

Efficient Removal of Ammonia-Nitrogen from Deliming Effluent by using Magnesium Ammonium Phosphate Precipitation Method

by

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Abstract

Ammonia nitrogen (NH₃-N) pollutant has received much attention in the leather industry. An efficient strategy for removal of NH₃-N from tannery wastewater was proposed by using a magnesium ammonium phosphate (MAP) precipitation method to remove NH₃-N from deliming effluent with the highest NH₃-N concentration among all leather-making effluents. Results showed that approximately 80% of NH₃-N was removed from deliming effluent when reacting at P/Mg/N mole ratio of 1.2:1.2:1.0 and pH 9.5 for 20 min. The NH₃-N and total nitrogen concentrations of tannery wastewater (a composite wastewater of all leather-making effluents) sharply decreased by treating deliming effluent with MAP precipitation, which greatly improved the biological treatment efficiency of tannery wastewater. The residual concentration of NH₃-N in the treated tannery wastewater was less than 2 mg/L. The total phosphorus concentration of tannery wastewater increased by less than 0.4 mg/L, indicating that secondary pollution of phosphorus did not occur after MAP precipitation treatment.

Introduction

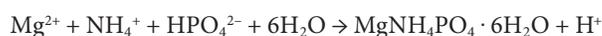
Beamhouse procedures are important for the removal of preserving salts, dirt, blood, hair, epidermis, non-structural proteins, and fat from raw hide and dispersion of hide collagen fibers.¹ However, the beamhouse procedures cause pollution in tannery wastewater. For example, deliming and bating procedures generally use ammonium salts such as (NH₄)₂SO₄ and NH₄Cl, resulting in high concentration of ammonia nitrogen (NH₃-N) in deliming and bating effluents (2,000–4,000 mg/L). The NH₃-N amount of deliming and bating effluents accounts for 60%–70% of the NH₃-N amount of tannery wastewater that includes all effluents released from leather-making procedures.² The high concentration of NH₃-N in deliming and bating effluents contributes to a low C/N ratio of the tannery wastewater, making it difficult to achieve an efficient biological treatment of tannery wastewater and a satisfactory NH₃-N removal efficiency.³ The high NH₃-N load in deliming and bating effluents deteriorates the tannery wastewater. If the tannery wastewater contains a large amount of NH₃-N, it will cause the eutrophication

of water, the low concentration of dissolved oxygen in water, and the death of fish and other organisms.^{4,5}

NH₃-N pollution caused by deliming and bating can be eliminated by replacing ammonium salts with ammonium-free deliming agents. However, existing ammonium-free deliming agents, such as carbon dioxide,^{6,7} acetic acid, lactic acid, citric acid,^{8,9} magnesium salts,¹⁰ peracetic acid,¹¹ glycolic acid,¹² and glycine,¹³ have small pH-buffering capacity, slow penetration in limed pelt, or high cost. Consequently, ammonium-free deliming agents only have small-scale applications, and ammonium salts with excellent deliming performance and low price are still popular for deliming and bating procedures in tanneries. Thus, an effective way to reduce the NH₃-N in tannery wastewater is the removal of NH₃-N from the deliming and bating effluents with high NH₃-N concentration and small volume before the two effluents are released into tannery wastewater.

Many methods involving ammonia stripping,^{14,15} ion exchange method,^{16,17} membrane technology,^{18,19} and chlorination^{20,21} have been developed to remove NH₃-N from wastewater. However, the ammonia stripping method requires large-scale heating to strip ammonia and strong acid solution (mainly H₂SO₄) to absorb ammonia.²² The ion exchange method is generally used to treat the wastewater with low concentration of NH₃-N because the ion exchange material usually shows a limited exchange capacity.²³ For the membrane technology, membranes are easily damaged by suspended solids in deliming and bating effluents. Chlorination uses a lot of chlorine and produces harmful byproducts.²¹ Therefore, these methods are not appropriate for the treatment of deliming and bating effluents.

The magnesium ammonium phosphate (MAP) precipitation method removes high concentration of NH₃-N from various wastewaters, such as aquaculture wastewater,²⁴ landfill leachate,²⁵ and human urine.²⁶ The formation of MAP proceeds through the following reactions:²⁷



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MAP precipitation method requires the addition of magnesium salt and phosphate into wastewater to make NH₃-N precipitate. The addition of phosphate has received considerable attention because it usually results in excessive phosphorus residue in wastewater after MAP precipitation treatment. The secondary pollution of phosphorus limits the application of MAP precipitation method in wastewater treatment. In fact, Tünay *et al.* reported NH₃-N removal with MAP precipitation in a composite wastewater of liming, deliming and bating effluents and tannery wastewater (a composite wastewater of all leather-making effluents).²⁸ However, the liming effluent with high sulfide and calcium concentrations made the composite wastewater undergo complex pretreatment and difficult to simultaneously achieve a high NH₃-N removal efficiency and a low residual phosphorus concentration. Additionally, the MAP precipitation treatment of the tannery wastewater was not economical and led to a high residual concentration of phosphorus in the treated wastewater (ranging from 19.3 mg/L to 199 mg/L) because the tannery wastewater has large volume and relatively low concentration of NH₃-N. It is well known that the NH₃-N pollution mainly comes from deliming and bating procedures rather than the other leather-making procedures. The deliming and bating effluents have lower sulfide and calcium concentrations than the liming effluent and much smaller volume than the tannery wastewater. Moreover, the use of phosphorus-containing chemicals in the whole leather-making processes is limited. Therefore, the introduction of phosphorus into deliming and bating effluents caused by MAP precipitation treatment will scarcely affect the total phosphorus (TP) concentration and C/N/P ratio of tannery wastewater. It is reasonable to speculate that MAP precipitation method can effectively remove NH₃-N from deliming and bating effluents without the secondary pollution of phosphorus. Besides, the MAP precipitate formed by treating the NH₃-N in the deliming and bating effluents can even be reused as slow-release fertilizer.²⁹

This study aims to effectively remove NH₃-N from deliming and bating effluents by using the MAP precipitation method. The effects of molar ratio of HPO₄²⁻ to NH₄⁺, molar ratio of Mg²⁺ to NH₄⁺, reaction pH, and reaction time on NH₃-N removal efficiency and residual phosphorus concentration of deliming and bating effluents were investigated. Finally, the effect of the treatment of deliming and bating effluents with MAP precipitation on the biological treatment of tannery wastewater was investigated.

Experimental

Materials

Deliming effluent with pH of 8.72 and NH₃-N concentration of 2,105 mg/L was collected after deliming. Bating effluent with NH₃-N concentration of 776 mg/L was also collected after bating. Analytical-grade MgCl₂·6H₂O and Na₂HPO₄·12H₂O were obtained

from Kelong Chemical Reagent Factory (Chengdu, China). High-range NH₃-N and TP test reagents were obtained from Fuzhou Fuguang Water Science & Technology Co., Ltd. (Fuzhou, China). Activated sludge used for biological treatment of tannery wastewater was provided by Chongzhou Fubang Leather Co., Ltd. (Chengdu, China).

Effect of pH adjustment method on NH₃-N removal efficiency

At room temperature, 2.43 g Na₂HPO₄·12H₂O and 1.51 g MgCl₂·6H₂O (P-to-Mg-to-N mole ratio [P/Mg/N] of 1.1:1.2:1.0) were added to 50 mL of deliming effluent. The pH of deliming effluent was separately adjusted using three different methods as follows: (1) no adjustment (control); (2) pH adjusted to 9.0 by using 1 mol/L NaOH solution before adding Na₂HPO₄·12H₂O and MgCl₂·6H₂O (Method A); and (3) pH maintained at 9.0 by using 1 mol/L NaOH solution after adding Na₂HPO₄·12H₂O and MgCl₂·6H₂O (method B). The reaction was performed with magnetic stirring for 15 min and standing for 30 min. Then, the concentration of NH₃-N in the supernatant of the reaction mixture was determined with high-range NH₃-N test reagent and water quality analyzer (DR6000, Hach, USA) according to the salicylic acid method (Method 10031).³⁰ The NH₃-N removal efficiency was calculated using Equation (1) as follows:

$$\text{NH}_3\text{-N removal efficiency} = \frac{X-Y}{X} \times 100\% \quad (1)$$

where X is the concentration of NH₃-N in deliming effluent before treatment, and Y is the concentration of NH₃-N in the supernatant of deliming effluent after treatment.

Optimization of MAP precipitation method for removal of NH₃-N from deliming effluent

Batch experiments were conducted at room temperature to investigate the effects of molar ratio of P to N (P/N), molar ratio of Mg to N (Mg/N), reaction pH, and reaction time on NH₃-N removal efficiency and TP concentration of deliming effluent after MAP precipitation treatment.

Effect of P/N

Different dosages of Na₂HPO₄·12H₂O (P/N 0.9, 1.0, 1.1, 1.2, 1.3 and 1.4) and 1.51 g MgCl₂·6H₂O (Mg/N, 1.2) were added into 50 mL of deliming effluent, and the reaction was performed at pH 9 with magnetic stirring for 15 min. After magnetic stirring, the reaction mixtures were left standing for 30 min, and the supernatants were collected to determine the NH₃-N and TP concentrations. To determine the TP concentration of the supernatant, we first digested the supernatant with potassium persulfate at 150°C for 30 min by using a digester (DRB200, Hach, USA). Then, the TP concentration of supernatant was measured using the TP test reagent and water quality analyzer according to the digestion-molybdenum antimony method (Method 10127).³⁰

Effect of Mg/N

Different dosages of MgCl₂·6H₂O (Mg/N, 0.9, 1.0, 1.1, 1.2, 1.3 and 1.4) and 2.66 g Na₂HPO₄·12H₂O (P/N, 1.2) were added into 50 mL of delimiting effluent, and the reaction was performed at pH 9 with magnetic stirring for 15 min. After magnetic stirring, the reaction mixtures were left standing for 30 min. Then, the NH₃-N and TP concentrations of supernatants were determined.

Effect of reaction pH

After adding 2.66 g Na₂HPO₄·12H₂O and 1.51 g MgCl₂·6H₂O (P/Mg/N, 1.2:1.2:1.0) into 50 mL of delimiting effluent, the pH of effluent was adjusted to a preset value (8.0, 8.5, 9.0, 9.5, 10.0, and 10.5) and then maintained throughout the reaction (magnetic stirring for 15 min). After the reaction, the mixtures were left standing for 30 min to determine the NH₃-N and TP concentrations of supernatants.

Effect of reaction time

The MAP precipitation reaction of delimiting effluent was performed at pH 9.5 and P/Mg/N of 1.2:1.2:1.0 with magnetic stirring for 10, 20, 30, 40, 50, and 60 min. Then, the reaction mixtures were left

standing for 30 min to determine the NH₃-N and TP concentrations of supernatants.

X-ray diffraction analysis of precipitate

The precipitate from delimiting effluent that was coprecipitated with Na₂HPO₄·12H₂O and MgCl₂·6H₂O was collected after reacting with P/Mg/N at a ratio of 1.2:1.2:1.0 and pH 9.5 for 20 min. The precipitate was washed thrice with distilled water and then dried at 45°C for 48 h to analyze the specific composition using an X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$; DX-2700, Haoyuan, China).

Aerobic biological treatment of simulated tannery wastewater

Three kinds of simulated tannery wastewaters were prepared for aerobic biological treatment experiment. A simulated tannery wastewater (control group) was prepared by mixing the effluents from each operation, except for chrome tanning, based on the amount of water used in each operation (Table I). Two other simulated tannery wastewater samples (experiment groups) were prepared using the same procedures, except that the delimiting or bating effluents were treated with MAP precipitation before mixing

Table I
Wastewater sampling from leather-making procedures

No.	Procedure	Sampling volume (L)		
		Control	Experiment 1	Experiment 2
1	Presoaking	2	2	2
2	Washing	2	2	2
3	Soaking	2	2	2
4	Liming	3.8	3.8	3.8
5	Washing	3	3	3
6	Delimiting	1	1 (MAP treatment)	1 (MAP treatment)
7	Bating	1	1	1 (MAP treatment)
8	Washing (3 times)	9	9	9
9	Pickling	0.5	0.5	0.5
10	Chrome tanning	No sampling	No sampling	No sampling
11	Washing	3	3	3
12	Rewetting	3	3	3
13	Washing	3	3	3
14	Neutralization	2	2	2
15	Washing	3	3	3
16	Retanning & Dyeing	1	1	1
17	Fatliquoring & Adding	1	1	1
18	Washing (3 times)	9	9	9
Total		49.3	49.3	49.3

into tannery wastewater (Table I). For experiment 1, the delimiting effluent was treated at P/Mg/N mole ratio of 1.2:1.2:1.0, pH 9.5, and room temperature for 20 min. For experiment 2, the delimiting and bating effluents were treated at P/Mg/N mole ratio of 1.2:1.2:1.0, pH 9.5, and room temperature for 20 min.

The three simulated tannery wastewaters were separately adjusted to pH 7.5 by using 2 mol/L sulfuric acid solution, mixed with activated sludge at a volume ratio of 3:1 (wastewater: sludge), and placed in a 2 L glass beaker. An aeration device (ACO-003, SunSun, China) was used to aerate the mixtures of activated sludge and simulated tannery wastewater at 25°C for aerobic biological treatment. After treatment for 0, 4, 8, 12, and 24 h, the concentration of dissolved oxygen (DO) was measured using a DO meter (HI9146, Hana, Italy), and the concentrations of mixed liquor suspended solids (MLSS) and sludge volume (SV) in the mixture of wastewater and sludge were determined using standard methods.³¹ Moreover, the mixtures were centrifuged at 5,000 rpm for 10 min, and the supernatants were used to determine the NH₃-N, total organic carbon (TOC), total nitrogen (TN), and TP concentrations. TOC and TN concentrations were determined using TOC/TN analyzer (Vario TOC, Elementar, Germany).

Results and Discussion

Effect of pH adjustment method on NH₃-N removal efficiency

According to the reaction equation of MAP formation (see Introduction section), the MAP precipitation process will release H⁺, causing a decrease in the pH of reaction system. The consumption of H⁺ helps the precipitation reaction proceed in the forward direction, which can increase the removal efficiency of NH₃-N. Therefore, we first investigated the effect of pH regulation on the removal of NH₃-N from delimiting effluent by using MAP precipitation method.

The data in Table II show that the pH of delimiting effluent sharply decreased to approximately 5.5 after the MAP precipitation reaction when the initial pH of delimiting effluent was not adjusted (control) or just adjusted to 9.0 by using a small amount of NaOH before adding Na₂HPO₄·12H₂O and MgCl₂·6H₂O (Method A). The removal efficiencies of NH₃-N from delimiting effluent by using pH adjustment Methods control and A were as low as approximately 50%. This was because the high concentration of NH₃-N in the delimiting effluent made the MAP formation release a large amount of H⁺ at the initial stage of precipitation reaction. Subsequently, the pH of the reaction system changed from alkaline to acidic pH, and this condition inhibited the continuous formation of MAP.²⁸ For Method B, the pH of the reaction system was maintained at 9.0 by continuously adding NaOH solution during the precipitation reaction. Thus, MAP precipitation was carried out more thoroughly, and the removal efficiency of NH₃-N was greatly increased to 78%. These results indicated that the pH of the reaction system mainly affects the removal of NH₃-N from wastewater by MAP precipitation, supporting the results obtained in previous studies.^{32,33} Keeping the pH of reaction system in an alkaline pH range is important for the efficient removal of NH₃-N from delimiting effluent.

Effects of reaction conditions on the removal of NH₃-N from delimiting effluent by using MAP precipitation method

MAP precipitation reaction conditions such as reaction pH, molar ratio of HPO₄²⁻ to Mg²⁺ to NH₄⁺, and reaction time influence the removal efficiency of NH₃-N and the composition and crystal structure of products. This section presents the effects of P/N, Mg/N, reaction pH, and reaction time on the removal of NH₃-N from delimiting effluent. The TP concentration of delimiting effluent after MAP precipitation treatment was also measured to determine whether secondary pollution of phosphorus occurred.

Table II
Effect of pH adjustment method on NH₃-N removal efficiency

pH adjustment method	pH of delimiting effluent after reaction	NH ₃ -N removal efficiency
Control	5.47±0.01	48.01±1.34%
Method A	5.48±0.01	50.20±1.54%
Method B	9.00	77.87±1.19%

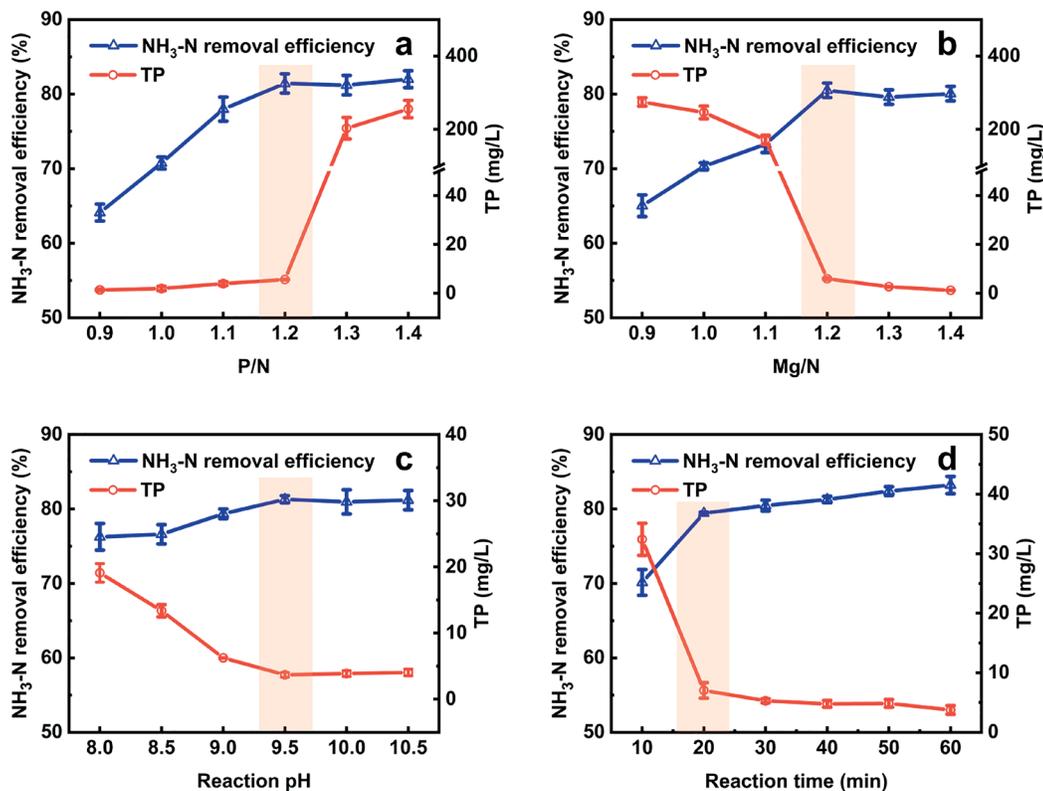


Figure 1. Effects of P/N (a), Mg/N (b), reaction pH (c), and reaction time (d) on the removal of $\text{NH}_3\text{-N}$ from deliming effluent and residual concentration of TP in treated deliming effluent by using MAP precipitation method

Figure 1(a) shows the effect of P/N on $\text{NH}_3\text{-N}$ removal efficiency and residual TP concentration of treated deliming effluent under Mg/N ratio of 1.2, reaction pH of 9.0, and reaction time of 15 min. When the P/N increased from 0.9 to 1.2, the $\text{NH}_3\text{-N}$ removal efficiency increased from 64.11% to 81.42%, and the residual TP concentration in the treated deliming effluent increased from 1.4 mg/L to 5.6 mg/L. When the P/N continued to increase to 1.3, the $\text{NH}_3\text{-N}$ removal efficiency scarcely increased, and the TP concentration rapidly increased and exceeded 200 mg/L. This phenomenon occurred because when the P/N was higher than 1.2, free $\text{NH}_3\text{-N}$ was mostly consumed, and the excess phosphate could not coprecipitate with $\text{NH}_3\text{-N}$ and remained in the deliming effluent. Therefore, the optimal P/N was 1.2, considering the chemical cost and phosphorus pollution.

The data in Figure 1(b) show that when the Mg/N increased from 0.9 to 1.2 (P/N=1.2, pH 9.0, reaction time 15 min), the $\text{NH}_3\text{-N}$ removal efficiency increased from 65.02% to 80.50%, and the residual TP concentration decreased from 274.9 mg/L to 6.0 mg/L. However, almost no increase was observed in the $\text{NH}_3\text{-N}$ removal efficiency, and the TP concentration slightly decreased when the Mg/N continued to increase. Thus, the optimal Mg/N of 1.2 was selected.

An alkaline pH of reaction system was conducive to the precipitation of MAP.³⁴ Therefore, the effect of reaction pH in the range of 8.0–10.5 on $\text{NH}_3\text{-N}$ removal efficiency and TP concentration of treated deliming effluent were investigated. As shown in Figure 1(c), at P/

Mg/N ratio of 1.2:1.2:1.0 and reaction time of 15 min, the $\text{NH}_3\text{-N}$ removal efficiency increased from 76.26% to 81.31% with the increase in pH from 8.0 to 9.5, and the TP concentration decreased from 19.1 mg/L to 3.7 mg/L. However, higher $\text{NH}_3\text{-N}$ removal efficiency and lower TP concentration were not obtained by continuously increasing the reaction pH. Hence, the reaction pH of 9.5 was appropriate.

The effect of reaction time on $\text{NH}_3\text{-N}$ removal and residual phosphorus at P/Mg/N ratio of 1.2:1.2:1.0 and reaction pH of 9.5 is shown in Figure 1(d). The reaction almost reached an equilibrium within 20 min at room temperature. The $\text{NH}_3\text{-N}$ removal efficiency was as high as 79.44%, and the residual TP concentration was as low as 7.0 mg/L after reacting for 20 min. The results indicated that MAP precipitate rapidly formed at the initial stage of reaction, which was consistent with kinetics of crystallization and dissolution of MAP.^{35,36}

Taken together, the MAP precipitation method was feasible for the removal of high-concentration $\text{NH}_3\text{-N}$ from deliming effluent within a short time at room temperature. The optimized precipitation conditions were P/N of 1.2, Mg/N of 1.2, reaction pH of 9.5, and reaction time of 20 min. Moreover, the residual phosphorus in the treated deliming effluent introduced by MAP precipitation method slightly influenced the TP concentration of tannery wastewater because of the small volume ratio of deliming effluent to tannery wastewater.

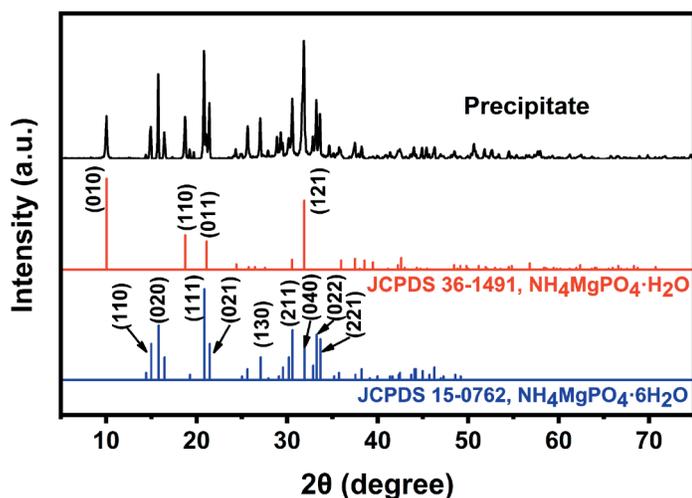


Figure 2. XRD pattern of the precipitate obtained from MAP precipitation treatment of deliming effluent

Characterization of precipitation

The precipitate formed by the MAP precipitation treatment of deliming effluent was collected under the optimum reaction conditions ($P/N=1.2$, $Mg/N=1.2$, pH 9.5, reaction time 20 min). The precipitate was first washed to remove the free organic matter and soluble salts and then analyzed by X-ray diffraction. As shown in Figure 2, the XRD pattern of precipitate shows sharp peaks, indicating that the precipitate was well crystallized.³⁷ Based on the comparison of the XRD pattern of precipitate and the standard XRD patterns of synthetic struvite (JCPDS Card No. 36-1491) and synthetic dittmarite (JCPDS Card No. 15-0762), the precipitate is a mixture of struvite and dittmarite. This result proved that the NH₃-N in the deliming effluent coprecipitated with MgCl₂·6H₂O and Na₂HPO₄·12H₂O and formed crystalline MAP monohydrate and hexahydrate.

Effect of MAP precipitation method on the biological treatment of tannery wastewater

This work aims to propose an effective method to achieve satisfactory biological treatment and NH₃-N removal of tannery wastewater. In this section, we investigated how the MAP precipitation treatment of deliming and bating effluents affects the aerobic biological treatment and pollution loads of tannery wastewater.

The concentrations of NH₃-N, TOC, TN, and TP in the control and experimental simulated tannery wastewaters are shown in Table III. The NH₃-N concentrations of Experiments 1 and 2 tannery wastewaters were merely 58.36% and 42.72% of the control one, respectively. This indicated that the treatment of high-concentration NH₃-N-containing deliming and bating effluents with MAP precipitation method greatly reduced the concentration of NH₃-N in the tannery wastewater. Considering that NH₃-N is an important source of nitrogen in tannery wastewater, the TN concentrations of experimental tannery wastewaters decreased with the decrease in NH₃-N concentration.³⁸ Although some phosphate was added into the deliming and bating effluents to remove NH₃-N, the TP concentrations of experimental tannery wastewaters slightly increased compared with the control one. This phenomenon occurred, because the TP concentrations of deliming and bating effluents after MAP precipitation treatment were lower than 7 mg/L. Moreover, the volume ratio of deliming and bating effluents to tannery wastewater was as small as 1:24. The sharp decrease in the initial TN concentration and the slight increase in the initial TP concentration of tannery wastewater caused by the MAP precipitation treatment of deliming and bating effluents improved the C: N: P ratio of tannery wastewater and should be beneficial to the biological treatment.

The simulated tannery wastewaters were subsequently treated with activated sludge to evaluate the performance of aerobic biological

Table III
Concentrations of NH₃-N, TOC, TN, and TP in simulated tannery wastewater before and after aerobic biological treatment

Simulated tannery wastewater		NH ₃ -N(mg/L)	TOC (mg/L)	TN (mg/L)	TP (mg/L)
Before treatment	Control	102.3±4.8	851.1±13.7	260.3±14.8	5.9±0.2
	Experiment 1	59.7±1.8	777.6±25.7	181.5±13.2	6.3±0.3
	Experiment 2	43.7±1.3	705.2±19.9	144.9±6.7	7.0±0.3
After treatment	Control	35.9±4.3	152.9±5.4	130.9±8.5	0.4±0.1
	Experiment 1	2.0±0.2	164.6±6.2	74.6±6.2	0.5±0.1
	Experiment 2	1.5±0.1	177.7±8.0	64.9±5.7	0.8±0.1

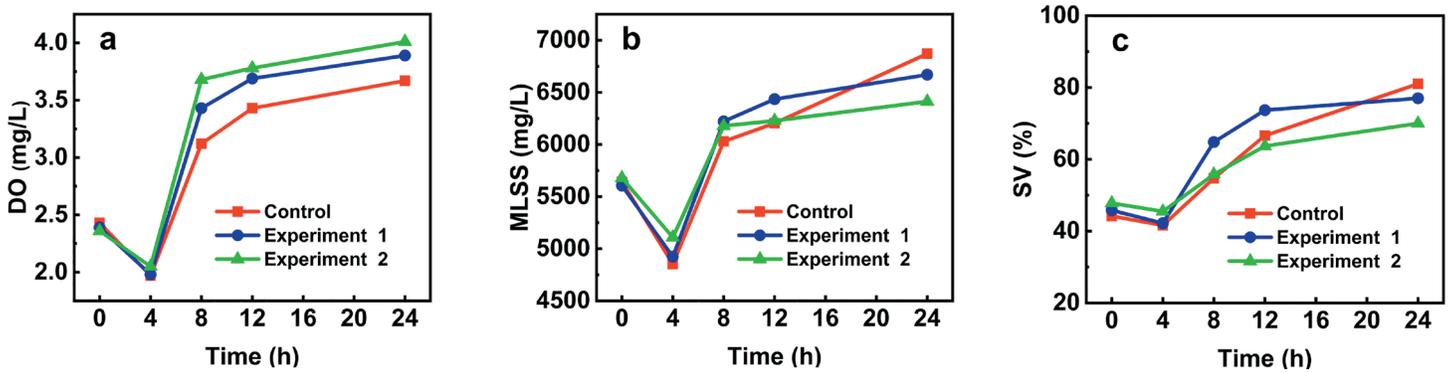


Figure 3. DO (a), MLSS (b) and SV (c) of activated sludge during aerobic biological treatment

treatment. During the treatment process, the DO, MLSS and SV concentrations were within normal ranges (Figure 3), indicating that the aerobic microorganisms in activated sludge grew well after cultivation and domestication.³⁹⁻⁴¹ The concentrations of $\text{NH}_3\text{-N}$ in the two experimental tannery wastewaters decreased to less than 25 mg/L within 8 h, and reached a very low level (below 2 mg/L) after treatment for 24 h, whereas the $\text{NH}_3\text{-N}$ concentration of the control group was 35.9 mg/L after treatment for 24 h (Fig. 4a and Table III). The TOC concentrations of the three tannery wastewaters decreased to 150–180 mg/L after treatment for 24 h (Fig. 4b). The residual TN concentrations of experimental groups after aerobic biological treatment were close to half of the control one (Fig. 4c). The low TN concentrations of experimental tannery wastewaters after aerobic biological treatment are helpful for the subsequent anaerobic

denitrification of tannery wastewater and complete and rapid TN removal.⁴² Figure 4(d) shows that although the initial concentrations of TP in experimental wastewaters were higher than the control group, they decreased more rapidly during treatment process. Additionally, the TP concentrations of experimental wastewaters were lower than 1 mg/L after treatment for 12 h, whereas the control group required a longer time to reach this TP concentration.

Overall, the aerobic biological treatment effects of the two experimental tannery wastewaters were better than that of the control group, because the MAP precipitation treatment of deliming and bating effluents decreased the initial $\text{NH}_3\text{-N}$ and TN concentrations of wastewater and improved the C:N ratio for biological treatment.

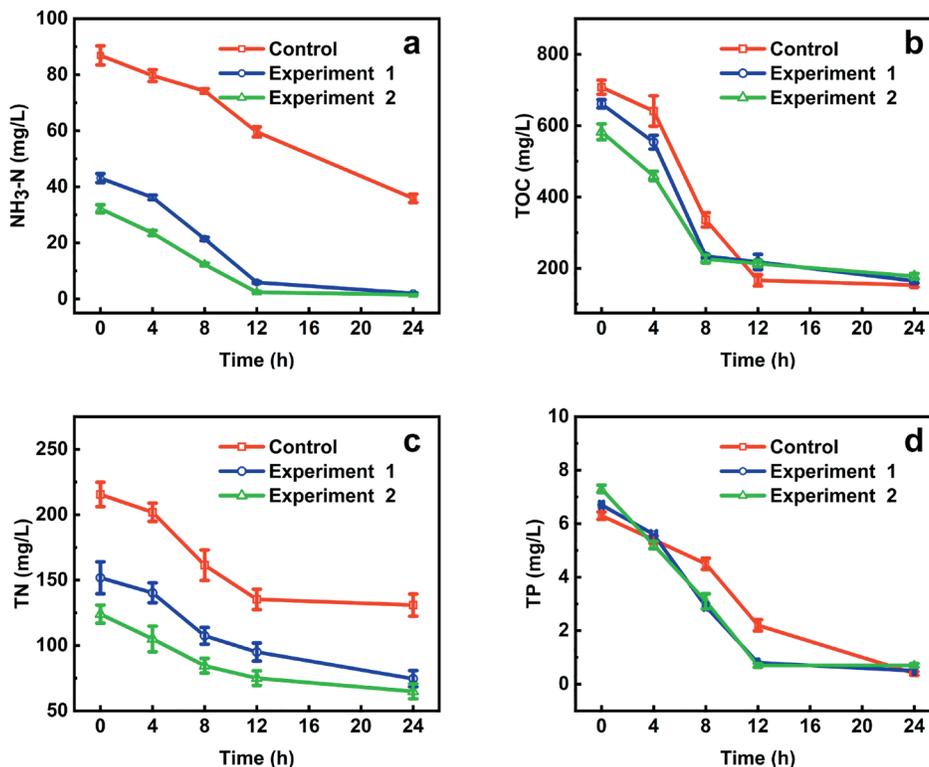


Figure 4. Effect of MAP precipitation method of deliming and bating effluents on aerobic biological treatment of simulated tannery wastewater: (a) $\text{NH}_3\text{-N}$ concentration; (b) TOC concentration; (c) TN concentration; and (d) TP concentration. Upon the addition of activated sludge, the initial $\text{NH}_3\text{-N}$, TOC, TN, and TP concentrations of simulated tannery wastewaters were slightly lower than the values shown in Table 3.

Conclusions

The MAP precipitation method is suitable for the treatment of delimiting and bating effluents with high concentration of NH₃-N and small volume. An efficient removal of NH₃-N from delimiting effluent and a low concentration of residual phosphorus in the treated delimiting effluent were obtained under the optimized experimental condition. The sharp decrease in the NH₃-N concentration of delimiting and bating effluents dramatically reduced the NH₃-N and TN concentrations of tannery wastewater and remarkably improved the C:N:P ratio of tannery wastewater and the efficiency of biological treatment. Therefore, the MAP precipitation treatment of delimiting and bating effluents can effectively remove NH₃-N from tannery wastewater without introducing secondary pollution of phosphorus. This work provides new insights into the efficient removal of NH₃-N and TN from tannery wastewater.

Acknowledgements

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