

REDUCTION OF WATER DEMAND AND TREATMENT COST IN TANNERIES THROUGH REUSE TECHNIQUE*

by

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ABSTRACT

Tannery industries employ great amounts of water; because most of their processes occur in an aqueous medium. This leads to the generation of high wastewater flowrates which will have to be treated due to the relatively high concentrations of some pollutant species. The attending paper presents this problematic throughout a case study in *Rio Grande do Sul*, state of *Brazil*. It establishes the water consumption in each stage of leather processing. In order to achieve the reduction in the total water consumption, herein it is proposed the water reuse technique in some stages of the process. Experimental results, on industrial scale, are shown so that the methodology is demonstrated to be successful. Water reuse reduces the load of the wastewater treatment plant as well as it reduces the costs.

Research on water demand in tanneries defines water consumption for each stage: beamhouse, tanning and pos-tanning operations. It is known that tanneries make use of water in an uncontrolled manner, usually higher than actually would be necessary. Additional, most of the stages use fresh waters from artesian wells or from rivers. Recycling technique is current in liming operation. This paper shows that reuse and recycle techniques could be applied for other operations.

Alternatives of water reuse were evaluated through the analysis of the process's wastewater to estimate the concentration of some contaminant parameters. The study was carried out on industrial scale. These parameters are indicators to evaluate the water quality according with the objectives of the reuse system.

During analysis, it was tested reuse in the pre-delimiting and delimiting stages, using 100% of the effluent from bating washing. The parameters analyzed in the process's wastewater with reuse practice did not present any considerable difference when one compared with the conventional process. It demonstrates the viability of reuse practice in tannery industry.

This study is of great importance to the environmental and to tannery industry, because the reuse technology aims at a solution to water minimization that results in the maximum environmental protection and cost reduction.

RESUMEN

Industrias de curtidos utilizan grandes cantidades de agua ya que la mayoría de los procesos ocurren en un medio acuoso. Esto conlleva a la generación de altos flujos de desechos acuosos los cuales deben ser tratados debido a relativas altas concentraciones de algunas especies contaminantes. Esta obra expone esta problemática a través de un estudio del caso en el estado de Río Grande do Sul, Brasil. Se estableció el consumo de agua en cada paso del procesamiento del cuero. Para lograr la reducción en el consumo de agua total proponemos la reutilización del agua como técnica en algunas etapas del proceso. Resultados experimentales, a una escala industrial, se exponen para así demostrar que la metodología sí tiene éxito. La reutilización del agua no solo reduce la carga para la planta de tratamiento, sino reduce los costos.

La Investigación sobre la demanda de agua en las curtiembres define el consumo en cada paso: ribera, curtido y operaciones posteriores. Es reconocido que las curtiembres utilizan agua descontroladamente, por

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lo general, más de lo que se requeriría. Adicionalmente, en la mayoría de las etapas se utiliza agua limpia proveniente de pozos artesianos o ríos. Técnicas de reciclaje son utilizadas hoy en día para la operación de encale. Esta publicación demuestra que técnicas de reutilización y reciclaje pueden ser también aplicadas en otras operaciones. Alternativas de reutilización de aguas fueron analizadas desde el punto de vista de los desechos del proceso para estimar los parámetros de concentraciones de algunos contaminantes. El estudio fue efectuado a nivel industrial. Estos parámetros son indicadores para evaluar la calidad del agua de acuerdo con los objetivos del sistema de reutilización. Durante el análisis de reciclaje, se reuso en el pre-desencale y desencale, el 100% del efluente del resultante del rendimiento y [siguiente] lavado. Los parámetros analizados con el reuso practicado no presentaron considerable diferencias comparados con el proceso convencional. Así queda demostrada la factibilidad de más extensivas prácticas del reuso en la industria de curtidos. Este estudio es de gran importancia a [los sectores] medioambientales y a la industria del curtido, porque esta tecnología de reutilización logra una minimización del empleo de agua y así resulta en incrementada protección ambiental en conjunto con reducción del costo.

INTRODUCTION

The tanning industry employs large amounts of water in unit operations of leather processing which occurs in an aqueous medium. In these processes, the water must be available in a sufficient amount, like a solvent medium, so that an interchange between the materials can be accomplished, which occurs essentially in solution.

Many previous studies were developed to estimate the volume and quality of this water. The literature shows the consumption varies of 15 to 40 L of water per kg of salty hide processed. Some studies indicate the quantity of water used for leather processing can be reduced from 40-50 m³ to 12-30 m³ for processing 1 t of bovine hides¹. The water consumption, for processing 1 t of hides, for each stage is: soaking = 9.0-12.0 m³; liming = 4.0-6.0 m³; delimiting = 1.5-2.0 m³; pickling = 1.0-1.5 m³; chrome tanning = 1.0-2.0 m³. This leads to a total consumption of 16.5-23.5 m³ in these stages².

Nazer et al.³ proposed some modifications on the liming stage in which the wastewater is reused, reducing the chemicals and water consumptions of this operation. The method proposed by the authors utilizes fresh water in the first hide batch. The wastewater generated by this batch can be recycled until four times, presenting no modification in the final leather quality. This process reduces economic and environmental costs.

Further, the large amounts of water employed, there is the high concentrations issue of some pollutant species present in the wastewater streams. The waters contamination is associated to

their physical, chemical and biological features. According to the state environment regulatory agency (*Fundação Estadual de Proteção Ambiental-FEPAM*⁴), the wastewater flowrate discharged by tanning industries located in the hydrographic area of *Rio Grande do Sul* varies from 300 to 2000 m³/day, with loads of up to 141 t/year of chemical oxygen demand (COD).

Environmental legislation establishes liquid effluent emission's criteria and standards of the polluting sources which can be discharged into water bodies, directly or indirectly. In the state of *Rio Grande do Sul*, the maximum limits of liquid effluent emission, for the discharge of companies with flowrate of 1000-2000 m³/day, are: pH = 6.0-8.5; biochemical oxygen demand (BOD) = 80 (mg.L⁻¹); NTK = 10 mg.L⁻¹, suspended solids = 80 mg.L⁻¹, total chromium = 0,5 mg.L⁻¹ and COD = 240 mg.L⁻¹.

The tanneries wastewater streams are treated in treatment plants. Usually, to obtain an effluent with constant features it is preferred to homogenize the outflow through a simple accumulation tank of adequate dimensions. A typical representation of a wastewater treatment plant of the tanney industry comprehends the stages of preliminary treatment, mechanical and physical-chemical treatment, biological treatment and sludge treatment or disposal. Complementary advanced processes of treatment are still not introduced.

The study of the wastewater contaminant parameters to accomplish a distributed treatment in tanneries has gained great attention so that water reuse or recycle could be allowed. The characterization of each wastewater stream allows one to identify the potentiality of reuse (direct) and recycle (after treatment) of the wastewater streams.

Initially, the object of this work is to investigate the amount of water employed in each stage of beamhouse, tanning and post-tanning operations. Furthermore, it will be analyzed some of the wastewater streams pollutant concentrations. The main objective is to propose some alternatives of reusing the wastewater streams in the processes. Considering that most of the tanneries already realized recycling in delimiting and tanning, this paper focus in the analyses of the reuse feasibility of the wastewater from washings, delimiting and bating operations.

EXPERIEMENTS

Water consumption research

In order to verify the water consumption, the stages: beamhouse, tanning and post-tanning from six tanneries located in the state of the *Rio Grande do Sul* were monitored and the water demands for the process formulations were investigated. These tanneries process the hides from its natural or conserved state until the finished leather, they are known as full tanneries. The study was carried through in the first semester of 2005 and it evaluated the amount of water used by each stage, as well as, the operations where recycling or reuse is already done.

TABLE I
Water consumption for the initial beamhouse operations
Water consumption (L) for processing 12000 kg of salty or green hides

Tannery	A	B	C	D	E	F
Pre-soaking	24000	36000	12000	12000	12000	0
Soaking	24000	12000	24000	12000	24000	0
Soaking washing	24000	12000	18000	12000	18000	0
Unhairing and liming	0	0	10800	0	10800	36000
Total	72000	60000	64800	36000	64800	36000
L of water per kg of hide	6	5	5,4	3	5,4	3
Employed water's origin	Dam	Brook	Dam	Dam	Dam	



Figure 1: Representation of the wastewater reuse system

Experiment to reuse technique

The implementation of wastewater reuse was realized in drums. Three experiment scales were evaluated: bench (with hide samples of about 1300 g), pilot plant (with half-hides) and industrial (with 4200 kg of hides).

The wastewater streams were characterized by the following parameters: pH, conductivity, calcium, fixed, volatile and total solids, and chromium. The wet-blue was characterized by the following analysis: dermic substance, volatile materials, extractable with dichloromethane (fats), chromium and calcium.

In preliminary bench tests, samples from the liquors of pre-soaking, soaking and soaking washing were collected. Each hide sample was dosed to 50% of the collected liquors and filled with fresh water; afterwards it fed the same processes of pre-soaking, soaking and soaking washing, respectively, inferring the feasibility of this kind of reuse⁵. In tests with half-hides, it was verified the viability of reusing the liquors from the 2nd bating washing into the 1st bating washing, from de 1st bating washing into the delimiting/bating operation and of reusing the liquors from the pre-delimiting washing into the pre-delimiting operation.

The industrial scale test was performed with green hides (no salt). It was so because the tannery, where was held the experiment, works with hides in this state. The soaked hides were processed and fleshed, according to the tannery ordinary process. Ten hides were separated and cut in half, as twin pairs: right side and left side.

The ten left sides were placed in a drum, summing the 4200 kg of hides. It was tested the reuse of the liquors from the 1st and 2nd bating washing mixed together, to form 100% of the pre-delimiting process and 100% of the delimiting process. Afterwards, the hides continue to the tanning stages, according to the representation below (figure 1). The ten right sides were processed in another drum; they follow the tannery ordinary production recipe, with no reuse. During the development of this experimental, liquors samples were collected at the end of each stage. The half wet-blue leathers, with reuse and with no reuse, were compared.

RESULTS

Water consumption in tanneries

Table I presents the water consumption by the beamhouse initial stages in the investigated tanneries. It is observed that the water consumption is very different among the tanneries. This indicates that the tanneries do not work with the minimum amount of water or that the hides processed have different salt content, since they are processing the same hide amount. The tannery F works with green hides, consequently its water consumption to the soaking stages is zero.

Table II presents the water consumption in the following stages, until the tanning stage. The values equal to zero, in the unhairing and liming stages, represents total recycle of the wastewater in these stages. The other tanneries perform partial recycle. The unhairing and liming recycles have great importance for the environment, besides the saving with chemicals used in these operations. The B tannery gives a good example; for the reason that it performs reusing of the tanning liquor for tanning the flesh splits leather. There could be other possibilities of recycling for tanning the grain split leather as well.

TABLE II
Water consumption for the following stages, until the tanning stage
Water consumption (L) for processing 5000 kg of limed hides

Tannery	A	B	C	D	E	F
Deliming	7500	1000	15000	1500	8000	10000
Washing	10000	10000	15000	5000	5000	5000
Bating	7500	0	4000	7500	5000	5000
Washing	10000	15000	30000	5000	5000	10000
Pickling	4000	1500	1500	5000	1500	2500
Tanning	4000	0	0	4000	0	0
Washing	0	0	0	0	0	5000
Total	43000	22500	65500	28000	24500	37500
L of water per kg of hide	8,6	4,5	9,3	5,6	4,9	7,5
Employed water's origin	Dam	Brook	Well/Dam	Dam	Dam	0

TABLE III
Water consumption for the retanning operations
Water consumption (L) for processing 2500 kg of wet-blue

Tannery	A	B	C	D
Washing	15000	12500	5000	2500
Neutralisation	1250	2500	5000	3750
Washing	15000	12500	3750	2500
Retanning	7500	2500	8750	7500
Dyeing	0	750	5000	0
Washing	15000	15000	5000	15000
Fatliquoring	0	3000	3750	0
Total	53750	48750	36250	31250
L of water per kg of hide	21,5	19,5	14,5	12,5
Employed water's origin	Well	Brook	Well	Well

Table III shows the water usage in the retanning operation. Tanneries C and D's water consumption is smaller than the others. Therefore, one insists that tanneries are able to investigate the possibilities of reducing the water usage, because the purpose of these stages is to promote the penetration of the chemical into the hide, accordingly the more concentrate the media the faster will be the diffusion of the chemical from the liquor to the hide.

Wastewater reuse analysis

The results obtained from the wastewater analysis, for the original process (without water reuse), are presented in table IV. The parameters analyzed show the contamination of the liquors and inclusively the liquor from the mixture of the bating washings. The conductivity, calcium concentration and fixed solids quantity are related with each other, as they indicate the salts which are in the waters that could interfere in the reusing practice. The analyses of the volatile solids quantify the amount of organic material in the liquors. The analysis chosen are of

quick and simple performance. In this condition, it is characterized the quality of the water for the practice of reusing.

The results presented in table V were obtained from the wastewater analysis after each stage for process with reuse form the wastewater from the 1st and 2nd bating washing mixed together to the pre-delimiting process and the delimiting process.

The calcium analyses ran for the reuse test resulted in higher values. It is due the fact the liquors reused contained some amount of residual calcium, although this gap was decreasing. The chromium oxide residual concentrations from both systems, with and without reuse, were very similar. For solids analyses, the sample from the reuse test showed higher levels of volatile solids in some stages and lower levels in others. The reason is the presence of hide fibers and organic material that are in the liquor. The fixed solids results are very similar for both systems. It can be observed that the liquors pH values

TABLE IV
Wastewater analysis of the beamhouse and tanning liquors
for the original process (without water reuse)

Stage	pH	Conductivity (mS/cm _{25°C})	Calcium (g.L ⁻¹)	Volatile Solids (mg.L ⁻¹)	Fixed Solids (mg.L ⁻¹)	Chromium (g.L ⁻¹)
Pre-delimiting	11,1	7,76	0,75	5948	6092	-
Pre-delimiting Washing	11,1	6,31	0,56	5580	4520	-
Delimiting/Bating	8,8	14,37	0,64	13118	8364	-
1 st Bating Washing*	9,6	10,41	0,53	5990	3694	-
2 nd Bating Washing*	9,5	6,96	0,30	2118	1378	-
Tanning	3,7	37,3	-	10342	68570	1,22
Tanning Washing	3,7	24,8	-	5408	31788	0,63
Bating Washing mixture*	9,00	9,16	0,43	4668	3950	-

*input for the reuse test

TABLE V
Wastewater analysis of the beamhouse and tanning liquors for the process with reuse
of the bating washing mixture into the pre-delimiting and the delimiting operations

Stage	pH	Conductivity (mS/cm _{25°C})	Calcium (g.L ⁻¹)	Volatile Solids (mg.L ⁻¹)	Fixed Solids (mg.L ⁻¹)	Chromium (g.L ⁻¹)
Pre-delimiting	9,91	10,8	1,38	11374	11120	-
Pre-delimiting Washing	9,96	7,6	0,75	5280	5638	-
Delimiting/Bating	9,10	12,6	0,92	15376	8084	-
1 st Bating Washing*	9,00	9,88	0,57	6492	3480	-
2 nd Bating Washing*	8,90	6,88	0,33	3956	1606	-
Tanning	3,02	35,4	-	8886	73410	1,35
Tanning Washing	3,68	23,8	-	5172	30180	0,567

TABLE VI
Wet-blue leather analysis

Wet-blue	Calcium	% Extractable with dichloromethane*	% Dermic substance*	% Chromium*
Half-hide 1- with reuse	#	0,79	92,33	4,17
Half-hide 1- with no reuse	#	0,96	92,86	4,29
Half-hide 2- with reuse	#	1,09	89,40	5,52
Half-hide 2- with no reuse	#	1,00	91,75	4,58

* dry basis # not detected

with reuse are lower than the values from the liquor without reuse. This is associated with a variation in the pH tanning. Even though, they are in the same recommended range to efficiency of each process stage. The results achieved to conductivity are similar, for both systems.

In table VI are shown the results of the wet-blue leather analysis. It can be observed the analytic values are very closed and the leather quality was not affected by the reusing system of wastewater adopted. The twin pairs from the ten hides were in a very similar aspect, no spots or any defect because of the wastewater reusing.

CONCLUSION

Although large amounts of water are employed in leather processing, observing this paper's results and the data from literature, these tanneries are in average regarding the water consumption. However, this is not enough. The search for water usage minimization and for clean technologies must be tireless by the companies that intend to continue in business for the next years.

The experiments showed the feasibility of reusing the wastewater directly, with no previous treatment. The reusing, proposed here, reduced about 30% the water consumption in the beamhouse stages. As soon as the reusing is adopted in other stages, segregated treatment systems can be implemented, and the quality of the water can be regenerated into the necessary condition, for instance solids precipitation and filtration. The developments must always be followed by analytical control to determinate the contamination limits of the water allowed for reusing. The main objective is to avoid the end-of-pipe treatment. As a result, the maximum water recovery and the prevention of its capture from the natural sources can be achieved, which must be preserved for essential uses of life.

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BIBLIOGRAPHY

1. Favazzi, A. O tratamento dos efluentes de curtumes (The treatment of the tanneries effluent). *International tannery*, 154, p.53-64, 2002. In Portuguese.
2. Rao, J. R. et al. Recouping the wastewater: a way forward for cleaner leather processing. *Journal of Cleaner Production*. **11**, 591-599, 2003.
3. Nazer, D.W. et al. Reducing the environmental impact of the unhairing-liming process in the leather tanning industry. *Journal of Cleaner Production*. **14**, 65-74, 2006
4. Fundação Estadual de Proteção Ambiental – FEPAM/RS/ Brazil. Diagnóstico da Poluição Hídrica Industrial na Região Hidrográfica do Guaíba (Diagnosis of the Industrial Hydro Pollution in the hydrographic area of Guaíba), Porto Alegre, 2001.
5. Passos, J. B et al. Análises e experimentos para reúso de água em curtumes (Analyses and experiments for wastewater reusing in tanneries). In: V Simpósio Internacional de Qualidade Ambiental: Gestão Integrada do Ambiente. Porto Alegre, v. 1, p. 1-10, 2006. In Portuguese.