, et al, but rarely on ammonium, so it is demanding for ammonium removal.

⃰ Corresponding author, Tel: 15829077070. E-mail: dingsl@sust.edu.cn

The wastewaters were collected from various sections (including soaking, liming, deliming, pickling and chrome tanning, wet finishing) during cattlehide leather-making process, then the effect of traditional activated sludge on each sample was tested, aiming to get scientific datas for ammonium prevention and cure, and provide theoretic foundation for cleaner production extension to decrease or eliminate pollution from the source.

2 Experiment

2.1 Materials

The wastewaters from each section were collected during a batch of cattlehide leather-making process in a tannery factory in Shandong Province. The samples included wastewater from soaking, liming, deliming, pickling, wet finishing, and a comprehensive one.

2.2 Methods

2.2.1 Cultivation and acclimatization of activated sludge

Firstly, strengthen oxygen supply by pneumatic pump, and add sufficient glucose, ammonia chloride, potassium dihydrogen phosphate to the sludge to promote microorganisms breeding according to Sawyer equation, BOD：N：P=100：5：1. Secondly, acclimatize the sludge to comprehensive and liming wastewaters gradually. During the acclimatization, remember to add nutrient substances, as well as mineral salt to the sludge in time, according to the changes of COD, nitrogen, DO, and sedimentation rate, etc. It was considered to be fully domesticated when the settlement ratio of the sludge was about 30%-50%, and the DO was about 1.5-2 mg/L.

2.2.2 Treatment of section samples with microorganisms

Take certain of wastewater sample, adjust its pH to 7.0 or so, and add some activated sludge to the sample, keep agitating at the speed of 500 rpm; a certain time later, collect some mixture of sludge and wastewater as samples, the monitoring methods included direct measuring by pH meter, distillation and titration method (GB 7478-87), determination of Kjeldahl nitrogen (GB 11891-89).

3 Results and discussion

3.1 pH changes of each sample

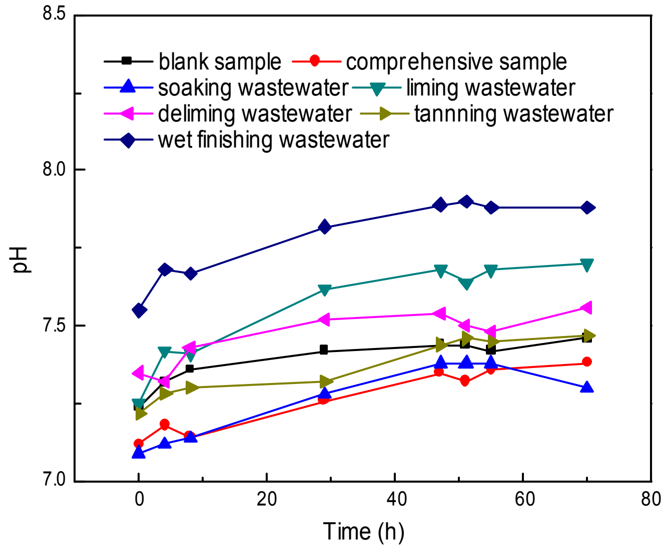


Fig. 1 pH changes during the treatment

Fig. 1 showed that during wastewater treatment by activated sludge, the pH increased slightly, staying at 7-8, which is suitable for aerobic microorganisms. The adaptive pH norm for most bacteria and protozoa is 4-10, and as the main body of activated sludge in aerating system, the zoogloea produce more stickum to get better floccule when the pH is 6.5-8.5. Therefore, the pH was suitable for microbial growth and breeding. Besides, little ammonium would transformed into alkaline air, and so the release of alkaline air was not considered during the experiment.

3.2 Ammonium changes of each sample

The ammonium concentration of each sample varied during activated sludge treatment, which was shown in Fig. 2.

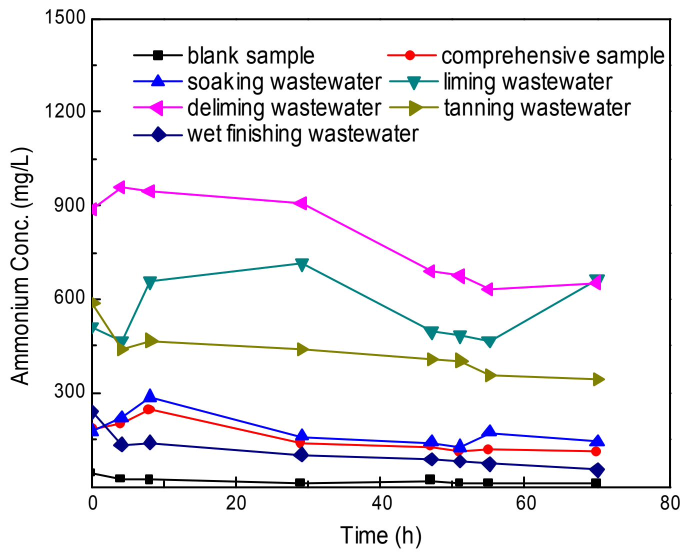


Fig. 2 Ammonium concentration changes during the treatment

It showed in Fig. 2 that the ammonium concentration of deliming wastewater sample was highest of all, which was above 900 mg/L at the beginnnig, and was about 600 mg/L at the end; the ammonium concentrations of samples from liming and tanning process were also higher, which was 400-750 mg/L;

the ammonium concentrations of samples from soaking, wet finishing and the comprehensive sample were 200 mg/L before the activated sludge treatment, and declined to 50-150 mg/L finally, with a not so high removal rate.

With the treatment of microorganisms, there were differentces among the ammonium concentration of each sample. Fig. 2 showed that at the beginning (0-4h), the ammonium concentration of liming, tanning, and wet finishing wastewater dropped down to some extent, the ammonium concentration of wet finishing wastewater

Fig. 2 showed that ammonium discharged from liming and deliming section resulted in high ammonium concentration in tannery wastewater. As the above description, the high ammonium in liming section resulted from massive scraps discharged into the wastewater, the macromocular materials were gradually decomposized, and the organic nitrogen was transformed into ammonium. Treated by the activated sludge system, such as oxidation ditch and biological contact oxidation process, the ammonium concentration of liming wastewater was rising, resulting in high ammonium in effluent. The ammonium in deliming section was mainly caused by the deliming technology with ammonium salt for the factory.

Cleaner production could be introduced to control the ammonium discharge from the source for liming and deliming operation. For example, take Hair-saving Unhair or oxidation methods for unhairing, it can not only guarantee efficient unhairing, but also make the hairs collectable for keratin solution or the extraction of cystine; partial or complete use of CO_2, organic acids for unhairing, could reduce the use of ammonium salt, and lower the ammonium concentration in the wastewater.

3.3 Organic nitrogen changes of each sample

The organic nitrogen concentrations varied among different samples during the microorganism treatment, as shown in Fig. 3.

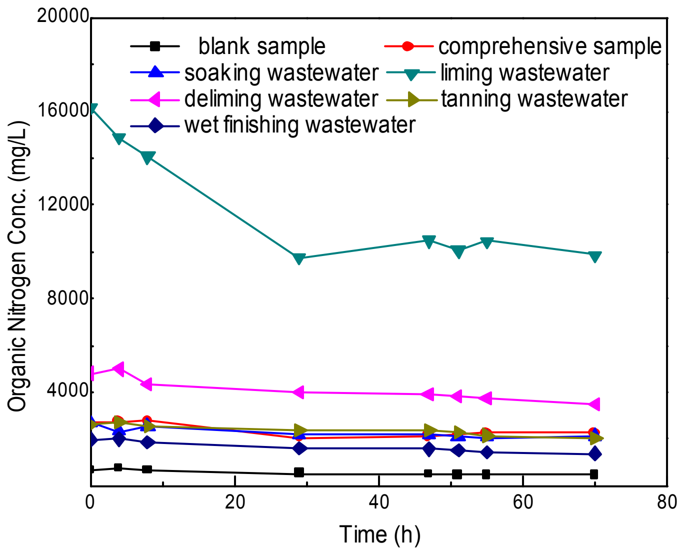


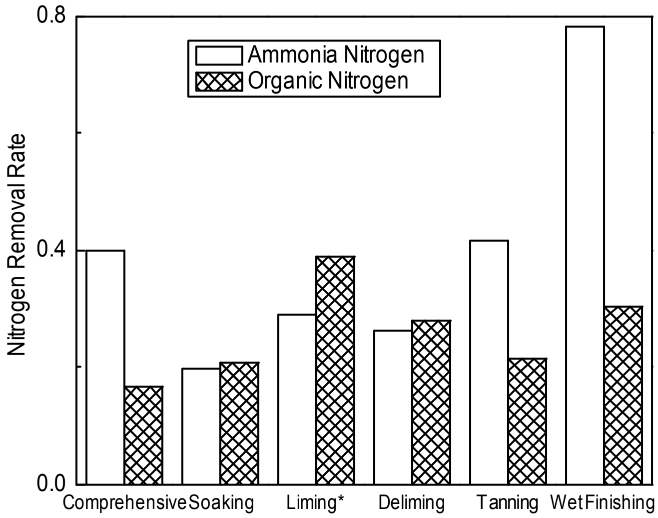
Fig. 3 Organic nitrogen concentration changes during the treatment

The organic nitrogen concentration of liming wastewater was much higher than that of other samples, during the process, the organic nitrogen decreased, but changed little at the later phase(treated for 30-70 hours). The organic nitrogen changed little after treated by microorganism. Fig. 3 showed the organic nitrogen concentration got a quick decrease before stabilization, meanwhile, the gradual decomposition of organic nitrogen resulted in large increase of ammonium concentration, which was consistent with Fig. 2. The organic nitrogen concentration was as high as 15000 mg/L, and it was high load for activated sludge system, besides, the chemicals including sodium sulfide used for liming would affect and do harm to microorganisms when discharged into wastewater.

3.4 Nitrogen transformation by activated sludge of each sample

The nitrogen removal rate for each sample was shown in Fig. 4.

Fig. 4 showed that the nitrogen removal rates differentiated greatly. Take ammonium removal rate for example, wastewater from wet finishing got the best removal efficiency, at 78.24%, followed by the comprehensive wastewater, tanning, deliming, soaking wastewater samples, which were 39.89%, 41.74%, 26.23%, 19.85% respectively. The ammonium concentration of liming wastewater rose by about 35%. As to the organic nitrogen removal rate, the liming wastewater got the best removal efficiency of 38.97%, and that of wet finishing, deliming, soaking, tanning wastewater and the comprehensive wastewater was 30.54%, 27.90%, 20.79%, 21.63%, and 16.64% respectively.



Note：The actual ammonium removal rate of liming was negative.

Fig. 4 Nitrogen removal efficiency before and after the experiment from each section

The diversity of nitrogen removal rates among different wastewater samples was mainly related with the characteristics of different samples. During the activated sludge treatment, the removal process of organic pollutants from wastewater is actually a process when the pollutants being ingested, metabolized, and utilized by microorganisms in the sludge. Firstly, the organic pollutants were adsorbed to the activated sludge surface, and contacted with the microorganisms. The micromolecular organics enter into the cells through the cell wall, and the macromolucular organics, such as starch and protein, were decomposed into micromolecular ones by ectoenzyme and hydrolase before ingested by microbes. The effluents from leather-making process contains lots of protein, resulting from scrap skin or hairs, but the details of wastewater samples usually differ in many respects, such as toxicity, so to the same activated sludge, they demanded different adaptation time, and different organic nitrogen removal rates. Fig. 4 showed that the organic nitrogen removal rates were around 16%-40% for each sample as the treatment went on.

The organic pollutants ingested into cells experienced complicated metabolic reaction by promotion of various endocellular enzymes, including dehydrogenase (DH) and oxidase. Some organics were used for synthesis of new cells, and some were transformed into stable inorganics, such as carbon dioxide and water by oxygenolysis, and produced energy for new cells synthesis. The decomposition of the organic nitrogen, lowered COD in the effluents, meanwhile, it would produce massive ammonium. From the experiment, it was found that except for the ammonium increase of liming wastewater, the ammonium concentration of other effluents dropped to tremendous different extent. The highest ammonium removal rate was that of the wet finishing wastewater, at 78%, and the lowest of soaking one, at about 20%.

3.5 Contrast on the characteristics of nitrogen

Various forms of nitrogen were existed in wastewater, including total nitrogen (TN), organic nitrogen, inorganic nitrogen (mainly ammonium), nitrates and sub-nitrates. When treated by aerobic microorganisms, there may be the metabolism, ammonia volatilization, nitrification and denitrification. The microbial metabolism makes organic nitrogen transformed into ammonium, and also synthesizes organic nitrogen with ammonium for cell growth and reproduction; the nitrification will convert ammonium into nitrates, sub-nitrates by, and the ammonia volatilization and denitrification will directly lead to the nitrogen loss. During the experiment, the effluent pH was at 7 to 8, little ammonia volatilization occurred, besides, the wastewater had been under aerobic conditions, so little sub-nitrates or nitrogen loss by denitrification. Therefore, there existed microbial metabolism and nitrification during the process.

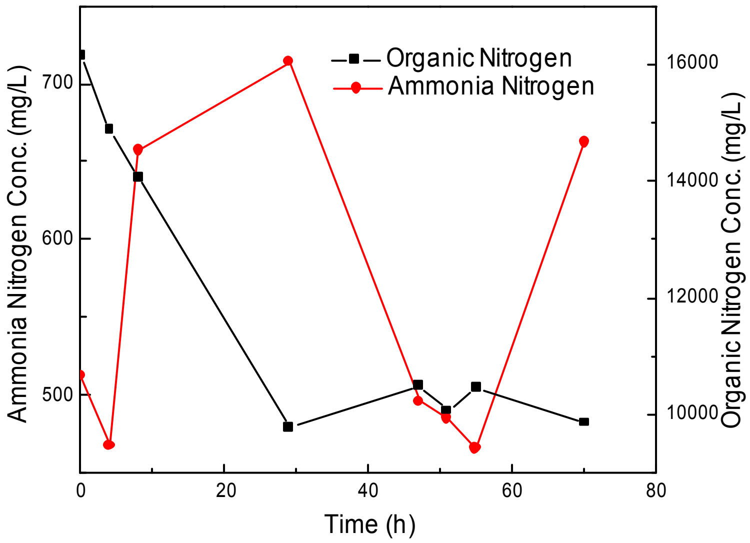


Fig. 5 Nitrogen Concentration in liming wastewater during the treatment

Fig. 5 showed the ammonium and organic nitrogen concentration in deliming wastewater. At the beginning (0-29h), the organic nitrogen declined significantly, and the ammonium increased. It was a time when the catabolism was stronger than anabolism for the microorganisms, and lots of organic nitrogen converted into ammonium. However, the decline in organic nitrogen was higher than the increase of ammonium according to calculation, which inferred the strong nitrification, and the ammonium transformed into nitrates later. At the middle phase (29-55h), the organic nitrogen kept stable, and the ammonium began a decline. It was a time when a balance between catabolism and anabolism began, but still with a strong nitrification, massive ammonium being converted into nitrates continuously, resulting in the ammonium decline. At the later phase (55-70h), there was a little decline in organic nitrogen, and the ammonium began to rise. It might be caused by the long-time nitrification, and the accumulation of nitrates might affect the nitrification, leading a new balance of metabolism.

4 Conclusions

During the treatment of activated sludge to effluents from leather-making sections, pH values of each sample rose slightly, staying at 7 to 8; wastewater from wet finishing got the best removal efficiency of ammonium, at 78.24%, followed by the comprehensive wastewater, tanning, deliming, soaking wastewater samples, which were 39.89%, 41.74%, 26.23%, 19.85% respectively. The ammonium concentration of liming wastewater rose by about 35%. As to the organic nitrogen removal rate, the liming wastewater got the best efficiency of 38.97%, and that of wet finishing, deliming, soaking, tanning wastewater and the comprehensive wastewater was 30.54%, 27.90%, 20.79%, 21.63%, and 16.64% respectively. Most ammonium was discharged from liming and deliming section, and traditional unhairing technology brought massive organic nitrogen into wastewater. It is necessary to implement cleaner production. The nitrogen transformation was mainly due to the microbial metabolism and nitrification, according to the experiment.

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