Assessment of water management in tanneries: State of Rio Grande do Sul case study

Patrice Monteiro de Aquim, Mariliz Gutterres, Jorge Trierweiler

Federal University of Rio Grande do Sul, Chemical Engineering Department,
Laboratory for Leather and Environmental Studies (LACOURO)
Rua Eng. Luiz Englert, CEP 90040-040 – Porto Alegre – RS – BRAZIL
Fax: +55 51 3308-3277, Phone: +55 51 3308-3954,
e-mail: pmaquim@gmail.com; mariliz@enq.ufrgs.br; jorge@enq.ufrgs.br

A B S T R A C T: This study evaluates the use of water during the processing of hide into leather. It investigates the environmental impact on water resources of tanneries in Rio Grande do Sul State, evaluating the water demand and concentrations of certain chemicals in the wastewater discharged from the beamhouse, tanning and retanning processes of this industry. Field research was required to formulate questions which could identify water management problems in tanneries, and the possible alternatives available to tanneries aiming at their improvement. A simple and objective application called IRGO (insufficient, regular, good and optimal) was developed. This evaluation offers a way for the tanneries with processes in the worst situation to find alternatives with less impact. Thus, after completing the questionnaire, the tanneries could check how distant they are from an ideal tannery and ascertain which actions must be taken to improve their performance. The IRGO was applied with collaboration from the Association of Tanneries Industries of Rio Grande do Sul (AICSul) which contacted 70 tanneries in the state, and 10 participated in the IRGO, i.e., 13% of the total. The results showed that there is a large demand for water in the process and little water is reused. The most conventional liming process employs sulfite, lime and amine and recycling is already applied to this operation in the state. The steps of washing, deliming and float use a large quantity of water, although the majority of the tanneries do not use ammonia in the deliming, this is due to environmental pressure for a reduction in nitrogen concentration in wastewaters. The tanning procedure most used employs chrome III without recycling. In relation to retanning, studies need to be carried out aiming to increase the efficiency of the absorption of chemicals. The wastewater treatment plants are satisfactory due to intense requirements of the environmental organizations.

Keywords: tannery assessment; water management; wastewater.

1. Introduction

The scarcity of freshwater is a topic that must be reassessed by all, but mainly by industries that use it as a replenishable resource. Brazil is considered to be a rich country in hydrological terms, since it has approximately 12 % of the freshwater that runs on the world´s surface. However, this volume is unevenly distributed: 70% of it is in the Amazon, a region which has less than 7% of the country´s population, 15% in the Centre-East region, 6% in the South & Southeast and only 3% in the Northeast of Brazil. This perception of water resources as a problem that needs attention only came about when there was a reduction in water available in places where, traditionally, it was abundant. Studies by UNO indicate that 40% of the world population will lack drinking water in 2050.

Leather processing involves a huge quantity of water in its different stages and therefore it generates a considerable amount of wastewater, which demands high investments and operational costs for effluent treatment to satisfy the discharge standards required by the environmental legislation. However, the leather sector is of great economic importance to Brazil and to the State of Rio Grande do Sul. In 2007, the leather production in Brazil was 45 million units and the world production was 330 million units, and Brazil is thus responsible for 13.6% of the world-wide production and is second in the world ranking for leather producers. In 2006, Rio Grande do Sul was the state with the most tanning establishments (217) and this business generated 15,821 jobs (Leather Brazilian Guide, 2008). Due to the economic importance of this state, it was chosen for this research study on the present situation in terms of water management in tanneries.

The objective of this study was to investigate procedures applied in tanneries during the processes which use water, in order to measure the environmental impact. The research was carried out through evaluations of the application of water resources during the processing of hides into leathers in the tanneries of the Rio Grande do Sul State, the water demand and the concentration of the residual floats from each step and the quality of wastewater discharged by these industries.

Leather processing consists of the transformation the raw hide into material that is called leather. Its manufacturing technology requires several stages of processing, with sequential additions of chemical products, alternating with washings and mechanical processes. The stages of this process can be grouped into: beamhouse, tanning, wet finishing and finishing.

The beamhouse process is responsible for high water consumption, since it has the function of cleaning the hide, removing the hair and preparing it for the tanning process. The operations comprising the beamhouse process that use water are: pre-soaking, soaking, dehairing/ liming, deliming, bating, and pickling, along with washings between the processes for better elimination of impurities and chemical products of the hide.

After the beamhouse operations, the hide receives the tanning agent, which provides the stabilization of the collagen structure. Subsequent to the tanning stage, the hide is called leather, and if the tanning is carried out with chromium the leather is described as "wet-blue" because of its humidity and coloration. After concluding the tanning process, the leather passes to the finishing phase.

The finishing can be subdivided into wet finishing and finishing. The function of the wet finishing is to define the quality required for the final article. This operation comprises: a) deacidification of the leather; b) retanning with synthetic tanning agents or chromium; c) fat liquoring with oils; which is important to give softness to the product; and d) dyeing. The finishing is not carried out with water, but rather by deposition of superficial covering layers based on polymers and resins onto the leather and thus the present study does cover this process.

Given that the majority of processes used to transform hides into leather use water and chemical products, there are many studies on the volume and the quality of the water used. Table 1 shows the results of studies carried out on water demand in tanneries, which reveal differences between the tanneries. According to Buljan (1995), a ton of raw hides generates 250kg of leather, that is, the ratio of water employed (l) to raw hides (kg) to produced leather (kg) is 120:4:1. Moreover, Ramirez et al. (2003) concluded that traditional processes use on average a 40-75% excess of chemical products, indicating that they do not use technology to minimize the chemical products and water consumption.

Table 1: Bibliographical review of water demand in tanneries

Author	Water demand in tanneries
Belavsky (1965)	50-60 l water/kg hide
Buljan (1995)	30 l water/kg hide
Center of Promotion of Sustainable Technologies (2003)	15-40 l water/kg hide
Ramirez et al. (2003)	35-40 l water/kg hide
Rao et al. (2003)	30-40 l water/kg hide

Gutterres et al. (2008)	10.5-28 l water/kg hide

Besides the large volumes of water, there is the problem of high concentrations of pollutants in the wastewater. The state environmental agency (FEPAM, 2001) selected the 100 industries with greatest river pollution potential in the state and of these 41 companies were in the leather business. The effluent discharge of these companies ranges from 300 to 2000/m³ per day with loads of up to 141 ton/year of COD (chemical oxygen demand).

Tania Floqi, Daut Vezi, Ilirian Malollari (2007) carried out a study to identify and evaluate water pollution from Albanian tanneries, and they had verified that they discharge 100 to 1000 tons of effluent into the watersheds. The physico-chemical indicators of these effluent were: BOD (biochemical oxygen demand) =965-1631 mg/l, COD=6168-11032 mg/l, total suspended solids =1264-9984 mg/l, sulfite=21-380 mg/l, total chromium=4.75-49.2 mg/l, and ammonia ions=10-102 mg /l. Baumgarten, Buer and Scholz (2004), also analyzed tannery effluent. RAO et al. (2003) reported results for the parameters of the residual floats to emphasize their environmental impact.

The wet finishing effluent contains chromium from the washings, along with oils from the fat liquoring, which are emulsified, making it difficult to separate these from the water. Other products found in the wet finishing are the dyes from the dyeing process. The wet finishing is responsible for generating an effluent with high COD concentration, since it uses innumerable chemical products to give the desired quality to the leather, these products being mainly oils from fat liquoring, which provide softness, dyes, and fixing and retanning agents.

Environmental legislation is the main motivation for the reduction in the environmental impact of industries. Unfortunately, most industries are reactive and not pro-active in relation to the minimizing their environmental impacts. The laws are continuously being improved, and therefore there is a growing need to update industrial practices to minimize the impacts on water resources. The current laws in Brazil relating to effluent control are: Resolution CONAMA 357/2005 (which classifies water bodies, offers environment guidelines, and establishes the conditions and standards for effluent discharge and other steps) and Resolution CONSEMA Nº 128/2006 (which sets emission standards for the discharge of liquid effluent to superficial waters in the State of the Rio Grande do Sul).

According to legislation effluents can only be discharged to water bodies, directly or indirectly, when they comply with the following conditions: pH between 6.0 and 8.5, Oils and Greases (Vegetable or Animal) 30 mg/l, Total Nitrogen ≤10 mg/l N, Sulfites ≤ 0.2 mg/l S, and Total Chromium ≤0.5 mg/l Cr. Resolution N.º 128 takes into consideration the outflows of the receiving rivers for the definition of emission standards for the physical and chemical parameters of the effluent discharged. Thus, the launching of effluent of high outflow will have restrictive standards of emission when launched into receiving bodies of low outflow. Rio Grande do Sul is the first Brazilian State to implement standards and criteria for the toxicity of effluents launched into superficial waters. Moreover, it revises, in another Resolution, the physico-chemical emission standards of effluent, taking into account the outflows of both the effluent discharge and the river (FEPAM, 2007).

2. Materials and methods

To evaluate the situation of the tanneries in the state of the Rio Grande do Sul in Brazil, an accessible and dynamic questionnaire was developed. Questions were formulated which could identify water management problems and propose possible alternatives for tanneries based on a wider previous study. This evaluation also indicates the way forward with respect to tanneries when the alternatives fall in the worse situation (alternative A), offering a situation of less impact (alternative D). Thus, the tannery will learn how distant it lies from the ideal tannery and which steps must be taken to improve its reality. The questionnaire can be applied to any tannery.

Four alternatives for responses represented by letters were stipulated, each one having different weightings and meanings. However, when answering the questionnaire the tanneries did not have knowledge of the meanings to avoid inducing certain responses. Table 2 presents these alternatives, with their meanings and weightings. The evaluation is called IRGO. In the same table, the points inform whether the tannery reached the end of the evaluation, for example, for an ideal complete tannery (excellent), the sum of points must be 124, since there are 31 questions multiplied by a weighting factor of 4, and for an insufficient tannery it is around 31.

Table 2: Evaluation of IRGO

Letter	Meaning	Weighting	Points for a complete tannery	Total points for a beamhouse and tanning tannery	Total of points for a finishing tannery
I	insufficient	1	31	23	12
R	regular	2	62	46	24
G	good	3	93	69	36
O	Optimum	4	124	92	48

The questionnaire is separated in 7 parts as follows:

Part I: referring to the state in which the hide arrives at the tannery;

Part II: referring to the processes of soaking and washing;

Part III: referring to the processes of dehairing and liming;

Part IV: referring to the washings and the processes of deliming and bating;

Part V: referring to the pickling and tanning processes;

Part VI: referring to the wet finishing processes;

Part VII: referring to the wastewater information.

For application of the IRGO, the cooperation of the Association of the Tannery Industries in Rio Grande do Sul was requested (AICSul). They contacted 70 tanneries in the state, of which, 10 participated in the evaluation, that is, 13%, of which 7 were complete tanneries, 2 were wet finishing and 1 was a beamhouse and tanning tannery.

Tanneries which carry out the operations of beamhouse, tanning and wet finishing were considered complete tanneries. Due to the amount of operations and volumes of water required, one tannery which was considered a complete company on the questionnaire will be qualified as that of greatest environment impact.

3. Results

The results for the evaluation of 10 tanneries will be presented below. Table 3 shows the results related to the condition of the hides arriving at the tannery (Part I of the questionnaire). The majority of tanneries receive the hide conserved with salt and some are acquired without shavings and appendices (parts of the hide that must be eliminated) or already washed to eliminate the blood. The tanneries can commission the storage rooms to remove the blood, shavings and appendices. Besides reducing the cost of the hide, the residues would be eliminated at source with other possibilities for exploitation (manufacturing of gelatin, animal feed, etc.).

Table 3: Results on how the hides arrive at the tannery

Alternatives	% tanneries which choose this option
I - conserved with salt and without shavings	67
R - conserved with salt and with shavings removed	0
G - raw hide, without shavings, with a lot of blood	33
O - raw hide, with shavings, without much blood	0

The percentages of water reported in the results are given in relation to the hide mass to be processed, for 1000 kg of hide processed 2000 l of water are added.

The results for Part II (soaking and washing processes) can be observed in Table **4**. The majority of the tanneries are in a good situation, they do not use excessive amounts of water to remove dirt. The tanneries that are classified as excellent are those that process raw hide, this providing the first benefit in terms of acquiring the hide without conservation agents or the need for water application and processing time to rehydrate the hide. Some tanneries already apply water reuse for these initial washings, normally derived from the effluent treatment and all tended to use biodegradable surfactants. Unfortunately, the majority present significant chloride concentrations in the float due to the salt used in the conservation, mainly for logistic reasons or due to the raw materials available in the market, whenever it has offer of hides these tanneries buy and make stock of it. The culture just in time still is precocious for the sector. Table 5 shows the results for the processes of dehairing and liming (Part III) carried out in the beamhouse. This stage was characterized as the stage with the most recycling and therefore it was mostly found to be in an excellent situation. The tanneries in this state changed their practices following strong pressure from the environmental agency, which led to water recycling, also having a positive economic result. The majority of the tanneries carry out dehairing with calcium/sulfite/amine and generate a residual float containing two important contaminants: sulfite and nitrogen. The nitrogen comes from epidermis of the animal hide and the amine. Since the state legislation concerning the

discarding of nitrogen is sufficiently strict to control problems of eutrophication in the receiving water bodies, it is important to minimize the use of products that contain it, highlighting the importance of recycling at this stage. However, even with recycling the use of sulfite in tanneries liberates gases with a strong smell, but due to the low cost they are reluctant to eliminate this from the process, although lower quantities are being used.

Table 4: Research results for soaking and washing processes

Alternatives	% Tanneries that chose this option
% Water demand in soaking and washing operations	
I - ≥400%	0
R - 300%	25
G - 200%	50
O - ≤100%	25
% Water demand in soaking and washing operations being used for a second time	
I- Reuse 0%	38
R - Reuse 25%	37
G - Reuse 50%	25
O - Reuse 100%	0
Surfactant type	
I - Non biodegradable	12
O – Biodegradable	88
Residual float from soaking (chlorides)	
I - with chloride	50
R - with some room for chloride reduction	25
G - with low chloride (up to 250 mg/L)	12
O - without chloride	12

Table 5: Research results for the dehairing and liming processes

Alternatives	% Tanneries that chose this option
Water demand	
I - >=300%	0
R - 200%	25
G - 100%	38
O - <=50%	37
% Recycled	
I - Reuse 0%	0
R - Reuse 50%	28
G - Reuse 75%	29
O - Reuse 100%	43
Dehairing and liming type	
I - Calcium and sulfite	0
R - Calcium, sulfite and amine	78
G - Calcium, sulfite and liming assistants	22
O - Auxiliary agents and enzymes	0
Residual float from dehairing and liming (sulfites)	
I - > 4000 mg/L	12
R - 2000 to 4000 mg/L	25
G - < 2000 mg/L	63
O – absent	0

Part IV (washing, deliming and bating): the results given in Table 6 show that the majority of tanneries obtained an acceptable water demand, although water reuse in these stages is not applied.

The majority of tanneries still use deliming products based on ammonia, despite the environmental pressure for a reduction in nitrogen concentration in the effluent.

Table 6: Research results for the deliming processes

Alternatives	% Tanneries that chose this option
Water demand	
I - >=700%	13
R - 600%	0
G - 500%	37
O - <=400%	50
% Water reuse	
I - Reuse 0%	87
R - Reuse 50%	13
G - Reuse 75%	0
O - Reuse 100%	0
Deliming type	
I - ammoniacal salts	0
O - deliming without ammonia	78

The results for the evaluation relating to Part V (pickling and tanning) given in Table 7 show that this stage is important. Although the water demand is not high, the effluent discharge contains chromium, and tanning achieves an excellent technological result, but with high environmental impact. The chromium used for tanning is CrIII, however, it can be oxidized to form CrVI which is dangerous in the environment. In the past it was common for the tanneries to reduce CrVI to CrIII for use in tanning, but currently none of the tanneries carry out this procedure, and thus, in the majority of the cases, there are traces of CrVI.

Table 7: Research results for the pickling and tanning processes

Alternatives	% Tanneries that chose this option
Water demand	
I - ≥100%	25
R - 50%	37.5
G - 25%	37.5
O - 0%	0
% Water reuse	
I - reuse 0%	62
R - reuse 50%	25
B - reuse 75%	13
O - reuse 100%	0
Salt from pickling	
I - with salt	100
O - without salt	0
Tanning type	
I - with chromium	89

O - without chromium	11
Does the tannery reduce chromium VI?	
I - Yes	0
O - No	100
Is the product analyzed for chromium VI?	
I - No	63
O - Yes	37
Residual float from pickling and tanning processes (chromium)	
I - No evaluation of chromium concentration in residual float	25
R - Evaluation, but no action taken for high concentrations (>1mg /L)	0
G - Evaluation, and studying ways to reduce high concentrations (>1mg /L)	38
O - Evaluation, and the concentration is relatively low (< 0.5mg/L)	37

The part VI of the evaluation (Table 8) raises some important issues regarding the wet finishing. The evaluation of this operation is more difficult, since there are many forms in which the leather article can be produced. This diversity reflects the fashion market, one of the biggest customers of tannery products, which changes within short time periods. In contrast to the previous operations where dirt and fat are removed, in wet finishing operations chemical products are incorporated into the leather.

Table 8: Research for the wet finishing processes

Alternatives	% Tanneries that chose this option
% Water demand in relation the wet-blue leather mass	
I - ≥1300%	25
R - 800%	50
G - 400%	25
O - ≤200%	0
% Water reuse	
I - Reuse 0%	67
R - Reuse 25%	22
G - Reuse 50%	11
O - Reuse 100%	0
Fat liquoring: percentage of added oil that penetrates the leather	
I - No information available at tannery	22
R - < 60%	0
G - 61 to 95%	67
O - > 95%	11
Dyeing: percentage of added dye that penetrates the leather	
I - No information available at tannery	22
R - < 60%	0
G - 61 to 95%	67
O - > 95%	11
Retanning with chromium	

I – With chromium	50
O - Without chromium and high exhaustion	50
Residual float from retanning (chromium)	
I - No evaluation of Cr concentration of residual float	22
R - Evaluation, but no action taken for high concentrations (>1mg /l)	0
G - Evaluation, and studying ways to reduce high concentrations (>1mg /l)	33
O - Evaluation, and the concentration is relatively low (< 0.5mg/l)	45
Are aromatic resins used? Is the use of these resins prohibited by internal regulations?	
I – Yes; no	0
G – No; no	56
O – No; yes	44
Are resins with formaldehyde, or formaldehyde as an auxiliary and setting agent used?	
I - No information available at tannery	0
R - Yes, but there is a plan to change these products	11
0 - Not, these products are prohibited at this tannery	89

The objective was evaluate at this stage concern regarding some products used in the wet finishing process which are being restricted by legislation as products that contain nitrogen and other dangerous chemicals that are required to leave circulation, such as aromatic and formaldehyde resins. The research showed that such resins are not used at the tanneries studied. Since azo dyes can be cleaved (one or more azo groups) under certain conditions, they can be reduced to form amino aromatic carcinogens. Formaldehyde has specified levels as a prerequisite of the label ECHO, of a maximum of 150 ppm in leather, and of the automotive sector, the current level required is less than 10 ppm (Reineking, C. et al., 2005).

For Stage VII (referring to the effluent), as shown in Table 9, most of the wastewater COD values were between 159 and 400 mg/l. The chromium discharges of the tanneries comply with the norms of the state, however, the majority do not separate the effluent with chromium, leading to its dilution and a reduction in its concentration.

Table 9: Research results for the wastewater treatment

Alternatives	% Tanneries that chose this option
Treatment water reuse: % water returned to the process	
I - Reuse 0%	45
R - Reuse 25%	44
G - Reuse 50%	11
O - Reuse 100%	0
Wastewater: chromium	
I - >0.5mg/L	0
R – 0.3-0.5 mg/L	44
G - < 0.3 mg/L	56
O - without chromium	0

Wastewater: COD	
I - COD > 700mg/L or no information available	0
R – COD of 400 to 700	0
G - COD of 150 to 400 mg/L	89
O - COD of <150 mg/L	11
Wastewater: Total nitrogen.	
I - > 1g/L	56
R - 0.02 to 1g/L	22
G - 0.01 to 0.02 g/L	11
O - < 0.01g/L	11

After evaluating the responses for the seven parts, the total IRBO points were obtained for the tanneries, as observed in the graphs in Figure 1 for the complete, beamhouse and tanning, and wet finishing tanneries. It was verified that the majority of the tanneries of the state lie within the regular and good categories. To improve this situation, the main recommendations regarding the measures which could be taken are: to remove shavings and appendices from the hides before acquiring or processing them; when logistically feasible process the green hide avoiding the hide conservation with salt; minimize the addition of chemical products, for example, verify possibilities for chromium reduction; substitute chemical products for less harmful products, e.g., change from ammoniacal delimers to those without ammonia and carry out pickling without salt; and invest in reduction techniques and water reuse /recycling.

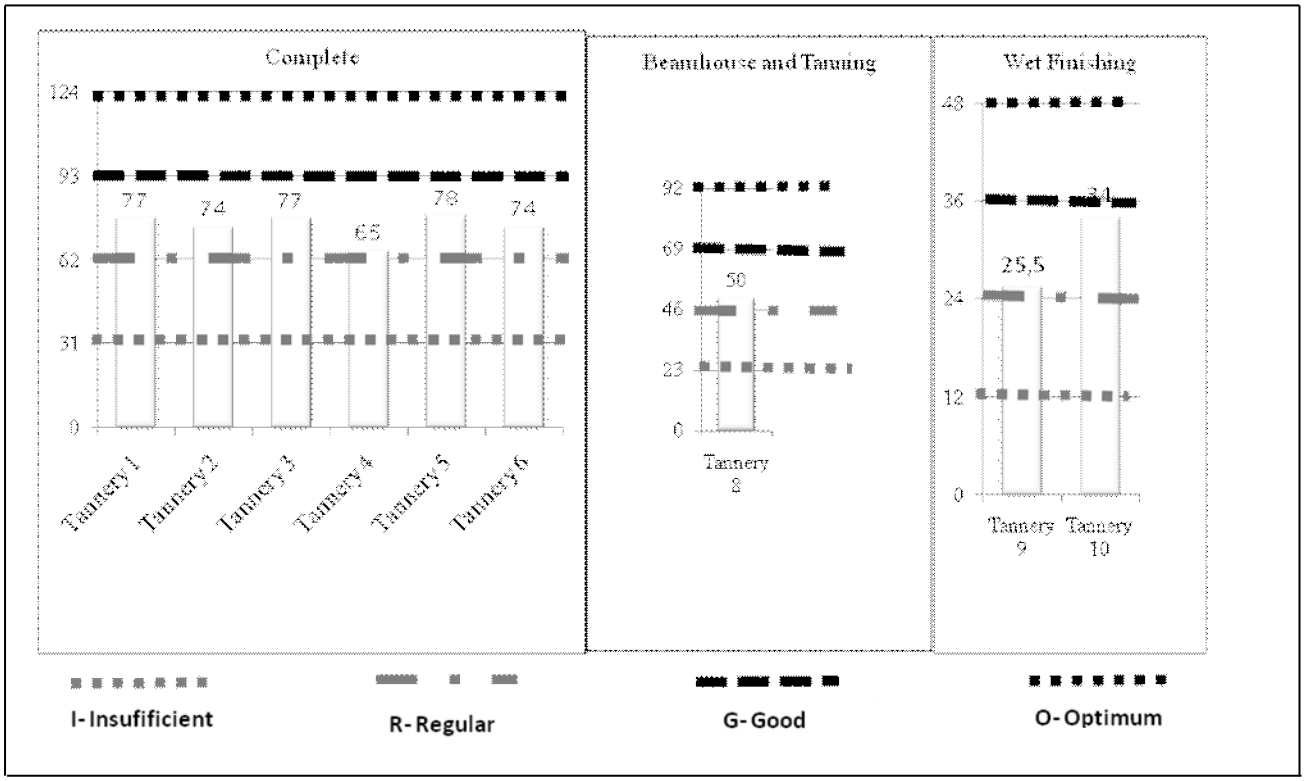

Fig. 1: Results from State Tanneries Research

4. Conclusions

The situation of tanneries in Rio Grande do Sul State was found to be regular to good, although many measures still need to be implemented. The IRGO tool was shown to be efficient and dynamic in its application to the tanneries, and each tannery could be quickly evaluated in terms of its current situation and where it must arrive in terms of implementing processes which address environmental concerns. Moreover, the tanneries were able to evaluate their own situations, and in this way it can be highlighted that many processes which become routine due to a high work load, in fact, require only small changes in order to maximize the process and to minimize the impact.

The results from the questionnaires showed that the tanneries evaluated consume, approximately, between 10 and 25 l water/kg hide. This shows that, compared to values reported in the literature, the tanneries investigated herein achieved better results, implying less water consumption. However, it was noted that many steps still need to be taken for them to become excellent tanneries and the water demand can still be reduced, to fulfill the environmental requirements to improve the performance of these process.

Acknowledgements

The authors gratefully acknowledge Association of the Tannery Industries in Rio Grande do Sul (AICSul), the tanneries consulted and the Brazilian government agency CNPq (CTHidro).

References

[1] Baumgarten, S, Buer, T. O. Scholz, W., 2004. Erfahrungen mit Membranverfahren in unterschiedlichen Prozess-stufen der Lederherstellung. Freiberger Kollagensymposium, 23- 24, Freiberg.

[2] Belavsky, E. , 1965. Tannery in Brazil. Livraria do Globo S. A. Porto Alegre- Brazil, p 22-23, p. 74.

[3] Buljan, J., Reich, G., Ludvik, J., 2000. Mass Balance in Leather Processing. United Nations Industrial Development Organization. Regional Programme for Pollution Control in the Tanning Industry in South-East Asia.

[4] FEPAM (*Fundação Estadual de Proteção Ambiental Henrique Luiz Roessler*), 2007. Accessed on-line in December ,2007 at: http://www.fepam.rs.gov.br/noticias/noticia_detalhe.asp?id=108

[5] FEPAM (*Fundação Estadual de Proteção Ambiental Henrique Luiz Roessler*), 2001. Diagnosis of the Industrial Hydro Pollution in the hydrographic area of Guaíba), Porto Alegre RS/Brazil.

[6] Floqi, Tania, Daut Vezi, Ilirian Malollari, 2007. Identification and evaluation of water pollution from Albanian tanneries. Desalination, Volume 213, Issues 1-3, Pages 56-64.

[7] Leather Brazilian Guide 2008. Brazilian Association of Leather Industry Chemists and Technicians).

[8] Center of Promotion of Sustainable Technologies (CPTS), 2003. Technical guide of Cleaner Production for Tanneries. Program of Danesa Cooperation to the Environment Sector, La Paz, Bolivia.

[9] Gutterres, M.; Aquim, P.; Passos, J. B.; Severo, L.; Trierweiler, J., 2008. Reduction of Water Demand and Treatment Cost in Tanneries through Reuse Technique. The Journal of the American Leather Chemists Association, v. 1, p. 138-143.

[10] RAMIREZ *et al*., 2003. *Proceso de Ribeira: Revisión a los Procesos Químicos*. XXVII IULTCS International Union of Leather Technologists and Chemists Societies Congress, Cancún, México.

[11] Rao, J. R. et al., 2003. Recouping the wastewater: a way forward for cleaner leather processing. Journal of Cleaner Production. 11, 591-599.

[12] Reineking, C., Walker, M., MA, S., 2005. *Formaldeído em couro – ocorrências e soluções*. XVII National Meeting of Chemists and Technicians of the Leather Industry, Gramado, Brazil.