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Environmental Developments and Researches in Brazilian Leather Sector

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Abstract

The importance of livestock in the production of meat and dairy products, as well as the tannery activity that uses hides and skins as raw material, is widely recognized. However, a considerable fraction of the raw material is discarded or sent to other industries because of its composition or limited value in terms of leather manufacturing. In order to modify this reality and improve production process technologies, many studies were conducted to reduce, reuse, recycle or dispose of tanning process waste. Alternatives are being implemented to ensure the adoption of environmentally safe methods that meet environmental laws, and to raise the awareness of the professionals involved in the sector. Brazil reportedly has the largest commercial cattle herd in the world, is the largest producer of bovine cattle in the world and the world's third largest producer and exporter of leather. Other significant data, as well as other indicators of the sector are presented. The present study characterizes the Brazilian industry regarding the leather articles produced, where the footwear articles are the main end-use of leather. However, other industrial uses have become increasingly important for leather manufacturers, such as the automotive and furniture sectors. A study in 224 Brazilian tanneries was performed with the purpose of finding out which are the most widely used tanning processes. This work reports the development and updating of the leather industry in Brazil. A typical representation of the wastewater treatment technology most frequently adopted in Brazil comprises the stages of preliminary treatment, mechanical and physical-chemical treatment, biological treatment, sludge treatment or disposal and nitrogen removal. The most advanced wastewater treatments and water reuse in tanneries are presented and discussed. The main uses for by-products generated in the leather processing are also presented. The work summarizes the research lines and developments conducted at the Federal University of Rio Grande do Sul, at the Laboratory for Leather and Environmental Studies, in order to obtain information on the latest technologies and improvements in the leather sector.
Keywords: leather technology, production data, liquid effluents, leather wastes, research lines in leather.

1. Introduction

The tanning industries in the developing countries are expanding, so that large amounts of good quality hides generated in the developed world are destined to countries that produce leather tanning, despite the poor quality due to improper storage and long periods of shipping and storage in unfavorable weather conditions.

Leather is a byproduct of the meat industry, in which the principal source of raw material for the leather industry is the cattle hide, which represents approximately 5% to 15% of the market value of an animal (ICT, 2011). Considering the importance of livestock activity toward the production of food, meat, milk and dairy tannery activity employ the hide as raw material, resulting, however, high amounts of solid waste that are not intended for manufacturing leather. The hide represents 7% of body weight of cattle and therefore. The fraction of raw hide that is effectively transformed into leather is 20 to 25%, remaining, therefore, others products and process intermediates in the form of by-products, characterized by high potential impact on environment. Therefore, remains of hide in the waste form deserve a commercial value.

It is of utmost importance to control and reduce the environmental impact by adopting environmentally friendly production cycles, use of materials with low environmental impact, energy save and pre-treatment or treatment of gas emissions, liquid effluents and solid wastes of the industry. Regarding solid waste management from tanneries, before the final destination for waste treatment, the possibilities must be considered to minimize the amount of waste generated by changes in the production processes, segregation, recycling and the use of waste from other industries.

2. Brazilian leather

2.1. Production and exports

The Brazilian leather industry has an important role in the national economy. Brazil is the third largest producer and exporter of leather in the world and holds the largest commercial cattle herd in the world (FAO, 2010 and ABQTIC, 2011). The leather industry in Brazil had, in 2009, 773 establishments, where the States of Rio Grande do Sul and São Paulo had a participation of respectively 28.4% and 26.6% in the number of tanning establishments (ABQTIC, 2011).

Brazil's share in the world production of leather has remained above 12.47%, over the last five years (see Table 1) (ABQTIC, 2011). However, Brazilian products in the wet blue stage are the most widely sold (low added value). It is estimated that because of these sales, Brazil will not achieve the expected trade income, once the industrial plants have favorable conditions to produce and export finished leather and crust product (more added value).

Table 1 shows the estimates of global bovine leather market in the 2005-2009 period compared to 2000. The growth of the Brazilian herd between 2000 and 2009 (20%) was much higher than that of the world's total herds (5%).

Table 1: Estimative of global bovine leather market 2005/2009 comparing to 2000 (in million of hides)

	Global bovine	Global hide production	Brazilian bovine herd	Brazilian hide production	Brazil's share in the global market (%)
2000	1.314,76	290,46	169,88	31,14	10,72
2005	1.349,24	301,51	207,16	39,43	13,08
2006	1.359,32	306,06	205,89	41,23	13,47
2007	1.357,84	310,11	199,75	42,33	13,65
2008	1.372,38	309,04	202,29	39,80	12,88
2009*	1.382,24	308,62	204,50	38,50	12,47

Source: ABQTIC, 2011.

Until 2006, the exports of cattle hides increased continuously, reaching a record 34.5 million of hides exported. From 2007 to 2009 occurred a decrease in the exports, which returned to growth in 2010 reaching a value of 27.3 million hides. Until 2007 the largest export volume of leather was in the wet blue stage, since surpassed by the finished leathers. The minor variations in terms of number of hides exported were found in the semi-finished products which grew almost linearly between 2002 and 2010 (MK, 2011).

Up to 2006, the exports of cattle hides increased steadily, reaching a record 34.5 million of hides exported. A decrease in the exports was observed from 2007 to 2009, and growth resumed in 2010 reaching a value of 27.3 million hides. Until 2007 the largest export volume of leather concerned the wet blue stage, surpassed by the finished leathers. The minor changes regarding the number of

exported hides were found in the semi-finished products, which grew almost linearly between 2002 and 2010 (MK, 2011).

The profile of Brazilian industry by type of leather in the first quarter of 2011, considering export value was as follows: finished (57%), wet blue (21%), crust (17%) and wet blue split waste (5%). Considering the volume exported in number of leathers, the distribution is as follows: finished (42%), wet blue (34%) and crust (24%). It is important to note the growth in the export value of finished and crust leather in this quarter, compared to 2010, with 39% and 29% respectively (Courobusiness Magazine, 2011).

Table 2 summarizes important data about the Brazilian leather in 2009.

Table 2: Data of Brazilian leather sector in 2009

Number of bovine animals: 181,193 in thousand heads
Number of sheep and lambs: 16,817 in thousand heads
Number of goats: 9,683 in thousand heads
Production of bovine hides and skins: 39,5 million pieces
Production of bovine hides and skins (wet salted weight): 789,3 thousand pieces
Production of sheepskins and lambskins: 5,0 million pieces
Production of sheepskins and lambskins (dry weight): 4,5 thousand tones
Production of goatskins: 2,6 million pieces
Production of goatskins (dry weight): 2,1 thousand tonnes
Production of heavy leather from bovine animals: 36,6 thousand tonnes
Production of light leather from bovine animals: 1594,9 million square feet
Production of light leather from sheep and goats: 56,2 million square feet

Source: FAO, 2010.

An analysis performed by the authors in 224 companies showed that the Brazilian tanneries use mainly retanning to finishing process (39.3%). Figure 1 shows the other processes most widely used in Brazilian tanneries according to this study, i.e., complete tanning (24.1%), beamhouse to tanning (25. 9%) and finishing process (10.7%). The same study (total of 88 tanneries) also showed the same tendency in the state of Rio Grande do Sul.

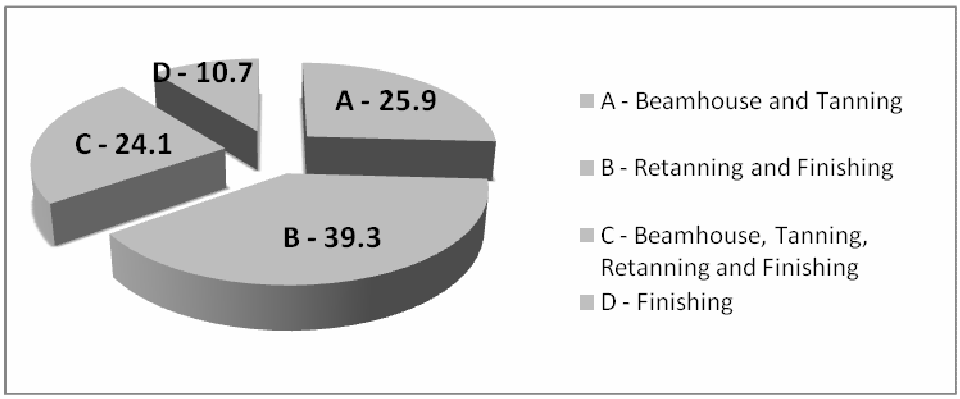

Figure 1: Distribution from the tanneries in Brazil according to their processing steps

2.2. Leather Articles

Historically, footwear articles are one of the main end uses of leather. However, other industrial uses have become increasingly significant for leather manufacturers, especially the furniture and

automotive segments. Although the share of the footwear industry in the leather sector has decreased, footwear production still accounts for 50% of world consumption of hides, according to FAO data (ICT, 2011).

Brazil is one of the world's largest footwear producers. It is estimated that about 65% of the world's leather production is used in leather footwear. This sector is among those that generate the greatest number of jobs in the country. The value of the leather produced for the automotive industry has been calculated at US$1,350 million internationally (ICT, 2011). The United States and the United Kingdom are the main buyers of Brazilian shoes, followed by Argentina, Venezuela and Italy. Although most large enterprises are based in Rio Grande do Sul, the Brazilian shoe manufacturing industry is now gradually expanding into the southeastern and northwestern regions of the country. Brazil produced in 2010 approximately 894 million pairs/year, 143 million being destined to exports (ABICALÇADOS, 2011).

3. Tanneries and the environmental legislations

Environmental legislation is the main motivation for the reduction in the environmental impact of industries. The laws are continuously being improved, and therefore there is a growing need to update industrial practices to minimize the impacts on water resources and waste generation. The current legislation on liquid effluent control in Rio Grande do Sul, Brazil follows:

a) CONAMA Resolution N° 357/2005: the National Council for the Environment classifies water bodies, offers environmental guidelines, and establishes the conditions and standards for effluent discharge and other steps.

b) Grant of the right to use water, Act N°. 10.350/1994: this act established the use of water resources in Rio Grande do Sul. The grant is regarded as an administrative act (concession, permission and authorization) of the use of water resources by the state government, aimed to ensure the quantitative and qualitative control of water uses and the effective exercise of rights of access to water by the various users (MMA, 1997).

c) CONSEMA Resolution Nº 128/2006: which sets the emission standards for the discharge of liquid effluents to surface waters in Rio Grande do Sul. According to the pertinent legislation, only effluents that comply with the emission standards shown in Table 3 can be discharged, directly or indirectly, to natural water reservoirs. The definition of the emission standards for the physical and chemical parameters of effluent discharges of Resolution Nº 128 takes into consideration, for different flow rates, the outflows of the receiving rivers. Thus, for higher flows, the discharge of effluent is subjected to more restrictive emission standards when effluents are discharged into receiving water bodies of low outflow.

Table 3: Emission standards for the liquid effluents of pollution sources

	Standard emissions	**Q (m^3/day)**
pH	6.0 to 9.0	
Oils and Greases (vegetable or animal)	≤ 30 mg/l	
Total Kjeldahl Nitrogen**	≤ 20 mg TKN/l	100 ≤ Q < 1.000
Sulphide	≤ 0.2 mg S^{2-}/l	
Total Chromium	≤ 0.5 mg Cr/l	
DBO_5	80 mg O_2/l	500 ≤ Q < 1.000*
DQO	300 mg O_2/l	500 ≤ Q < 1.000
SS	100 mg/l	500 ≤ Q < 1.000

Source: CONSEMA Resolution Nº 128/2006 (FEPAM, 2007).
*The flow rate exemplified corresponds to medium-sized tanneries in Rio Grande do Sul.

According to the referred resolution, the variation of emission standards for Total Kjeldahl Nitrogen (TKN) must either observe the concentration values established or operate at a fixed minimum efficiency (75%), as a function of flow rates. In order to comply with the minimum efficiency fixed for the Total Kjeldahl Nitrogen, removal must also observe the maximum limit of 20 mg/L Ammoniacal Nitrogen for any flow of effluent discharge (Table 3).

d) CONSEMA Resolution N° 01/1998: specifies the conditions and requirements for the self-monitoring system of pollution from industrial activities performed in the State of Rio Grande do Sul, including the completion of a form of SISAUTO Ordinance N° 01/85-SSMA of 29.07.85, which ratified the Technical Norm N° 01/85- SSMA.

e) CONSEMA Resolution N° 129/2006: this resolution applies to liquid effluents discharged to surface waters of the State of Rio Grande do Sul, the first Brazilian State to implement standards and criteria for the toxicity of effluents discharged in surface waters (FEPAM, 2007 and Aquim, 2010).

f) ABNT NBR-10004/2004: this standard classifies solid waste and its potential risks to the environment and public health, so that they can be properly managed. If local recovery is not possible, this waste is sent to landfills. The use of Cr salts in tanning process, generating waste containing chromium, which according this Brazilian standard are classified as Waste Class I - Hazardous, requiring treatment and specific disposal. The residues after tanning process are a management problem for the industry.

4. Wastewater treatment in tanneries

One of the distinguishing characteristics of the tanning industry is the use of large amounts of water and chemicals in its production process. The generation of high volumes of effluents with high loads of nitrogen, BOD, COD, sulphide and chromium is due to the need for execution of many extraction and chemical treatments of the raw hide (cleaning of the hide in beamhouse operations and chemical x collagen substrate reaction by tanning and pos-tanning steps), performed in an aqueous system in batches. In order to modify this reality and improve production process technologies, there are many studies to reduce, reuse, recycle or dispose of tanning process waste. According to Ganem (2007), the volume of liquid waste generated in the tanning process corresponds to 67.6% in the beamhouse, 21.7% in the tanning and 10.7% in the finished process (Sammarco, 2004 and BLC, 2009).

In wastewater treatment plants, preliminary mechanical devices precede physicochemical and/or biological treatment and are used to remove sand, grit, fibers, floating substances and materials in order to avoid obstructions and to enhance the performance of the subsequent treatment stages. Detention tanks also control wastewater flow. Physicochemical treatment is added to aid sedimentation in the chemical coagulation/flocculation of non-settleable matter from water, either to remove flocs or to break them down to less complex and less hazardous compounds. Biological treatment, mainly by activated sludge treatment is usually necessary to remove soluble and colloidal organic material from wastes. The liming baths are oxidized before being sent to the joint treatment and precipitation of chromium from tanning baths is often performed.

Besides performing the above mentioned steps, the tanneries in Rio Grande do Sul widely adopt the reuse of liming baths and operating systems with activated sludge with aerobic and anaerobic phases for nitrogen removal. The present concerns regard monitoring methods, toxicity analyses and the use of advanced treatment to remove nitrogen pollutants in wastewater in order to meet the emission standards for discharge of effluents into rivers and water bodies.

4.1. Advanced wastewater treatment and water reuse in tanneries

Advanced wastewater treatment processes are also called tertiary treatment processes because are used beyond the traditional secondary treatment to produce high quality water (Roing *et al*., 2008). These methods remove more contaminants from wastewater after conventional physicochemical and/or biological treatments. Common advanced methods remove phosphorous from solutions, oxidize ammonia to nitrate (nitrification), convert nitrate to nitrogen (denitrification), and remove or inactivate pathogenic bacteria and viruses (disinfection). In water reclamation, the objectives may be expanded to include the removal of heavy metals, organic chemicals, inorganic salts, and the elimination of all pathogens.

The ongoing development on advanced treatment systems enables wastewater regeneration requirements for segregated or integrated water recycling or reuse and the removal of difficult contaminants to meet environmental regulatory standards for discharge. Treatment systems such as sand filtration, ion exchange, adsorption, disinfection, advanced oxidation processes, membrane filtration, reverse osmosis, and advanced oxidation meet the requirements of recycling and reuse. All these systems basically lead to the segregation of depurated water flows that can be reused for any purpose or recycled in the industrial process.

The microbial processes involved in nitrogen transformations have traditionally been described by aerobic nitrification, anoxic/anaerobic denitrification and aerobic/anaerobic ammonification. However, intensive studies, often aimed at processes responsible for nitrogen removal from wastewaters, revealed or confirmed many other microbial processes responsible for nitrogen transformations like as anaerobic ammonia oxidation and aerobic denitrification (Vymazal, 2008). Nitrification is usually defined as the biological oxidation of ammonium to nitrate with nitrite as an intermediate in the reaction sequence. The process is influenced by temperature, pH value, alkalinity of the water, inorganic C source, moisture, microbial population and concentrations of ammonium-N and dissolved oxygen (Vymazal, 1995). Denitrification is most commonly defined as the process in which nitrate is converted into nitrogen gaseous via intermediates nitrite, nitric oxide and nitrous oxide.

Adsorption is one of the most commonly used methods for treatment of wastewater contaminated with heavy metals in coloring agents. In this process, the soluble substances are collected in a fluid and soaked in adsorbent material. The advantages of the adsorption processes for wastewater treatment are low initial investment, simple operation of the project, no-toxicity and greater efficiency compared to the conventional processes. Besides, the adsorption process is reversible, and, thus, changes in temperature or other process conditions may cause the easy removal of the absorbed solute, making its recovery and reuse possible. Studies are being conducted on the possible use of the adsorption process for the removal of other pollutants (ammonia, nitrite and nitrate). In the case of tanning wastewater, the studies on the adsorption process were focused on the removal of chromium and dye from the tanning and dyeing stages.

Membrane based processes offer a cleaner technology in the treatment of various industrial processes for separation, purification, concentration and fractionation of the solutes. The application of nanofiltration to the effluent from the liming and the ultrafiltration from the degreasing unit has been reported. The use of ultrafiltration and reverse osmosis to treat the soaking, deliming/bating and pickling effluents are conceptualized (Cassano *et al.,* 2001). The treatment of the chromium rich tanning effluents using ultrafiltration and nanofiltration is mostly studied (Saalan *et al.,* 2001; Scholz and Lucas, 2003; Cassano *et al*., 2003) for the recovery and reuse of tanning chemicals. However, application of the membrane based processes to treat each of the beamhouse effluent becomes is cost intensive. Hence, it is envisaged that the combined effluents coming from all the beamhouse processes can be treated by a two-step membrane based process (nanofiltration followed by reverse osmosis) after proper pre-treatment (using gravity settling, coagulation, and coarse filtration) (Cassano *et al.,*

2001). Kasparkova *et al*. (2009) extracted gelatinous proteins from untanned solid wastes generated by tanneries after elimination of hair and greases with chemical treatment.

There are other advanced wastewater treatments, such as the constructed wetland systems, which can be potentially used to enhance the overall biological performance, or else be an alternative to the conventional biological treatment.

Wastewater reuse is a rational practice that contributes to environmental protection. This technique is being implemented to reduce water consumption and the high costs of water treatment. Therefore, more than an environmental measure, water reuse has an economic impact. By the water reuse techniques, including recycling, the same water is used for different purposes or for the same purpose. A study (Gutterres *et al*. 2008, 2010) provided tools for the minimization of water consumption at tanneries by applying the reuse of water at some stages of the process. Water consumption and concentration of some contaminant parameters for each stage of beamhouse, tanning and pos-tanning operations are given and alternatives of water reuse were evaluated. A study was carried out on pilot and industrial scale to demonstrate the viability of reuse practices in the tannery industry, which has shown the feasibility of wastewater streams reuse in beamhouse steps of leather processing. Finally, a mathematical program for mass integration was applied to solve the problem of water reuse in the beamhouse steps.

5. Solid wastes generated in the leather processing

Solid waste released untreated into the environment may cause serious harm due to heavy metal pollution, the presence of pathogens, toxic substances and the high organic load. Chrome-tanned waste makes it difficult to handle effluent sludge separated from unwanted waste with decanting centrifuges. On the other hand, the solid waste from vegetable tanning processes generates great amounts of nitrogen and organic matter for agricultural use. The economic disposal of sludge from industrial waste treatment processes is often one of the most difficult problems encountered. The combination of operations for sludge treatment (conditioning, dewatering, drying, incineration, materials recovery) and the disposal techniques required in a particular situation will depend on many variables. Alternatives are being sought to address environmentally safe methods, in order to ensure that waste treatment meets the current environmental laws and to raise the awareness of the professionals involved in the sector.

The solid waste produced by industry tannery is major source of environmental contamination due to organic matter, salts, sulphides, heavy metals (mainly Chromium), and sludge treatment plant effluent. When processing 1 ton of hide salted are produced approximately 200 to 250 kg of finished leather, consuming 500 kg of chemicals products, 15 to 50 m^3 of water and 2.600 to 11.700 kWh of energy and generating an average of 600 kg of solid waste (Ganem, 2007, BLC, 2009). Therefore, only 20% of the raw material is processed into finished leather and over 60% of chromium used in the process is discarded in solid and liquid wastes (Kolomaznika *et al*., 2008).

5.1. Valorization of solid wastes generated in tanneries

The international leather literature abounds with suggestions of options for conversion of solid wastes into by-products: bovine hair for fertilizer, goat hair for felt manufacture, raw trimmings for glue, fleshings for glue and tallow, poultry feed supplement, biogas, composting, splits and trimmings (can undergo extraction for the preparation of dispersions of collagen transformed later into gels, films, pomades, powder, etc. for cosmetic and medical applications by exploiting, respectively, regenerating properties and cicatrizing character of collagen), dog chews; wet blue shavings and trimmings for leather board and hydrolysis (for the preparation of gelatins usable in food and photographic industries), vegetable and Cr leather shavings for leather board, sludge for composting, gasification

and briquetting etc. Controlled incineration and pyrolysis of combined wastes have been proposed, tested and there are a few industrial scale plants in operation. However, in reality, there are fewer alternatives. Typically, tanners in industrialized countries pay to have the waste removed; in developing, they are often able to sell them. In general, untanned solid wastes are subjected to a biological degradation, which creates problems of transport and handling, and difficulties of discharge in landfill (UNIDO, 2007 and Kasparkova *et al*., 2009).

In Brazil, the main uses of untanned wastes include the production of oils and fatliquors, pet bone, sticks, dog-toy, agricultural use of limed sludge from treatment plants. As for the tanned wastes, chromed leather shavings have recently been used in fertilizer products for export, as well as in intensive research of controlled incineration of residual waste, showing good results for chromium recovery and energy generation. Unfortunately, most leather wastes are disposed in special landfills for hazardous materials.

6. Researches in Laboratory for Leather and Environmental Studies

The research group from the Laboratory for Leather and Environmental Studies (LACOURO) at Chemical Engineering Department of Federal University of Rio Grande do Sul (UFRGS) works for the development of effluent and waste treatment alternatives and eco-friendly technologies to avoid environmental impacts by the leather production, such as innovative technologies for improvement in leather sector. The principal subjects and the corresponding researches developed in last ten years are summarized in Table 4:

7. Conclusions

This article addressed the importance of the tannery activity in Brazil, reporting the most significant information on the Brazilian leather sector and other indicators. The major environmental problems faced by the Brazilian leather industry were discussed, as well as the current environmental laws on effluent control. Tannery industries generate a considerable amount of sludge, shavings, trimmings, hair and other general wastes, as a natural consequence of leather production. Solid wastes such as sludge, tanned and untanned waste materials are inevitable by-products of the leather manufacturing process. Thus the main uses of leather by-products were reported aiming at their valuing. One study performed by the authors showed that Brazilian tanneries employ mainly the retanning to finishing (39.3%), beamhouse to tanning (25.9%) and complete tanning process (24.1%). The waste water treatment, advanced treatment and wastewater reuse with greater potential were presented in this work. Other studies and the main research lines and developments conducted at UFRGS, in the Laboratory for Leather and Environmental Studies/LACOURO, aimed to obtain information on the latest technologies and improvements in the leather sector, were also reported.

Table 4 - Summary of researches at LACOURO-UFRGS

Subject	Researches
Applications of biotechnology	- Enzyme characterization, screening and isolation of bacterium, producers of proteases to be used in leather unhairing and other applications (Dettmer *et al.* 2011); - Tests of biotechnological routes for leather waste treatment (Gutterres *et al*., 2009).
Developments on leather retanning, fatliquoring and dyeing	- Leather retanning with hydrolyzed protein (Gutterres and Silva, 2010); - Study of the fatliquoring with high exhaustion (Santos and Gutterres, 2007; Gutterres and Santos, 2009); - Development of novel natural dyes for eco-friendly leather.
Material balance, water management and wastewater reuse in tanneries	- Characterization of inlet and outlet streams in steps of beamhouse and tanning processes in order to make a material balance to reduce the environmental and economical impacts in tanneries; - Assessment of water management and clean technologies in tanneries (Aquim *et al.,* 2011); - Alternatives for wastewater reuse in pilot and industrial scales (Gutterres, *et al*., 2008 and Gutterres *et al*., 2010).
Effluent treatment	- Evaluation of nitrogen contamination of residual baths in tannery and biological nitrogen removal (Gutterres *et al*., 2010); - Adsorption of dyes and other contaminant substances.
Olein production	- Olein production from the residue constituents of hide pre-fleshing (Priebe and Gutterres, 2010).
Thermal treatment of wastes	- Incineration of leather and footwear wastes and chrome recovery from the ashes; (Godinho *et al*., 2007); - Control of atmospheric emissions and vapor generation from the incineration process.
Chromium recovery from leather wastes	- Chemical and enzymatic treatment for chromium and peptides recovery from leather wastes (Gutterres *et al.*, 2009); - Obtaining sodium chromate from ashes of thermal treatment of leather and footwear industry wastes (Dettmer *et al*., 2010a, Dettmer *et al*., 2010b and Dettmer *et al*., 2010c).
Gas emissions in landfills	- Quantification of atmospheric pollutants (biogas) generated in landfills.

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