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SOME ASPECTS OF A TREATMENT OF THE WASTE WATER FROM THE BEAMHOUSE OPERATION IN TANNERY

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Abstract

Waste water from a tannery shows high pollution load which mainly arises from organic substance in a process of presoaking, soaking, liming and reliming. Acidification of the effluent from each process were separately carried out and clarification of the waste water mainly about elimination of pollution load due to organic substance was studied in comparison with disposal of the effluent by mixing and sedimentation. Composition of crude proteins recovered from the effluent by the acidification was also examined. Results are as follows: 1) In acidified effluent from each process separately, elimination rate of suspended solid (SS) was more than 90%, total nitrogen (TN) 38–92%, and chemical oxygen demand (COD) 44–86%. This elimination rate was so high in the effluent from liming process as follows; suspended solid 97%, TN 92% and COD 86%. 2) Pollution load could be reduced by mixing and sedimentation of effluents from each process, the elimination rate, however, was comparatively low as follows; SS 57%, TN 22%, and COD 25%. By acidifying the above effluent, SS 98%, TN 45% and COD 74% were observed. When the acidification was applied on each effluent from various process separately, elimination rate increased so high as follows; SS 92%, TN 49% and COD 77%. Also, recovery rate of protein was raised by the acidifying of effluent from each process separately, and was 14.1% to the quantity of skin and other organic substance used. 3) From the above results, it can be considered that elimination of organic pollution load in the effluent from beamhouse process could be carried out more effectively by acidifying effluent from each process separately. 4) Purity of the proteinous substance, estimated for the composition of amino acid contained in recovered proteinous substances, from presoaking and soaking processes were 30%, but from liming process was more than 60% and from reliming process was more than 50%.

Introduction

Normally, waste water from a tannery are mixed in one from various processes and settled before chemical and biological treatment being applied.

Effluent from beamhouse processes in a tannery shows considerably high pollution load and it is known that about 80% of pollution load with oxygen-consuming substances and nitrogen-containing materials in all effluents from a

tannery arises from soaking and liming.⁶⁾

Consequently, a considerable cost for treatment of effluent is expected as a quantitative pollution load can still be observed at the stage of chemical treatment which is also accompanied by the formation of large quantities of sludge.

In this study experiments were carried out on clarification of effluent by acidifying waste water from various processes separately, and by coagulating those proteinous substances dissolved from hides.

Comparison of acidification and mixing-sedi-

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mentation regarding clarification of effluent was also made mainly on reduction of chemical oxygen demand (COD), total nitrogen (TN) and organic substances.

Analysis of those coagulated crude proteinous substances were carried out on their properties and amino acid composition.

Materials and Methods

Raw hide used in this experiment is Holland wet salted kip skin (9.8 kg), and beamhouse processes were carried out by using testing drum (diameter 79 cm, width 51 cm, 16 rpm) as shown in Fig. 1.

Effluents from each processes were collected separately through 60 mesh screen, and then mixed-sedimentation and acidification were applied. Mixing-sedimentation were carried out by sampling a same quantity of effluent from each process separately, then combined and have sedimented by settling overnight.

Supernatant fluid and precipitates were separated by centrifugal separator (4,000 rpm, for 15 min).

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- Materials : Holland wet salted kip skins (9.8 kgs.)
 Presoaking : 500% water (16–18°C) (% based on salted weight) keep for an hour, run for 20 minutes and keep standing for 4 hours, then fleshing.
 Soaking : 500% water (16–18°C) (% based on fleshed weight), keep it for 16 hours.
 Liming (Lime-sulfide-unhairing) :
 500% water (25°C)
 1% sodium sulfide
 2% calcium hydroxide, run for 20 minutes and keep standing for 40 minutes.
 2% calcium hydroxide
 1% sodium sulfide
 1% sodium hydrosulfide, run for 20 minutes, keep standing for 60 minutes, run for 20 minutes, and steep in the bath for 2 days, with rotation 8 times a day for 10 minutes each.
 Reliming : (% based on limed weight)
 500% water
 2% calcium hydroxide, run for 10 minutes, keep it for 16 hours.
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Fig. 1. Outline of soaking and liming process

The effluents from various processes separately and mixed-settled fluid described above were slowly acidified to pH 4.2 with 3 N sulfuric acid solution. These experimental procedure were shown in Figs. 2 and 3. The pH value 4.2 was determined on the fact of effectiveness in eliminating COD and TN contained in lime-sulfide unhairing effluent which showed high pollution load at the time of preliminary experiments.

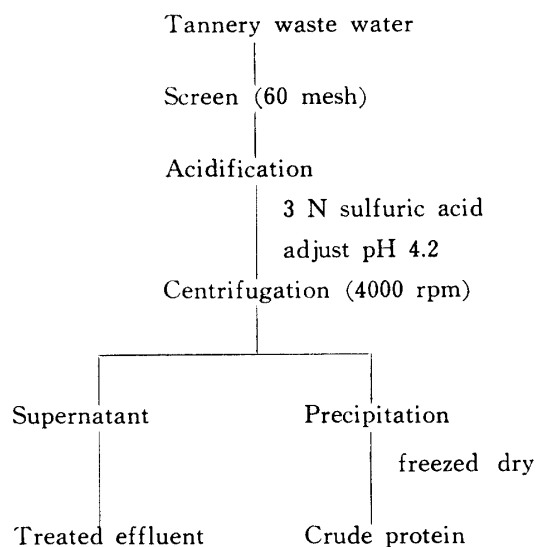


Fig. 2. Clarification of the effluents from each process by acidification

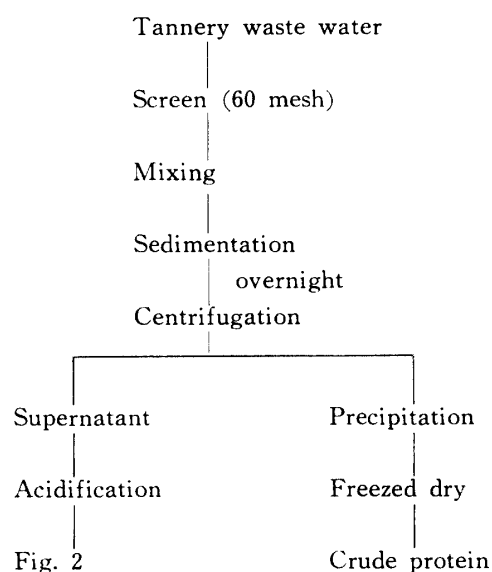


Fig. 3. Clarification of the effluents by mixing-sedimentation, and then acidification

Yields of protein and reduction of pollution load from lime-sulphide effluent were reported to be highest at pH 4.0 by BLAZEJ.¹⁾

These pH value agree with the optimum pH range 3.5–4.5 which was experimented on the recovery of the proteinous substances by NIWA,⁵⁾ van MEER,⁸⁾ HAPPICH,⁹⁾ and others.^{4,9)}

The coagulated proteinous substances and precipitates separated centrifugally were freeze-dried as recovery materials, and supernatant were collected as treated effluent.

Analysis of Effluent and Treated Effluents

The testing methods for industrial waste water in the Japanese Industrial Standard (JIS-K0102, 1974) were used for the determination of transparency, pH, total residue of evaporation (total solids), evaporation residue of soluble matters (soluble solids), residue of strong heating in total evaporation residue (total ash), strong heating loss in total evaporation residue (ignition loss), suspended solids (SS), total nitrogen (TN) and chemical oxygen demand (COD) by potassium bichromate method in effluents and treated effluents from beamhouse processes.

Analysis of Recovery Materials

Precipitate from effluent were freeze-dried immediately and moisture, total nitrogen, fat (ether extracts) and total ash were determined by the A. L. C. A. official method of the testing method for leathers.

Quantitative analysis of amino acid composition of the recovery protein was carried out by hydrolyzing in 6 N hydrochloric acid solution for 24 hrs, and measured with Hitachi KLM 3 B amino acid analyzer. And quantitative analysis of tryptophane was based on OKUYAMA's method.⁷⁾

Results and Discussion

Acidification of Effluents from Each Process of Beamhouse Operation

The composition of the effluent and the acidified effluent from each process, presoaking, soaking, liming, and reliming, and a quantity of acid used for acidification, and also the

efficiency of pollutant removal are shown in Table 1. In this effluent, no acid treatment was applied to the effluent from deliming and bating but only combined and settled. The effluent from various processes can be clarified to a certain degree by the acidification.

Transparency varies in each process, and in soaking and reliming showed depth of 30 cm. The elimination rate in total solids is low, and this can be observed also in total ash, and this is presumably effect of salt brought by hide in soaking, and of lime used in liming, also of sulfuric acid in acidification. The elimination rate in suspended solid by the acidification showed considerably high and in each process it showed more than 90%. The elimination rate in total igniter loss, presumably of organic substance, was high except the effluent from soaking, and was more than 51%. TN and COD also showed high elimination rate. The effect of the acidification on the effluent from various process, especially to lime-sulfide unhairing effluent showed remarkably high, and the elimination rate showed 97% of suspended solid, 72% of total igniter loss, 92% of total nitrogen and 86% of COD.

Comparison of the Effluents Mixed-Settled and Acidified with the Effluents Acidified at Each Process.

The load on the effluent mixed and settled and its load after acidified, the effluent load acidified at each process separately, and elimination rate of these load by settling and acidification to the total load are shown in Table 2. The effluent load from deliming and bating were measured separately and added in each study but these effluents were inclusively in the case of mixing-sedimentation.

Some clarification could be observed when the effluents were mixed and settled, then 57% of suspended solid and more than 20% of total nitrogen and COD were eliminated. But the above figures are far lower comparing with the effluent acidified at each process. Acidifying effluent mixed and settled, a prominent clarification was observed such as 98% of suspended solid, 35% total igniter loss presumably of organic substances, 45% of total nitrogen and 74% of COD.

Table 1. Acid treatment on effluent from each process (1)

		Presoaking			Soaking		
		Effluent	Acidified	Removal%	Effluent	Acidified	Removal%
Quantity, water used	l	49			46		
Quantity, waste water	l	43	43		44	44	
Quantity, acidified	ml		216			37	
Transparency	cm	1.5	5.0		1.4	30.0	
pH		7.60	4.19		7.00	4.22	
Total solids	mg/l	40.425	37.230		6.875	6.277	
	g	1.738	1.609	7	303	276	9
Evaporation residue	mg/l	37.087	36.980		6.394	6.237	
	g	1.595	1.598	—	281	274	—
Suspended solids	mg/l	3.338	248		481	40	
	g	144	11	92	22	2	91
Total ash	mg/l	34.773	34.463		5.034	4.928	
	g	1.495	1.489	—	221	217	—
Total ignite loss	mg/l	5.652	2.767		1.841	1.349	
	g	243	120	51	82	59	28
Total nitrogen	mg/l	466	263		180	108	
	g	20	11	45	8	5	38
COD	mg/l	10.794	3.052		2.679	1.050	
	g	464	132	72	117	66	44

Table1. 1. Acid treatment on effluent from each process (2)

		Liming			Reliming		
		Effluent	Acidified	Removal%	Effluent	Acidified	Removal%
Quantity, water used	l	46			45		
Quantity, waste water	l	44	44		43	43	
Quantity, acidified	ml		2.042			830	
Transparency	cm	0.4	3.6		0.7	30	
pH		12.65	4.18		11.92	4.21	
Total solids	mg/l	17.961	13.782		3.972	2.642	
	g	790	634	20	171	116	32
Evaporation residue	mg/l	12.578	13.652		2.790	2.630	
	g	553	629	—	120	115	—
Suspended solids	mg/l	5.383	130		1.182	12	
	g	237	6	97	51	1	98
Total ash	mg/l	9.358	11.490		2.517	2.280	
	g	412	529	—	108	100	—
Total ignite loss	mg/l	8.608	2.292		1.455	362	
	g	379	106	72	63	16	75
Total nitrogen	mg/l	1.417	117		94	23	
	g	62	5	92	4	1	75
COD	mg/l	14.659	1.903		1.287	332	
	g	645	88	86	55	15	73

Comparing this with the acidification at each process, the elimination rate on total solid and suspended solid are more prominent while the elimination rate on organic substance and total nitrogen are less.

This is presumably because of denaturation and reduction of a protein while ageing for mixing.

From the above results, when the effluent was mixed and settled, the clarification rate is

Table 2. Effect of acidification on the road of tannery effluents

		Effluent		Mixed/Settled		Acidified		Acidified on each process	
		Load		Load	Removal%	Load	Removal%	Load	Removal %
		A		B	$\frac{A-B}{A} \times 100$	C	$\frac{A-C}{A} \times 100$	D	$\frac{A-D}{A} \times 100$
Transparency	cm			1.0		19.8			
pH				9.22		4.20			
Total solids	mg/l	14.332		12.898		12.286			
	g	3.110		2.799	10	2.680	14	2.743	12
Evaporation residue	mg/l	12.143		11.966		12.246			
	g	2.635		2.597	—	2.671	—	2.709	—
Suspended solids	mg/l	2.189		932		40			
	g	475		202	57	9	98	42	92
Total ash	mg/l	10.618		9.610		9.824			
	g	2.304		2.085	—	2.143	—	2.403	—
Total ignite loss	mg/l	3.714		3.288		2.462			
	g	806		713	12	536	35	340	58
Total nitrogen	mg/l	682		532		378			
	g	148		115	22	82	45	76	49
COD	mg/l	6.756		5.066		1.763			
	g	1.466		1.099	25	384	74	338	77

Table 3. Amount and composition of recovered substances from effluent acidified

		Presoaking	Soaking	Liming	Reliming	Total	Mixed/Settled & Acidified
Quantity Recovered ¹⁾	g	123	23	273	47	466	270
Recovery Rate ²⁾	%	3.7	0.7	8.3	1.4	14.1	8.2
Moisture	%	3.1	5.3	5.6	9.2		5.8
Total nitrogen ³⁾	%	4.7	6.2	11.2	9.4		9.2
Total ash ³⁾	%	19.8	8.7	10.3	15.3		13.4
Total fat ³⁾	%	42.2	48.4	12.4	16.6		22.1
Purity of protein ⁴⁾	%	27.8	32.8	64.7	54.5		52.2

Weight of skin used : 9.8 kg, Moisture : 48.90%, Total ash : 17.47%, Organic substance : 33.63%.

1) Quantity recovery (g) = Ignite loss of effluent - Ignite loss of treated water.

2) Recovery rate (%) = Amount of recovery / Skin used $\times$ 100.

3) Moisture free basis.

4) Estimated from analysis of amino-acid composition.

comparatively low with 57% of the elimination rate of suspended solid while the pollution load is considerably high and suffering later treatments to be applied on the effluent. The acidification after mixed and settled can not compete with the solution applied separately on the effluent from each process on the effect of elimination except of suspended solid.

Consequently, the effluent from the beam-house process should be acidified on each process enabling other treatments more easily and effectively. At least, the acidification on the effluent from liming process which brings high elimination effects should be applied well in advance.

Composition of Crude Protein Recovered from Beamhouse Effluent

The quantity and the composition of the substance recovered from the effluent acidified at each process and from the effluent mixed-settled then acidified are listed in Table 3.

The amount of the substance recovered regarded as organic substance is shown in comparison

with the quantity of ignite loss of the effluent, while the recovery rate is shown at a ratio of a quantity recovered to the skin and other organic substance used. The quantity of organic substance recovered from the effluent acidified at each process was 466 gs. in total, and the recovery rate was 14.1% while 270 gs. and 8.2% were observed from the effluent mixed-settled then acidified.

From the above, it is more effective to acidify the effluent from each process separately. The protein purity of the substance recovered from the effluents from presoaking and soaking processes were more or less than 30%.

Total fat, however, was found more than 40% which was more than expected. It is estimated that these fat arise flocculation at the time of coagulating those proteinous substance during acidification. The recovery from the effluent from liming and reliming contained, on a moisture-free basis, more than 10 % of total nitrogen, more than 10% of total ash, and more than 12% of total fat, and high protein purity of more than 50% was observed. The composition of the substance recovered

from the effluent mixed, settled, and then acidified was similar to the average figure of those from acidified on each process separately, and the protein purity was almost 50 %. Amino acid composition of recovered substance from the effluent are shown in Table 4.

As shown in Table 4, the effluent from each process contained a considerable amount of Glu, Asp, Arg, Leu, Ser, and all of essential amino acids.

In comparison with whole egg protein,²⁾ ratio of contents of Val, Met, Ileu, and Phe are rather low, although Tyr has a nutritive substitution effect to Phe, and Cys has a same effect to Met.²⁾ Consequently, the recovery, containing those substitutes

Table 4. Amino acid composition of recovered substance from effluent

	Presoaking	Soaking	Liming	Reliming	Combined (M/S)
Lys	1.6	2.0	2.8	3.0	2.4
His	0.6	0.8	1.0	1.0	0.8
Arg	1.7	2.2	5.3	4.2	4.3
Asp	2.5	2.8	5.2	4.9	4.3
Thr	1.2	1.4	3.4	2.4	2.6
Ser	2.0	2.5	4.8	3.3	3.6
Glu	4.9	5.7	10.8	9.2	8.9
Pro	1.2	1.4	4.6	3.4	3.3
Gly	1.8	2.3	3.4	3.3	2.6
Ala	1.5	1.4	2.4	2.4	2.1
Cys	0.5	0.6	2.5	0.8	2.0
Val	1.3	1.5	3.1	2.7	2.5
Met	0.7	0.6	0.8	1.0	0.8
Ileu	1.2	1.4	2.4	2.2	2.0
Leu	2.1	2.5	5.2	4.7	4.3
Tyr	1.2	1.5	3.5	2.6	2.8
Phe	1.2	1.4	2.4	2.4	2.0
Trp	0.6	0.8	1.1	1.0	0.9
Total	27.8	32.8	64.7	54.5	52.2

Weight %—Moisture free basis.

are irrespective of quantities, can possibly be used as an ingredient of cattle and poultry feeds.

The amino acid composition of the substance recovered from the effluent combined, settled, then acidified were similar, and being considered to be effective as well.

From the above results, and in our continuous studies for future, it is considerable that once the purity of proteinous substance could be refined and recovered eliminating mixture of salts as well as other impurities, they could possibly be utilized as cattle and poultry feeds.

In order to recover such useful substances from the effluent, it is more effective to apply the acid treatment on the effluent from each process of beamhouse operation separately.

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皮革準備工程の排水処理に関する一知見

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要 約

皮革製造における準備工程の排水中で、有機物による汚染度の高い予備水漬、本水漬、脱毛石灰漬と再石灰漬の各排水を酸性化処理して、水質の浄化の程度を主に有機物による汚濁負荷の除去効果から、各排水の混合・沈降処理と比較検討した。また酸性化処理により回収された粗蛋白質の性状を調べた。その結果は次の通りである。

1) 準備作業の各工程別排水の酸性化処理によるSSの除去率は90%以上であり、TNで38~92%、CODで44~86%であり、特に脱毛石灰漬排水における除去率が高く、SSで97%、TNで92%、CODで86%であった。

2) 準備工程の各排水は混合・沈降処理により、汚濁負荷は削減されるが、主なものの除去率はSSで57%、TNで22%、CODで25%に過ぎない。さらにこの排水を酸性化することによりSS98%、TN45%、COD74%とそれぞれ除去率が高くなる。しかし、各工程別に酸性化処理をするとSS92%、TN49%、COD77%と除去率はさらに高くなる。また蛋白質の回収率も工程別に排水を酸性化する方が高くなり、原料皮有機物を基準として14.1%であった。

3) 以上の結果から、製革排水の有機汚濁負荷の削減は、工程別に個々の排水を酸性化処理した方が効果的であろうと考えられる。

4) 回収蛋白質のアミノ酸組成より推定した蛋白質純度は、予備水漬と本水漬排水からのもので30%前後であるが、脱毛石灰漬で60%以上、再石灰漬で50%以上であった。