Investigation on the distribution of COD and nitrogen emissions during cattlehide leather-making process

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Abstract: The pollutants, mainly COD and nitrogen (including organic nitrogen and ammonia nitrogen), distributed in soaking, unhairing, deliming, tanning, finishing sections during cattlehide leather-making process, were evaluated. The results showed that COD and organic nitrogen discharge were much higher than that of ammonia nitrogen in a single section. The preparation phase was the major pollutant-generated one, with a percentage beyond 85%, resulting from unhairing, and deliming sections. The experimental results were closely related with the actual production in the tannery.

Keywords: cattlehide leather-making; COD; organic nitrogen; ammonia nitrogen; discharge; distribution

1 Introduction

A great many operations will be needed for raw cattlehide to be leather, such as soaking, liming, unhairing, deliming, bating, pickling, tanning, finishing, etc. It not only makes massive solid wastes that can be collected, but also produces plenty of wastewater which may contain splits and shavings. Some of those splits can be removed by the grid, others may enter into the biological treatment phase.

The research is attempted to test various effluents from different sections during the leather-making process, and to determine the specific distribution of COD and nitrogen, getting a general idea about the characteristics of the wastewater.

2 Experimental section

2.1 Materials

Effluents from various sections were collected in a tannery in Binzhou, Shandong Province. All the chemicals used were for analysis.

2.2 Experimental preparation

Five sections were selected according to the actual situation in the tannery in this experiment: soaking, unhairing, deliming, tanning, finishing. The first three were involved in the preparation phase, and tanning in the tanning phase, while finishing in the finishing phase. The water samples were collected when an operation was finished, during the wastewater discharging. Table I showed the specific unit operations and the section wastewater emissions.

Table I Section selection and wastewater emissions in each section

Phase	Section	Unit operations
Prepareation Phase	Soaking	Pre-soaking
	Unhairing	Liming
		Unhairing

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	Deliming	Washing
		Deliming
		Bating
		Washing
Tanning Phase	Tanning	Pickling & tanning
Finishing Phase	Finishing	Washing tightly closed and Rinsing
		Retanning & neutralization
		Washing with flowing water
		Filling
		Top dyeing
		Washing tightly closed

2.3 Analytical methods

Determine COD, ammonia nitrogen & organic nitrogen concentrations of the wastewater collected from each section. COD was measured with Dichromate method (GB 11914-89). Ammonia nitrogen was measured by Distillation and Filtration (GB 7478-87). Organic nitrogen was determined according to the Determination and Kjeldahl nitrogen (GB 11891-89) .

3 Results and discussion

3.1 Charateristics of water samples from different sections

The charateristics of water samples from different sections were shown in Table II.

Table II Charateristics of water samples from different sections

Section	COD (mg/L)	N-NH_4^+(mg/L)	Organic Nitrogen(mg/L)	Wastewater emissions (t)
Soaking	8177.56	182.26	2873.92	13.20
Unhairing	36914.64	529.60	18789.46	9.70
Deliming	5324.09	1101.11	6561.42	36.00
Tanning	2961.84	590.06	2565.42	4.00
Finishing	2911.27	177.63	1609.74	31.45

3.2 Pollutant distribution analysis

The pollutant emissions from different sections were shown in Figure 1. The distributions of pollutants in sections were shown in Figure 2.

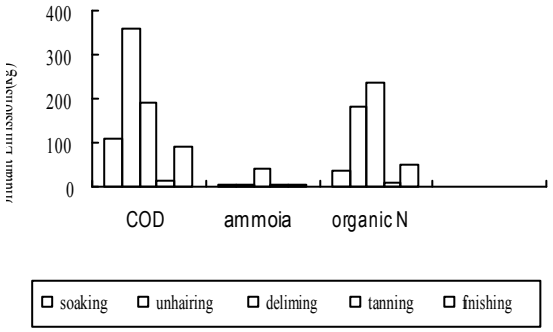

Figure1 Pollutant emissions from different sections

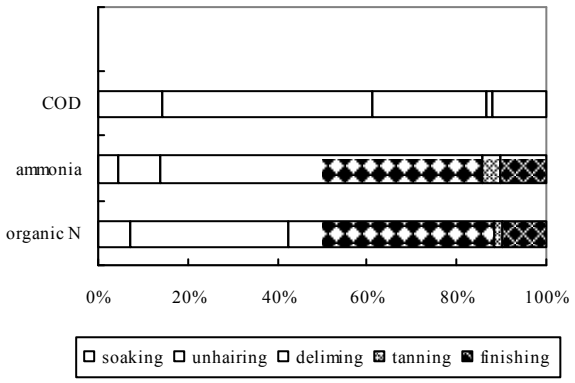

Figure 2 Distribution of pollutants in different sections

As shown in Figure 1, the ammonia nitrogen concentration was much lower than that of COD and organic nitrogen in each section. COD emissions were mainly from unhairing, deliming, soaking and finishing sections, while ammonia nitrogen from deliming, organic nitrogen from unhairing, and deliming.

As shown in Figure 2, the preparation phase generated the majority of the three pollutants, with a percentage beyond 85%, and the tanning phase about 5%, the finishing phase 10%~15%. During the preparation phase, the pollutants mainly came from unhairing, deliming sections, with a ratio of 70%~80%. The quantities of COD, ammonia nitrogen, and organic nitrogen from unhairing section were 358.22kg， 5.14kg， 182.33kg respectively, accounting for 47%, 9% and 35% of total COD, ammonia nitrogen, and organic nitrogen. As to deliming section, the pollutants were 191.67kg，39.64kg，236.21kg，and the ratio 25%, 72%, and 46% separately.

The experimental results were in accordance with the actual leather-making process in the tannery greatly.

Soaking wets back for the raw hide, as well as removes salts, blood, sewage, non-fibre proteins and proteoglycan for the following operations. The cattlehide was wet-salted, with less water lost, and pre-soaking was done in the intermittent rotating rotor for 4.1 h. Degreaants, soaking assistants were used in this section. The wastewater samples were collected after soaking, without consideration of fleshing, so the suspended solid in the effluents were mainly blood, sewage, etc. adhered to the surface of the hide. In fact, splits and little meat could be seen to settle down in the collected samples after a period of time, which resulting in high COD concentration (8177 mg/L), organic nitrogen concentration (2873 mg/L), and relatively low ammonia concentration (182 mg/L).

Liming and unhairing aims at unfolding fibrous tissues, getting rid of epidermis and hairs. The fibrous tissues were interspersed by structural destension, and with the further effect of alkaline, the S-S bonds in the epidermis and hairs were decomposed, converting into pulp, which caused the high pollution of COD and organic nitrogen. The cattlehide was treated by sodium sulfide unhairing in the tannery, so there were lots of hairs discharged into the effluents, and the COD and organic nitrogen emissions during this section reached half of total pollutants.

Deliming is a process to adjust pH to the required extent for dating, balancing the alkaline, lime, and sodium hydrate from the liming operation, generally by deliming agents, such as ammonium sulfate or chloride. Enzyme was added during bating operation to get rid of some dirts, including hair root, pigment, and other unnecessary protein residues. In this tannery, ammonium sulfate was introduced not only during deliming process, but also bating, which made high ammonia concentration in the effluent, much higher than other four sections, with the ammonia emission percentage of 72%.

In tanning sections, chromium powder was used for tanning after pH adjustment by formic acid and sulfuric acid, and the hide was converted to leather by tanning agents crosslinking with skin collogen. The agents used could not be completely adsorpted, leaving some pollutants in effluents, less than the other sections and the rate was below 10%.

The finishing section includes retanning, filling, top dyeing, etc. Chromium powder, sodium formate, baking soda were used for retanning, grease, acrylic acid, filling agents, dyes, protein for filling, and dyes, formic acid, grease for the top dyeing operation. Thus dyes, grease, organic acid, etc. were the main pollutant in the effluents for this section. The chemical materials could not be fully adsorpted, and the rest would be pollutants in the wastewater. Besides, there were relatively many unit operations, consuming more water, so the percentage of pollutants was about 15%.

To solve the pollution during leather-making process, researchers have investigated on the cleaner production for the industry, and have developed some practical technologies. The implementation of cleaner production, on the one hand reduce the use of raw materials and chemical agents, lowering production cost, on the other, decrease the pollutant emission, relieving pollution by leather-making industry. Based on the experimental results, cleaner production could be introduced in the liming and deliming sections. Take liming & unhairing section for example, the Xeno two-bath unhairing process could recycle unhairing effluent as well as hair recovery, decreasing COD emission by 15%~20%, total nitrogen (TN) 20%~30%; while unhairing by enzyme, reducing COD emission by 30%~60%, BOD 40%~70%, and eliminate sulfide pollution. As to deliming & bating, reduction in ammonium salt use or deliming by CO_2 would cut down or avoid ammonia pollution.

4 Conclusions

According to the experimental results, conclusions were drawn as follows,

(1) COD and organic nitrogen emissions were larger than that of ammonia nitrogen in various sections. The majority of COD discharge came from liming & unhairing, deliming & bating, soaking, and wet finishing sections, and the ammonia nitrogen from deliming & bating, while organic nitrogen from liming & unhairing, deliming & bating.

(2) The preparation phase was the dominant pollutant-production phase, with the pollutant emission percentage beyond 85%. The COD, ammonia and organic nitrogen emission percentages of liming section, were 47%, 9% and 35% respectively, and as to the deliming section, the corresponding ratios were 25%, 72% and 46%.

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