Evaluation of Chemical Products in Leather Post-tanning Process and Their Influence in Presence of Neutral Salts in Raw Tannery Effluent

by

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Abstract

In the leather industry, several chemical products are used for the transformation of the raw hide into the demanded final product. The production flow and the post-tanning of wet-blue leathers may vary according to the available technologies and the type of final item produced. Previous operations and processes are also relevant, particularly the steps of unhairing-liming and tanning process. During the effluent treatment process, there is a great difficulty in removing soluble salts, such as sodium chloride and sodium sulfate in conventional effluent treatment stations. These salts might compromise the biological treatment of tannery wastewater and adversely impact the receiving water bodies, causing environmental pollution. Further, the presence of chlorides and sulfates might interfere in the implementation of the bath reuse system or in the recycling of the treated effluents in the post-tanning process. Therefore, this work aims to investigate the measures used to control the production of sodium neutral salts, such as the sodium chlorides and sulfates, contained in the chemical compounds uses in the industry that performs post-tanning in bovine wet-blue leather, mostly for automotive and furniture upholstery. The work was carried out following the production of the factory for six months, with approximately 1485 whole wet-blue leathers being processed per day, with an average production of 7500 m^2 of crust leathers per day. The work methodology was based on the diagnosis of the initial situation of the tannery, chemical analyses of the supplies employed and in proposals of action based on this initial profile. The work also involves the checking of the water consumption and the evaluation of the residual baths. The identification of the chemical products in the formulation that contribute directly to the presence of neutral salts in the gross effluent and their presence in the residual baths were among the main results observed in the present work. In order to determinate sodium, chlorides and sulfates, two methodologies were tested (ion chromatography, for chlorides and sulfates; and absorption spectroscopy, for sodium), showing similar results.

Introduction

Leather production has been a highly relevant activity in many countries since ancient times and currently leather industry plays an important role in the economy of several developing countries.[1] Brazil, China and India have the biggest cattle herd in the world.[2] On the other side, leather industries are also one of the major polluters worldwide due to its highly toxic constituents and thus, adequate treatment is required to manage the pollution risks.[1,3–5] The transformation of hides in leather involves several chemical and mechanical operations that deeply clean the hide and improve its appearance and physical and chemical properties.[6] The current literature has many examples of important articles about the control and reduction of the environmental impact of the beamhouse and tanning processes, which does not occur, with the same frequency, for the post-tanning process and finishing of leathers.

During the post-tanning, leathers are submitted to the steps of setting-out, classification, standardization, cutting-out, washing, conditioning, neutralization, retanning, dyeing, fatliquoring, fixation, and washing.[7] The effluents of the wet-blue post-tanning plants consists in an aqueous solution of the products not fixed in these processes and the products of the reactions that take place in these steps. However, the processes and the chemical supplies involved in the post-tanning depend on the type of tanning performed and on the kind of leather that is intended to be produced, which directly affect the emissions.

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Among the chemicals used in the post-tanning of leathers for automotive upholstery, are the cationic agents, such as the formic acid and chrome salts; the anionic agents, such as formate and sodium bicarbonate; surfactants; vegetable tannins, and synthetic tannins; resins; oils and oil emulsions; dyes; fungicides and fillers.[8] In general, about 15% of the chemical products used are estimated to be retained in the leather, while most of them are lost in the liquid effluents and solid wastes.[9]

The post-tanning effluent is difficult to characterize, since the technology and products used may vary widely from industry to industry and according to the market segments: automotive upholstery, furniture, footwear, artifacts, and clothing.[10] Although the presence of neutral salts, such as sodium chloride and sodium sulfate, is usually associated to the steps of beamhouse and, more specifically, to the deliming, pickling and tanning steps, these salts might be present in the post-tanning chemical supplies such as the retanning agents, the dyes, and the dispersants. When hides are processed without conservation by salt, the chloride pollution from the post-tanning step corresponds to 11% and that from the tanning step corresponds to 66%. Regarding the sulfates, these anions result mainly from the tanning (53 to 60%) and from the post-tanning (20 to 22%) processes.[11] The presence of sodium sulfate in the chemical supplies is frequent in the chrome sulfate, synthetic tannins or, even in the dyes, with the purpose of helping in the dispersion of substances to the leather. However, sodium sulfate might also be formed by the reaction of neutralization of the leather. The presence of sodium chloride in the post-tanning is usually lower than that of sodium sulfate.[11,12]

The gross effluent of a post-tanning industry is composed, in a higher or lesser degree, by the following components: residues of leather fibers; surfactants; chrome (Cr^{+3}); cations such as sodium, ammonium, calcium, magnesium, silicon, and aluminum, present in chemical products or resulting from the process. Anions such as sulfates, chlorides, bicarbonates or carbonates; dyes usually anionics (acid and direct); vegetable tannins (chestnut, tara, acacia); and synthetic tannins (phenolic and naphthalene); acrylic, melamine, and styrene maleic resins, and polyurethanes; oils and oil emulsions; fillers; preservatives (fungicides) used in fatliquoring and also present in chemical products, and organic solvents.[8,12,13]

The components of the homogenized effluent, after screening, in industries that process leather in the post-tanning step are shown in Table I. The parameters are presented in kilograms of pollutant per ton of processed leather, and the production of effluents is in m^3 of effluents per ton of processed leather.

Table I

Components of the effluent of post-tanning tanneries of wet-blue leathers.

Parameters	IULTCS (2008)[14]	Black et al. (2013)[12]	
	Tanneries that adopt good practices	Conventional Process	Advanced Techniques
Effluent	4-8 m^3/t	7-13 m^3/t	3 m^3/t
Suspended Solids (SS)	10-20 kg/t	6-11 kg/t	1-2 kg/t
Total Chrome ($Cr+^3$)	1-2 kg/t	1-2 kg/t	0,1-0,4 kg/t
Chemical Oxygen Demand (COD)	15-40 kg/t	24-40 kg/t	10-12 kg/t
Biochemical Oxygen Demand (BOD_5)	5-15 kg/t	8-15 kg/t	3-5 kg/t
Total Kjeldahl Nitrogen (NTK)	1- 2 kg/t	1-2 kg/t	0,2 -0,5 kg/t
Ammoniacal Nitrogen $N\text{-}NH_4^+$	-	0,3-0,5 kg/t	0,15 kg/t
Chloride (Cl^{-1})	5-10 kg/t	5-10 kg/t	3-6 kg/t
Sulfate $(SO_4)^{-2}$	10-40 kg/t	10-25 kg/t	4-9 kg/t
Oils and Fatliquors	3-8 kg/t	-	-
Total Dissolved Solids (TDS)	40-100 kg/t	-	-

Table I shows the usual characterization of the post-tanning effluent that presents variations due to the type of article produced: automotive upholstery, furniture, footwear and others. The data shows the low biodegradability of the effluent, observed by the relationship between BOD values and COD values, which is usual in these processes. With respect to the amount of chloride and sulfate in the effluent, it is verified that there is predominance of the sulfate anion in relation to the chloride anion. In addition, the adoption of advanced techniques in the post-tanning process has a more direct impact on the reduction of the anion sulfate than on the reduction of the chloride anion in the effluent.[12] This can be expected since the presence of the chloride is usually more characteristic in the processes of preservation of the hides and in the steps of riverside and tanning, although its removal continues in the post-tanning stages, especially in the washes. Total dissolved solids (TDS or neutral electrolyte) has become a major problem in many countries. For example, some have set up regulations to limit the concentration of salts in effluents after waste water treatment; such as South Africa (1350 mg/l of TDS), Italy (1200 mg/l of chloride, 1000 mg/l of sulfate), India (2100 mg/l of TDS, 1000 mg/l of chloride, 1000 mg/l of sulfate). These limits apply for effluent from all industries, not just the leather industry.[14]

For tanneries with implemented good manufacturing practices, the environmental committee of IULTCS observed that the water consumption varies from 4 to 8 m^3/ ton of leather.[14] Besides, tanneries that employ advanced techniques reach up to 3 m^3/ ton of leather and the traditional ones from 7 to 13 m^3/ton of leather.[12] Water consumption in industries that process leather from wet-blue, according to different authors[11,13,15] vary from 6 to 21.5 m^3/ ton of leather. The water consumption in leather processing industries might be separated in at least four parts: water for the leather processing, cleaning, operation of the effluent treatment station (ETS), and energy generation.

In face of this context, the present work aims to investigate control measures and minimization strategies for sodium neutral salts, such as chlorides and sulfates, present in the chemical products found in an industrial plant that performs the post-tannery of bovine wet-blue leathers, mostly for automotive and furniture upholstery. In order to determinate sodium, chlorides and sulfates, two methodologies were tested (ion chromatography, for chlorides and sulfates; and absorption spectroscopy, for sodium), and the analysis of ashes content by gravimetric method.

Experimental

This work was performed in an industry that produces mainly crust bovine leather for automotive upholstery and furniture from standardized wet-blue leathers. The study was conducted from January to June 2015 (six months) with approximately 1500 whole leathers produced per day, with an average daily production of 7500 m^2 of crust per day. Besides the post-tanning, pre-finishing, drying, and finishing of leather facilities, the company has an ETS with the preliminary, physical-chemical and biological treatments, lacking the ability to remove significant amounts of soluble dissolved solids.

The study consisted of the selection of the most produced leathers, and the listing of the chemical substances used, considering their amounts without, however, revealing the formulation of the article. The work also involved the checking of the water consumption and the evaluation of the residual baths.

Gathering of Production Data

The first part of the methodology was the identification of the tannery profile, through the selection of the most produced items, and its formulation with the identification of the chemical supplies.

Identification and Characterization of the Main Chemical Supplies Used

The selection of the chemical products was based on the following criteria:

- Identification of all the chemical products employed;
- Descending order of the products in terms of their amount used;
- Selection of the products with the highest amounts in the formulation until the minimum of 85% of the total mass of the all chemical supplies used;
- Removal from the study of the chemical products that do not reveal the potential presence of sodium, sulfate and chloride in their formula;
- Evaluation of the chemical products regarding the presence of neutral salts such as sodium sulfate and sodium chloride.

Characterization of the Critical Chemical Products Regarding the Presence of Neutral Salts

The characterization of the selected chemical products (dyes, synthetic tannins and vegetable tannins) consisted of sulfate and chloride analyses by ion chromatography, sodium analysis by absorption spectroscopy and the analysis of ashes content by gravimetric method. Stoichiometric calculations were performed in order to compare the two methods (ion chromatography and absorption spectroscopy) used to determine the ions of interest.

Characterization of the Residual Baths and Water Consumption Measurements

The characterization of sodium sulfate and sodium chloride was performed in the baths of the post-tanning steps of the leather for automotive upholstery. The sulfate and chloride parameters were determined by ionic chromatography and the sodium by atomic absorption spectroscopy.

The measurement of water consumption was made through the instruments present in the tannery. The "*Aqua-mix*" meter was used to measure the water volumes consumed in the productive process and a hydrometer was employed to determine the volume of the gross effluent sent to the ETS.

Results and Discussion

Production Data

The major raw material of the tannery is whole wet-blue leathers, tanned and standardized between 1.1 and 1.2 mm thick. The average monthly production of leathers in the period was 154,778 m^2, which was equivalent to 7,500 m^2 (80,729 ft^2) of crust leathers produced per day, characterizing a medium-sized tannery in Brazil. The leathers for automotive and furniture upholstery are sold in crust and the leathers for shoes are finished in the plant itself. Regarding the segmentation of the investigated period, the result can be seen in Figure 1.

The formulation of the automotive upholstery in the data sampling period corresponded to an average of 67%, while leather for shoes represented 16% and furniture upholstery 17%. Therefore, automotive upholstery was the formulation chosen to be evaluated.

Chemical Supplies Used in the Formulations

The analysis of the formulation of the automotive leather shows that 18 chemical supplies were employed in the post-tanning step. The percentage of the products over the hide mass in the formulation was 47.55%. These values are referred to the mass of wet-blue leathers (with an average water content of 45% in the investigated industry). Table II shows the chemical products employed in the formulation of the automotive leather in decreasing order of use.

The twelve first products identified in Table II are the most consumed supplies with amounts varying from 2 to 8.5% over the leather mass. These products amount to 43.1% of the total of 47.5% of the chemical products used, representing 91% of the total mass. Among the chemical products most consumed, those with a higher potential of presenting sodium salts were heuristically identified. These chemical products are presented in Table III.

The six products identified in Table III are the most consumed supplies with a higher potential of presenting sodium salts.

Characterization of the Critical Chemical Products Regarding the Presence of Neutral Salts

Table IV shows the characterization of the retanning agents and the acid dye used in the evaluated tannery regarding the presence of chloride, sulfate, and sodium, besides the content of ash.

From the concentrations of chloride and sulfate anions by ion chromatography, stoichiometric calculations were performed to determine the concentration of the sodium chloride and sodium sulfate salts. The concentrations calculated of these neutral sodium salts are shown in Table V. Some stoichiometric calculations from the sodium concentrations obtained by absorption spectroscopy were also performed in order to compare the two analytical methods.

For the acid dye, usually employed with the amount of 2.3%, the amount of ash in the product was 66.1%. This result was confirmed by the ion chromatography of the chloride and sulfate anions that represented the result of 67.1% of salts (61.6% of sodium chloride and 5.5% of sodium sulfate). Thus, sodium chloride and sodium sulfate correspond, approximately, to total ash found. In addition, the sodium present in the sodium chloride is equal to the difference between the sodium chloride calculated and the chloride found analytically (61.6% - 37.4%), which is equivalent to 24.2% of sodium. Sodium present as a sulfate is equal to the difference of the calculated sodium sulfate and the sulfate found in the analysis (5.5% - 3,7%), which is equivalent to 1,8%. The sum of both sodium salts is equal to 26%. This also confirms the result found for sodium directly by absorption spectroscopy (26.2%), showing a good equivalence of the two adopted methods (ion chromatography and absorption spectroscopy). The results reflect high load of salts in the dye,

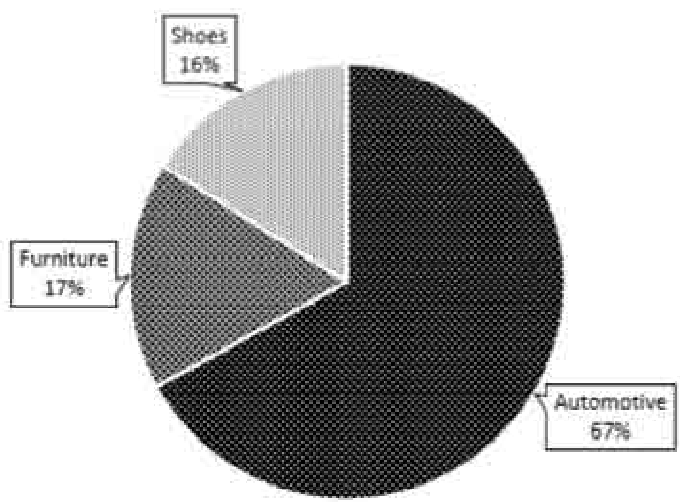

Figure 1. Types of leather items produced in the period evaluated in this work.

which does not mean dyeing power. Therefore, the methodologies used allowed the detection of soluble salts in the supplies and, in this case, showed the low efficiency of the acid dye regarding its dyeing power and the presence of chloride salts, especially sodium chloride.

For the synthetic tannin, employed with the amount of 6, the presence of sodium in the product was recorded as 12.3% in mass, by absorption spectroscopy, of which 37.3% are in the form of sodium sulfate (by stoichiometry) and 25% of sulfate. In this product, the amount of sulfate by ionic chromatography was 25.2%, very similar results. The amount of identified sodium chloride was lower than 1% and, therefore, is not considered significant. These values are compatible with the result of the gravimetric analysis of 41.6% of ash and reveal a high load of inorganic matter in this product.

For the Neutralizing synthetic tannin, employed with the amount of 3.5%, the sodium content obtained by absorption spectroscopy was 9.2% and, stoichiometrically, 28.4% of sodium sulfate. For this product, the amount of sulfates analyzed by ion chromatography was 19.2%, which also represents 28.4% of sodium sulfate, which validates the results. The content of sodium chloride recorded in this item, lower than 1%, was not significant.

Table II
Chemical products in descending order of use.

Item	Chemical product	Role in the process	% mass
1	Synthetic and natural oil (liquids)	Softness, Resistance to Fogging	8.5
2	Synthetic retanning agent (powder)	Filling	6
3	Tara vegetable tannin (powder)	Elasticity Reduction, Solid in Light	4.5
4	Neutralizing synthetic tannin (powder)	Buffering Neutralizer	3.5
5	Styrene-maleic resin (liquid)	Filling of Empty Parts	3.5
6	Acrylic resin (liquid)	Grain Filling and Filling of Empty Parts	3
7	Natural, synthetic, and emulsifying oils (liquid)	Softness, Resistance to Fogging	3
8	Formic acid (liquid)	Fixation, Acid Wash	2.8
9	Acid dye (powder)	Color	2.3
10	Chromium hydroxide sulfate III (powder)	Dechroming	2
11	Sodium formate (powder)	Buffering Neutralizer	2
12	Compact retanning agent (powder)	Discrete Filler	2
13	Neutralizing synthetic tannin (liquid)	Buffering Neutralizer	1.5
14	Direct dye (powder)	Dye Intensifier	1.2
15	Sodium bicarbonate (powder)	Neutralizer	0.6
16	Surfactant (liquid)	Tensoactive	0.1
17	Sulphited fish oil (liquid)	Softness, Penetration	1.0
18	Fungicide (liquid)	Avoid fungi	0.05
	Total		**47.5**

The product Tara tannin, used with the amount of 4.5%, showed no significant amounts of sodium chloride and sodium sulfate and only 4.2% of ash. Therefore, this product does not present high levels of sodium neutral salts.

The product Compact retainer, employed with the amount of 2%, presented no chlorides, but 12.2% of sodium sulfate and 36.6% of ash, which reveals a high inorganic load, although with a lower content of sulfate and chloride.

Assembling the results of the chemical analysis it was possible to calculate the amount of sodium chloride and sulfate chloride that is consumed in the post-tanning step per ton of wet-blue leather from the retanning agents and from the dye. The result of this compilation is shown in Table VI.

Concerning the chrome salt, used in the amount of 2%, and identified as monobasic chromium sulfate III ($CrOHSO_4$), no test was made to determine the concentration of sodium sulfate in this supply, since the composition provided by manufacturer was used: 25-26% of Cr_2O_3, 33.3%-35.0% of basicity and on average 22% of sodium sulfate (Na_2SO_4), which is equivalent to 14.87% of sulfate (SO_4^{-2}). The present mass balance does not consider the sulfate of the monobasic chromium sulfate.

Therefore, according to the mass balance of the main formulation carried out during the evaluation period, a ratio of sulfate (27.36 kg/ton of wet-blue leather) is observed at least three times higher than that of chloride (8.70 kg /ton of wet-blue leather). The chloride supply is directly connected to the dye used.

The sulfate and sodium ions are present in all the baths. Although sodium sulfate and sodium chloride might be used for

Table III
Chemical products with higher potential of sodium salts presence.

Chemical Product	% mass
Synthetic retanning agent (powder)	6
Tara vegetable tannin (powder)	4.5
Neutralizing synthetic tannin (powder)	3.5
Acid Dye (powder)	2.3
Chromium hydroxide sulfate III (powder)	2
Compact retanning agent (powder)	2
Total	**20.3**

Table IV
Characterization Analyses of the retanning agents and of the dye.

Products	Anion Chloride (%)*	Anion Sulfate (%)*	Cation Sodium (%)**	Ash (%)***
Synthetic tanner (powder)	0.04	25.2	12.3	41.6
Tara vegetable tannin (powder)	0.15	0.08	0.07	4.2
Neutralizing synthetic tannin (powder)	0.02	19.2	9.2	32
Compact retanning agents (powder)	0.02	8.29	3.9	36.6
Acid dye (powder)	37.4	3.7	26.2	66.1

* Ion chromatography
** Absorption spectroscopy
*** Gravimetric analysis.

Table V
Sodium chloride and sulfate concentrations in the retanning agents and dye, obtained from stoichiometry.

Chemical Products	NaCl*	Na_2SO_4**
	(Stoichiometry from ion chromatography)	(Stoichiometry from ion chromatography)
Synthetic retanning agent	0.07%	37.28%
Tara vegetable tannin	0.25%	0.12%
Neutralizing synthetic tannin	0.03%	28.4%
Compact retanning agent	0.03%	12.26%
Acid dye	61.6%	5.5%

*Stoichiometric conversion: anion Cl^{-1}(atomic mass: 35.5) to NaCl (molecular mass: 58.5).
**Stoichiometric conversion: anion SO_4^{-2} (atomic mass: 96) to Na_2SO_4 (molecular mass: 142).

dispersion, they do not connect to leather fibers, therefore, their main destination is the effluent. Besides that, in excess, they might even hinder the passage and dispersion of products like dyes and retanning agents, particularly in the fatliquoring emulsions with low stability to electrolytes, causing an effect opposed to the intended one. The neutral salts are extracted by washing and are not removed adequately in the conventional ETS.

The calculated chloride value of 8.7 kg/ ton of wet-blue leather, is within the range indicated by Black *et al.* (2013),[12] of 5 to 10 kg/ ton, for tanneries with conventional processes. In practice, the chloride value is mainly due to the acid dye. In this case, the use of acid dyes with a lower amount of salts, is indicated.

The recorded value for sulfate, 27.36 kg/ton of wet-blue leather, is higher than those presented by Black *et al.* (2013),[12] of 10 to 25 kg/ ton, for tanneries with conventional processes, being comparable to the values indicated in the document of IULTCS (2008)[14] of 10 to 40 kg/ton. In these calculated values the sulfate from other chemical compounds is not included, such as the sulfate of chrome salts, which by hydrolysis goes to the residual baths. Regarding this parameter, the direct influence of the synthetic retanning agent was recorded, since 25.2% of this item is composed of sulfate that represents more than 50% of the sodium sulfate provided by the products analyzed in the formulation.

In the cases of the dye and of the synthetic retanning agent, as well as in the other products, there is no indication of the presence of sodium chloride or sodium sulfate in the technical information and Material Safety Data Sheet (MSDS) provided by the manufacturers.

Table VI

Sodium chloride and sodium sulfate of the retanning agents and the dye per ton of wet-blue leather.

Chemical Product	Formulation (%)	Mass (kg)	Cl^- (%)	Cl^- (kg)	SO_4^{-2} (%)	SO_4^{-2} (kg)
Synthetic retanning agent	6	60	0.04	0.02	25.2	15.12
Tara vegetable tannin	4.5	45	0.15	0.07	0.08	0.04
Neutralizing synthetic tannin	3.5	35	0.02	0.01	19.2	6.72
Compact retanning agent	2.0	20	0.02	0.00	8.29	1.66
Acid dye	2.3	23	37.4	8.60	3.7	0.85
Chromium hydroxide sulfate III (Na_2SO_4 content: 22%)*	2.0	20	-	-	14.87	2.97
Total				**8.70**		**27.36**

* Calculation based on the technical specifications of the manufacturer.

Table VII

Water consumption in litters per m² of wet-blue leather.

Period	Nº Leathers/ day	Water Volume (m^3/ day)	Area (m^2/day)	Weight (kg/day)	Liters/m^2 (L/m^2)	Liters/kg (L/Kg)
April *	1463	136218	6790	7469	20.1	18.24
May*	1580	141739	7402	8142	19.1	17.41
June*	1413	149211	6890	7579	21.7	19.69
Average	**1485**	**142389**	**7028**	**7730**	**20.29**	**18.42**

*Monthly averages.

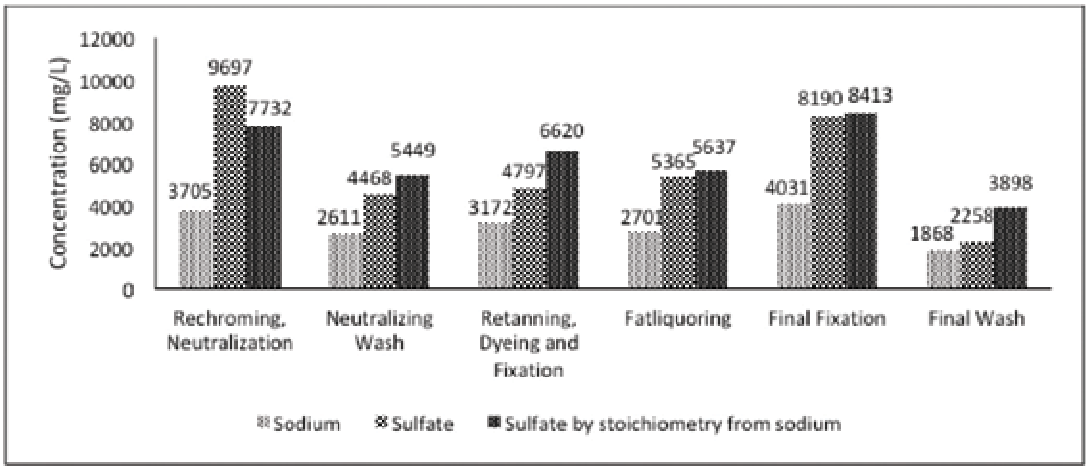

Figure 2. Presence of sodium and sulfate ions analyzed and the stoichiometrically calculated sulfate from the sodium content.

Water Consumption

Water consumption in leather processing industries can be separated into at least four parts: water for leather processing, cleaning, operation of effluent treatment plants (ETS) and power generation. The quantification of each consumption separately was not the object of this work.

The water consumption monitoring was daily assessed from April to June 2015. The values obtained are presented in Table VII.

In the practice of this tannery, the wet-blue leather mass is determined by a factor that relates the footage of the lot (m^2) with weight (kg). The factor depends upon the type of leather produced, with a factor of 1.1 being adopted in this work. For this company, the daily processing of 1485 wet-blue leathers, approximately 7028 m^2 of wet-blue, means an average production of 7500m^2 of crust leathers per day.

Average monthly values from 17.41 up to 19.69 liters of water per leather kilogram are compatible with the values appointed by Gutterres (2008),[16] but higher than those indicated by Black *et al.*[12] for conventional tanneries, between 7 to 13 m^3/t.

Thus, considering the processing in the period of 7.73 tons of wet-blue per day, being 2/3 of the production destined for automotive upholstery, and then 5.18 tons of wet-blue are used for automotive upholstery. The sulfate balance, shown in Table VI, shows 27.36 kg of the anion sulfate per ton of wet-blue leather, which equals 141.7 kg of sulfate are used in the process per day. Considering the water consumption of 142389 liters, shown in Table VII, it is estimated that 995 mg of sulfate per liter of water are provided in the process for this formulation.

Characterization of the Residual Baths

The concentration of sulfate, chloride and sodium ions in the post-tanning residual baths comes from at least four sources: wet-blue leathers, the chemicals used in these steps, the quality of the water used and the reactions occured in the process, as, for example, in the deacidulation (neutralization) step. They also depend on specific operating conditions such as drainage of the drum at the end of each stage, and the operational conditions such as water volume, temperature and process time. Thus, the extrapolation of the results to different post-tanning processes should consider the conditions previously stated.

Figure 2 shows the characterization of sodium and sulfate in the baths of the post-tanning steps of the automotive leather. The wet finishing steps that contribute to the effluent of these plants are the following: neutralization, rechroming, dyeing, fixation, fatliquoring, and washes. Also presented in this Figure is the sulfate obtained by stoichiometric calculation from the sodium.

Comparing the sulfate found directly in the analysis with the sulfate calculated from the sodium analyzed, it is observed that the same levels of concentration are found in different residual baths. In the rechroming, the highest amount of sulfate found in the residual bath analysis of this step is due to the hydrolyzed sulfate from the basic chromium III sulfate ($CrOHSO_4$) used in the process. Then, in the neutralization baths (washing) and dye fixation, the amounts of sulfate found are lower than the calculated values from the sodium. This derives from the presence of the neutralizers formate (HCOONa) and sodium bicarbonate ($NaHCO_3$), and because of that, the calculated values are higher than the values found in the residual baths. The increase of the amounts of sulfate in the final grease baths is justified by the presence of the synthetic retanning agents in the formula, which have a high amount of sodium sulfate. Usually, the presence of neutral salts in the chemical supplies is not identified by the vendors of these products or, when that happens, their quantification is very rare. In order to reduce the presence of sulfate, chloride and sodium, the use of liquid dyes and tannins, due to the lower amount of salts is recommended.[14]

In addition, the usual practice of retanning increases the sodium sulfate content, due to the presence of this salt in the chromium product in the form of powder. The use of a mixture of chromium salt with synthetic tannin in liquid form is a recommended practice, once it does not change the characteristics of the article to be produced.

Conclusion

Current processes are moving towards reducing water consumption, which can in many cases increase the concentration of dissolved solids such as chlorides and sulfates. Attention should be given not only to the concentration of dissolved solids (TDS) from the chloride and sulfate anions found in the mixed effluent, but mainly to the reduction of TDS at the source, especially the amount present in the chemicals. However, the important role that neutral salts play when present in adequate amounts in the formulation should be considered.

The present study detected the presence of neutral sodium salts, such as chloride and sulfate, in chemical products frequently used in the leather industry, especially in the post-tanning step. In the case herein reported, the high amounts of chloride were derived from the acid dye used and the sulfate concentrations are due to the synthetic retanning agents. The use of these chemical products contributes to the presence of high concentrations of chloride and sulfate ions in the residual baths, which are not removed in the conventional treatment of liquid effluents and, hence, increase the pollutant load released in the water bodies. In order to reduce the presence of sulfate, chloride and sodium, the use of liquid dyes and tannins, due to the lower amount of salts is recommended.

The analytical methodology used in the present work was efficient to detect the presence of the sulfate, chloride, and sodium ions, as well as to estimate the ash content. It is worth highlighting that the analytical techniques are simple and easily replicable, optimizing the use of these in other application in the leather industry.

Although it is less feasible to recycle post-tanning baths, compared to beamhouse and tanning baths, knowing the characteristics of post-tanning residual baths allows the identification of the chemicals at the source, increasing the efficiency of the process and creating ways of practicing the reuse or recycling of liquid effluents, as well as the reduction of the amount of contaminants in the raw effluent. The management model of chemical products traditionally implemented largely in industrial plants is a model in which the chemical products are sold to clients in order to fulfill certain functions in the process and, usually, it is more profitable to sell chemical products with higher prices or in large amount. In many cases, this is related to the release of products that are problematic to the environment and with negative consequences to the future availability of resources.

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