

NON-AMMONIA DELIMING USING SODIUM HEXAMETAPHOSPHATE AND BORIC ACID

by

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ABSTRACT

The use of ammonium salt in the deliming process is the primary reason for high ammonia nitrogen content in tannery wastewater. To reduce ammonia nitrogen pollution, a composite of sodium hexametaphosphate (SHMP) and boric acid (BA) was employed for non-ammonia deliming. The synergistic effect of SHMP and BA on deliming of limed cattle hide was investigated by analyzing the pH of deliming liquor, the extent of removal of calcium in pelt and the concentration of total nitrogen (TN) in the effluent. The experimental results indicated that the lowest pH of float during SHMP and BA deliming process was 7.08 and the concentration of hydroxyproline in the deliming liquor was lower than that of ammonia sulfate deliming, which suggest that deliming by SHMP and BA can reduce the damage of pelts. The extent of calcium removal from pelts delimed by using 3% SHMP and 1% BA was comparable to that of the pelts delimed with 3.5% ammonium sulfate. FESEM images and EDS analysis indicated that the deliming by SHMP and BA produced clearer grain with less calcium salts. Compared with ammonium sulfate deliming, TN concentration in SHMP and BA deliming float was reduced by 85%.

RESUMEN

El uso de la sal de amonio en el proceso de desencalado es la razón principal de alto contenido de nitrógeno amoniacal en las aguas residuales de curtiembres. Para reducir la contaminación del nitrógeno amoniacal, un compuesto de hexametafosfato de sodio (SHMP) y ácido bórico (BA) se utilizó para desprender el calcio sin amoníaco. El efecto sinérgico de SHMP y BA en el desencalado de cueros vacunos encalados fue investigado analizando el pH del licor de desencalado, la medida de remoción de calcio en la piel y la concentración de nitrógeno total (NT) en el efluente. Los resultados experimentales indican que el pH más bajo de la flota durante el proceso de desencalado con SHMP y BA fue 7.08 y la concentración de hidroxiprolina en el licor de desencalado fue menor que la del desencalado con sulfato de amoníaco, lo que sugiere que el desencalado con SHMP y BA puede reducir el daño de las pieles. El grado de remoción de calcio a partir de pieles desencaladas utilizando 3% de SHMP y 1% de BA fue comparable a la de las pieles desencaladas con 3.5% de sulfato de amonio. Imágenes FE-SEM y análisis EDS indicaron que el desencalado con SHMP y BA produjo una flor más clara con menos sales de calcio. En comparación con el desencalado con sulfato de amonio, la concentración de NT en la flota del desencalado con SHMP y BA se redujo en un 85%.

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Manuscript receive January 14, 2011, accepted for publication March 25, 2011.

INTRODUCTION

Excessive discharge of ammonia nitrogen from wastewaters results in eutrophication of lakes, rivers and coastal waters and depletion of dissolved oxygen in receiving waters.¹ Therefore, the tannery wastewater that usually has high ammonia nitrogen content, needs to be treated by biological methods comprising nitrification/denitrification to remove ammonia nitrogen before discharge. To achieve effective removal of COD and ammonia nitrogen in wastewater by biological treatment, the ratio of C:N:P in wastewater should be approximately 100:5:1 for aerobic treatment and 250:5:1 for anaerobic treatment.² So the biological treatment of tannery wastewater containing high ammonia nitrogen content needs an external carbon source to meet the proper carbon/nitrogen ratio in the wastewater, which increases treatment costs.³ In fact, with the high ammonia nitrogen concentration in the effluent, it is usually difficult to meet the discharge standard even after biological treatment. So the reduction or elimination of ammonia nitrogen in production processes is undoubtedly an effective approach from the viewpoints of economic and environmental considerations.

As we know, the ammonium salt used in delimiting process is the main source of ammonia nitrogen in tannery wastewater. Thus, non-ammonia delimiting technology is an effective way to reduce ammonia nitrogen pollution.⁴ Many non-ammonia delimiting approaches have been reported, such as CO₂ delimiting, magnesium salts delimiting, and weak acids delimiting.⁴⁻⁸ These technologies can significantly reduce ammonia nitrogen content in tannery wastewater. But some disadvantages of these technologies have restricted their practical application. For example, CO₂ delimiting needs special equipment and only suits limed split. The delimiting with formic acid, citric acid or lactic acid may lead to acid swelling of pelts because these acids can create localized areas of low pH, especially when they are added in excess.⁵ Sodium hexametaphosphate (SHMP) is widely used in water treatment, food industry, beneficiation industry, etc. It has an excellent ability to chelate alkaline earth metals such as calcium and magnesium.⁹⁻¹³ Thus, it is reasonable to hypothesize that SHMP can be used for delimiting and a high extent of calcium removal can be expected. It was found in our preliminary experiment that the pH of 1% (w/w) aqueous solution of SHMP is about 5.6, which is very suitable for the delimiting process. On the other hand, boric acid (BA) can act as a buffering agent in delimiting liquor in the pH range of 8-9 and can penetrate into pelts very quickly.^{8, 14} Therefore we suppose that delimiting with both SHMP and BA can avoid acid swelling of pelts and other problems that may arise. In addition, SHMP can act as a source of nutritive element phosphorus for the biological treatment of wastewater. It can be inferred that the introduction of phosphorus will benefit the biological treatment.²

In this study, the composite of SHMP and BA was employed as a delimiting agent. The pH of delimiting liquor, the extent of removal of calcium in pelt and the concentrations of hydroxyproline (Hyp), total nitrogen (TN) and total organic carbon (TOC) in delimiting effluent were analyzed and compared with those of conventional delimiting using ammonium sulfate.

EXPERIMENTAL METHODS

Materials

Limed cattle hide with the thickness of 4.0 mm was produced by conventional soaking, unhairing and liming processes and was used for the delimiting trials. All the chemicals used for the conventional processes were of commercial grade. SHMP ((NaPO₃)₆) and BA (H₃BO₃) used for delimiting, and the chemicals used for the analyses of delimiting effluents and delimited pelts were of analytical grade.

Delimiting Processes

The limed pelt was washed and divided into four groups numbered as shown in Figure 1. Each group includes four pieces of limed pelt taken from neck, back, belly and butt areas respectively. Delimiting was performed in the solution of X% delimiting agent (X represents amount of delimiting agent, as listed in Table I), 0.2% nonionic degreasing agent and 150% water at 32°C for 2 h. After delimiting, the pelts of groups 1 and 3 were bated, pickled and chrome tanned according to the conventional procedures. In addition, the pilot experiments for the delimiting of five split cattle hides (thickness 2.0 mm) and ten goat skins were performed by using the non-ammonia delimiting method in the same procedures as above.

Analyses of Effluents and Pelts

The liming pH (pH=13.31) was recorded as the initial pH of delimiting liquor, and pHs of both control and experimental delimiting liquors were measured by precise acidometer at 5, 10, 20, 40, 60, 90 and 120 minutes during delimiting process.

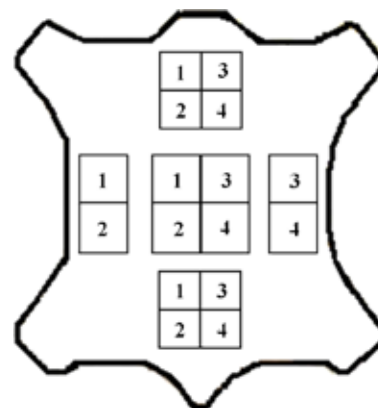


Figure 1. Sampling of limed cattle hide for delimiting trials

After delimiting, the concentrations of Hyp, TN and TOC in delimiting effluents were analyzed. The back pieces of groups 1 and 3 were used for determining the extent of calcium removal. The back pieces of groups 2 and 4 were split to obtain grain layers with thickness of 0.6 mm, and the residual calcium content in the grain layers was analyzed. After freeze-drying, the grain of delimited pelts was observed by Field Emission Scanning Electron Microscope (FESEM, S-4800, Hitachi, Japan), and the elements on the grain surface were investigated by using Energy Dispersive X-ray Spectroscopy (EDS, IE 250, Oxford, UK). After chrome tanning, the shrinkage temperature (Ts) of leather products was measured by using a shrinkage temperature recording instrument. Then the chrome tanned leather products were piled for 24 h and their chromium contents were analyzed.

Estimation Methods

Determination of Hyp concentration

Delimiting liquors were filtered by using 100 mesh filter cloth, and their Hyp concentrations were determined by the method described in literature.¹⁵

Determination of TN and TOC concentrations

Delimiting liquors were centrifuged at 8000 RPM for 10 min. The supernatant liquors were taken for the measurement of TN and TOC concentrations by using TOC / TN analyzer (LiquiTOC, Elementar, Germany).

Determination of calcium content and extent of calcium removal¹⁶

8 g of limed pelt or delimited pelt was dried to constant weight (Wc) at 102°C. The dried sample was calcined at 700°C for 8 h in a muffle furnace. The ash obtained from the dry sample was successively mixed with 2 mol/L HNO₃ (20% of ash weight). The mixture was heated at 110°C for 5 h and then filtered. The concentration of calcium in the filtrate was determined by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100DV, PerkinElmer, USA). The calcium content and extent of calcium removal were calculated as:

$$\text{calcium content} = \frac{\text{weight of calcium in pelt}}{W_c} \times 100\%$$

$$\text{extent of calcium removal} = \frac{\text{calcium content of limed pelt} - \text{calcium content of delimited pelt}}{\text{calcium content of limed pelt}} \times 100\%$$

Determination of chromium content

150 mg of chrome tanned leather was digested with 5 mL of 65% HNO₃ and 1 mL of 30% H₂O₂ by using microwave digestion system (MDS-8, Sineo, China) according to the following program: step 1 – 120°C for 10 min; step 2 – 150°C for 10 min; step 3 – 180°C for 10 min; step 4 – 200°C for 10

TABLE I
The delimiting agents used for delimiting^{a, b}

Number of group	Offer of delimiting agent
1 and 2 (control trials)	3.5% ammonium sulfate
3 and 4 (experimental trials)	3% SHMP and 1% BA

a - Percentage is based on weight of limed pelt.

b - The offer of delimiting agent is the optimized amount according to our preliminary trials.

min. Then the digestion mixture was filtered and the concentration of chromium in filtrate was determined by using ICP-AES. The moisture content of chrome leather was initially analyzed and the chromium content was calculated as:

$$\text{chromium content} = \frac{\text{Cr}_2\text{O}_3 \text{ weight in chrome leather}}{\text{dry weight of chrome leather}} \times 100\%$$

RESULTS AND DISCUSSION

pH of Delimiting Liquors

One of the purposes of delimiting is to decrease the pH of limed pelt from 12-13 to around 8 so that bating process can be properly performed. But the acid swelling of pelts and the production of toxic hydrogen sulfide may occur if the pH of delimiting liquor is excessively decreased.⁵ So delimiting agents are usually required to have a buffer action to control delimiting pH in a suitable range. In general, the desired pH range of delimiting is 7-9. In this study, the effect of SHMP and BA composite on the delimiting pH was first investigated.

The pH variations of both control and experimental delimiting liquors are shown in Figure 2. The lowest pH was 7.08 at 5 min during experimental delimiting process, showing that the

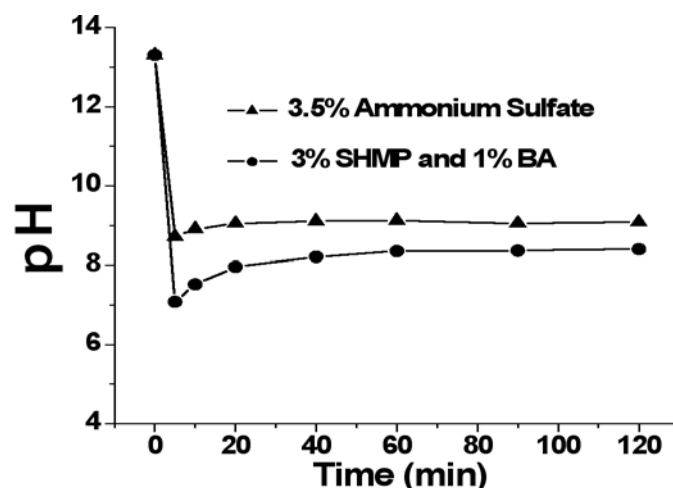


Figure 2. Variations of pH of delimiting liquors in delimiting process

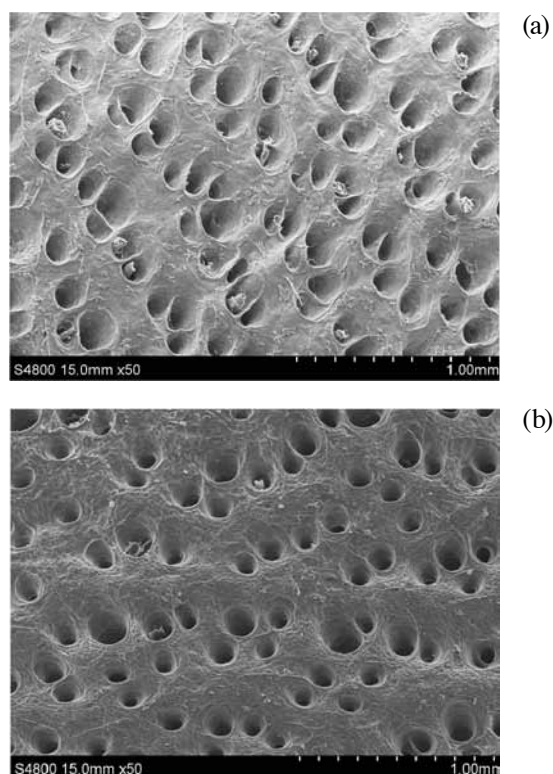


Figure 3. Grains of delimed pelts observed by FESEM at a magnification of 50: (a) delimiting with ammonium sulfate; (b) delimiting with SHMP and BA.

reduction in pH by using SHMP and BA is more moderate than those using formic acid, lactic acid, and CO_2 .⁵ The desired pH of 8.0 was reached in 20 min and an equilibrium pH of about 8.4 was attained in almost 40 min. These phenomena imply that SHMP and BA are prone to form a buffering system with the alkali in limed pelts. The equilibrium pH of experimental delimiting liquor was lower than that of control delimiting liquor (about 9.1), but was kept at a pH higher than 7.0. Therefore, the acid swelling did not occur. As shown in the FESEM photos (Figure 3a and 3b), hair pores of both the control and experimental delimed pelts were visible and clear, which indicates that SHMP and BA did not damage the grain because of its comparable buffering action to ammonium sulfate. The concentrations of Hyp in

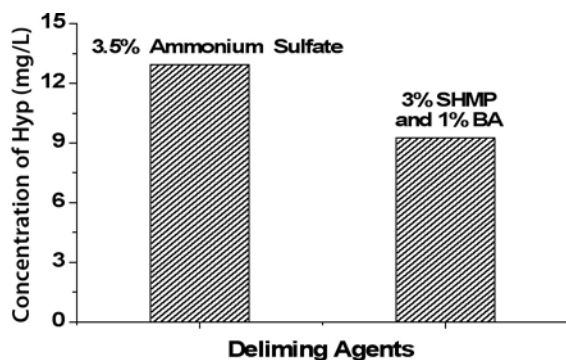


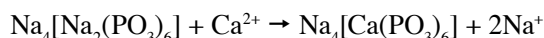
Figure 4. Concentration of Hyp in delimiting liquors

control and experimental delimiting liquors are shown in Figure 4. It was found that the concentration of Hyp in experimental delimiting liquor was lower than that in control delimiting liquor, which suggests that SHMP and BA lead to less collagen damage compared with ammonium sulfate.

Extent of Calcium Removal from Pelts

Surplus calcium salts remaining in delimed pelts have a negative effect on leather quality, such as uneven reaction with dyes and fatliquors in tanned hides. Furthermore, a large number of calcium salts precipitated in pelts or on the surface would result in “cracked grain” and poor strength.¹⁷ So the extent of calcium removal from pelt is a key parameter to evaluate the property of a delimiting agent.

As shown in Figure 5, the extent of calcium removal from pelts delimed by using 3% SHMP and 1% BA was comparable to that using 3.5% ammonium sulfate, indicating that delimiting with SHMP and BA can meet the requirement of calcium removal. The magnified FESEM photos of grains of both control and experimental delimed pelts are given in Figure 6 and 7. It can be observed that many particles were deposited on the grain surface of control delimed pelt (Figure 6), while the surface of experimental delimed pelt was very clean (Figure 7). Furthermore, EDS analysis indicated that calcium, carbon, oxygen and sulfur were all present on the grain surface of control delimed pelt (Figure 6), while only carbon and oxygen were present in the experimental delimed sample (Figure 7). These facts indicated that the particles on surface of control delimed pelt were precipitate of calcium salts. As shown in Figure 8, the calcium content of grain layer of experimental delimed pelts was 35 percent less than that of control delimed pelt. These results suggest that the composite of SHMP and BA has a stronger action for removing calcium in grain layer and therefore, could effectively eliminate defects of lime blast and uneven dyeing and fatliquoring. The strong action of SHMP on removing calcium could be due to the fact that SHMP can form water-soluble complexes with Ca^{2+} because of its pronounced chelating ability. The reaction between SHMP and calcium is shown below:¹⁸



The chromium content and Ts of the experimental chrome tanned leather were nearly the same as those of the control (Table II). This means that delimiting with SHMP and BA will not obviously affect the chrome tanning.

The total residual calcium content in experimental delimed pelt was almost the same as that in the control delimed pelt (Figure 5). However, the residual calcium content of experimental grain layer was remarkably less than that of the control, as shown in Figure 8. Hence the residual calcium content in the middle layer of experimental delimed pelt

should be higher than that of the control. This may be due to the fact that the molecular size of SHMP is larger than ammonium sulfate and therefore, SHMP has a slower penetration rate in pelt. Thus, the splitting of limed pelt should be performed if SHMP and BA composite was employed as delimiting agent. In the pilot experiments, it was observed that the composite of SHMP and BA was very effective for delimiting of goatskins and split cattle hides.

TN and TOC in Delimiting Effluents

In this study, ammonium sulfate was replaced by SHMP and BA for the purpose of reduction or elimination of ammonia nitrogen in tannery effluent. The concentrations of TN and TOC in both control and experimental delimiting effluents are shown in Figure 9. The concentration of TN in ammonium sulfate delimiting effluent was 3238 mg/L, while it was greatly reduced to 492 mg/L in experimental effluent. This means that TN was reduced by about 85% when ammonium sulfate was replaced by SHMP and BA. The nitrogen in non-ammonia delimiting effluent is most likely produced by the degradation of proteins in pelt. At the same time, the unpleasant ammonia odor was eliminated by using SHMP and BA as delimiting agents. Furthermore, the concentration of TOC in experimental delimiting wastewater was lower than that in ammonium sulfate delimiting wastewater, and the C/N ratio was significantly increased.

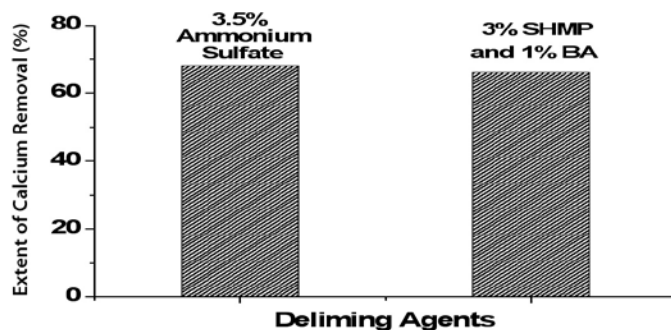


Figure 5. Extent of calcium removal from delimited pelts

TABLE II
Chromium content and Ts of chrome tanned leathers using control and experimental delimiting processes

Samples	Cr ₂ O ₃ content (%)	Ts (°C)
Control	7.26	107
Experimental	7.19	105

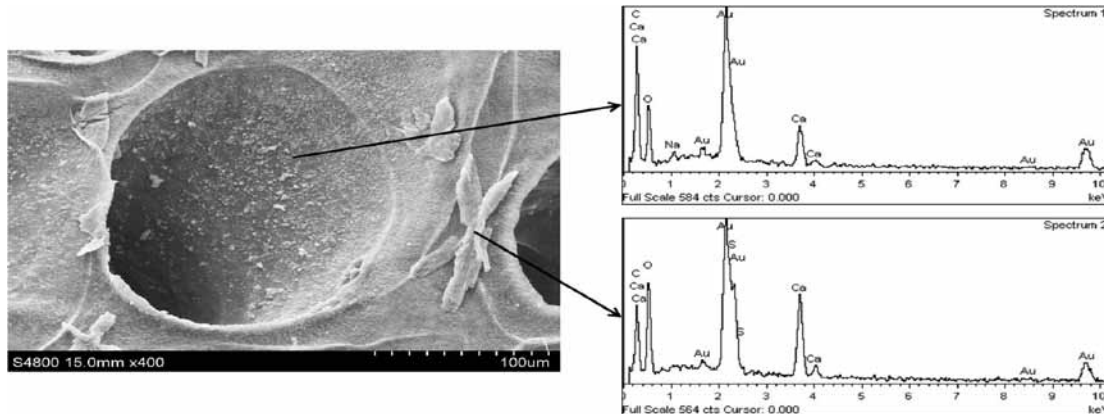


Figure 6. Grain of ammonium sulfate delimited pelt observed by FESEM at a magnification of 400 and element distribution maps of surface obtained by EDS

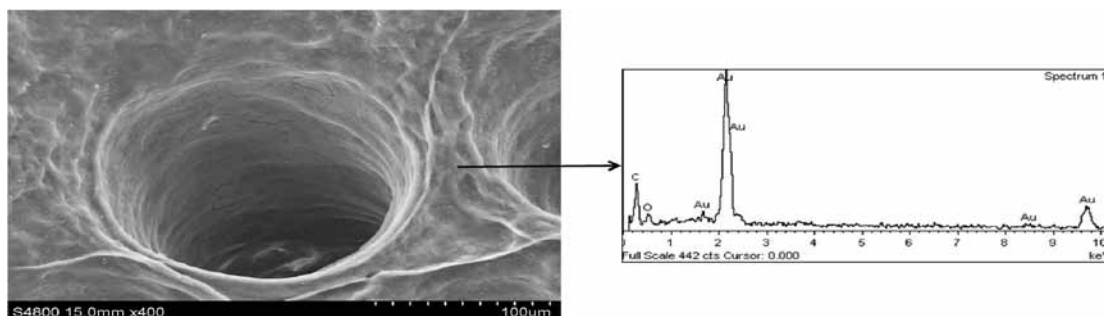


Figure 7. Grain of SHMP and BA delimited pelt observed by FESEM at a magnification of 400 and element distribution map of surface obtained by EDS

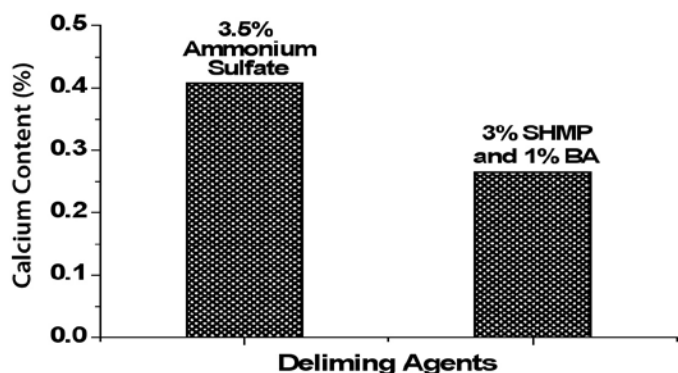


Figure 8. Calcium content in grain layer of delimed pelts

The use of SHMP seems to lead to phosphorus pollution. But, as we know, the deliming wastewater will be mixed with the wastewaters from other leather-making processes before biological treatment. It was estimated that the ratio of N:P in total wastewater would be approximately 5:1 when SHMP is used, which is suitable for the biological treatment. To effectively remove COD and ammonia nitrogen from wastewaters by biological treatment, it was recognized that the ratio of C:N:P in wastewater should be approximately 100:5:1 for aerobic treatment and 250:5:1 for anaerobic treatment.² Therefore, the phosphorus mixed into total wastewater could act as a source of nutritive element that increases the effectiveness of biological treatment of total wastewater, and theoretically, phosphorus itself will be consumed during the biological treatment. But this speculation, as well as the practical content of phosphorus in wastewater and in the discharged effluent, needs to be further investigated.

CONCLUSIONS

As a deliming agent, the composite of SHMP and BA has satisfactory buffering action. It can maintain the pH of deliming liquor in the pH range of 8~8.5 and thus prevent pelts from the risk of encountering acid shock. SHMP is effective in removing calcium salts from the limed pelts because of its good chelating ability with calcium. Deliming by SHMP and BA can greatly reduce TN concentration in deliming float, and thus increase C/N ratio of tannery wastewater. Meanwhile, the use of SHMP will introduce phosphorus into wastewater. Theoretically, as a kind of necessary nutrient, the introduction of phosphorus would favor the biological treatment of total wastewater. But the consumption of phosphorus during the biological treatment and the residue of phosphorus in the discharged effluent need to be further investigated.

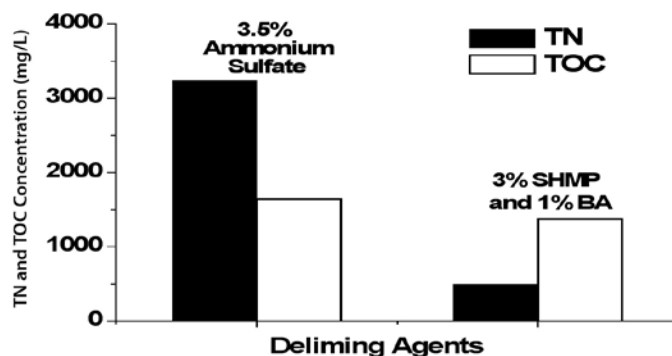


Figure 9. TN and TOC concentrations in deliming effluents

ACKNOWLEDGEMENT

This work was supported by the Key Program of Haining, Zhejiang Province (2010132) and the National High Technologies R&D Program (2011BAC06B11).

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