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Liming Baths Recycling, Case Study Of An Algerian Tannery

Tabak Messekine Djamila*[1], Dilmi Fatiha[2]

[1,2]Faculty of sciences of nature and life University of Mascara, Algeria

Correspondingauthor*:E-mail:messekinedjamila@gmail.com

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Abstract

The tanning industry is among the most polluting industries worldwide, negatively impacting the environment. Indeed, two main factors are at play: the volume of effluent as well as the significant resultant pollution load contained within. In this context, a study is critically needed to safeguard both the environment and the quality of leather, which must retain its aesthetic value. Therefore, we have undertaken to conduct an in-depth study to meet this objective.

The aim of this study was to assess the feasibility of recycling liming baths generated by industrial tanneries, in response to industry concerns that this method may not be practical at an industrial scale and could affect the quality of leathers produced.

Analysis of the raw effluents revealed pollutant concentrations far exceeding regulatory limits. A 21-cycle recycling process of bath reuse was then tested. The results show that this process enables the recovery of 66.87% of sulfides and 71.50% of lime while significantly reducing pollutant loads. Above all, extensive physicochemical tests certify that the reuse of recycled baths does not affect the characteristics and technical performance of the obtained leathers, which meet current quality standards.

Thus, in addition to its environmental benefits, this closed-circuit bath recycling process addresses industry concerns regarding large-scale feasibility and impact on leather quality. This should alleviate their reluctance towards broader adoption of this promising approach. This study thus clearly demonstrates the ecological and economic merits of liming bath reuse.

KEYWORDS : Pollution; Waste water, Recycling baths, industrial waste water, Tannery waste.

INTRODUCTION

Tanning is all the operations aimed at transforming raw hides, extremely putrescible material, into a stable material, leather, which is then used for the manufacture of all kinds of products and articles. The process consists of a series of complex chemical and mechanical operations resulting in a huge volumes of waste water (Dantas et Castro, 2004), in addition to a large amount of inorganic and organic chemicals (Lofrano and Meriç). This activity consumes a lot of water, more than 40 million m3/year in Italy (Cassano, 1998).

In Algeria, average discharges from the tannery (T.A.M.E.G) vary according to the method of tanning, discharges range from 40 to 120m^3/tone for the leather factory to over 60 to 80 m3/tone for the sole leather factories (T.A.M.E.G Report, 2001) . These effluents consist essentially of a mixture of biogenic matter from the skins (hair, lipids, proteins, etc.) and chemicals (see figure below). (Aloy,1976).

These various loads create conditions such that this pollution cannot be absorbed in the natural environment and, on the contrary, stops the phenomena of self-purification, on one hand, because of various heavy organic loads, and the other hand, due to the presence of large quantities of toxic elements (Akinola and Ekiyoyo, 2006), which negatively affect plant growth, as well as their physiological and biochemical attributes (Asaad Bashir and al, 2020).

The cleaning up of tannery effluents is delicate and costly, because of the large volume of water to be treated, as well as the wide variety of pollutant compounds they contain. Strict implementation of environmental regulations requires certain tanneries to close down permanently due to inefficiency or failure to comply with strict guidelines for the disposal of toxic and other wastes (Kanagaraj and al., 2015; Gomes and al., 2017).
The aim of this study is to characterise the waste water generated by an industrial tannery plant at the main panel and the liming workshop and possibilities of treatment of liming effluents for reuse in the manufacturing process.

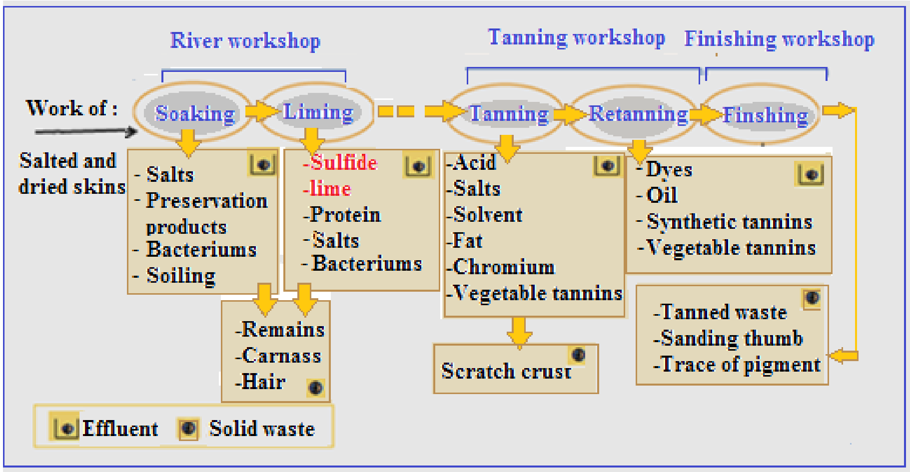


Figure 1 : The nature of the effluents and solid wastes discharged for leather.

MATERIALS AND METHODS

Wastewater analysis

Sampling points

This study concerns the recycling of liming baths (recovery of sulphides). The sampling points are chosen according to the technical organization of the unit and the workshops where the sulphide is ejected (see Figure 2).

The first point concerning the liming baths (2) and the second at the main collector (5) provide us with the overall composition of the effluent ejected. It is important to note that the production of the unit is not constant, which implies intermittent pollution leading us to carry out pollution balances over several days. The most significant are:

- Flush Sampling: 6 am
- After rinse samples: 10 am.

All samples are taken manually. The bottles used in glass or polyethylene are filled completely without agitation and by immersion in the water to be analysed, to not modify the oxygen content.

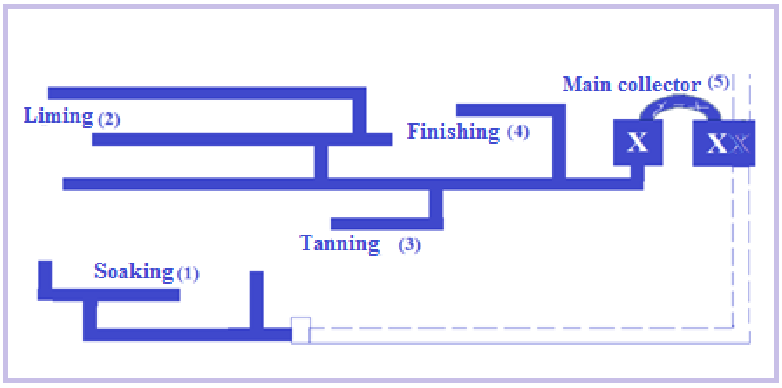


Figure 2 : Production workshop gutter.

Analyzed parameters

The parameters adopted for the establishment of the balance sheets concern oxidizable materials: (COD, BOD), suspended matter, toxic substances: (sulphide, chromium and chlorides), conductivity, total nitrogen Kjeldahl (NTK), turbidity (NTU), temperature, and PH. These last two parameters are measured at the sampling sites. For other measurements, the samples are transported in vials, stored at 4°C and analysed according to AFNOR (AFNOR, 2001).

Liming bath recycling process

Principle of treatment

This treatment consists in recovering all the sulphide effluents and reusing them without any treatment other than sieving (because of the presence in the waste bath of solid waste such as the pieces of skin, practically whole hair) and a readjustment of the concentration of reagents necessary for the liming operation.

Elbow liming

The operation was carried out on passes of six to seven average goat pieces, sampled, about 11Kg at each cycle (Figure 3).

After a 48-hour re-quench with 400% water (T=18 to 20°C) and 2% antiseptic (the percentages are relative to the weight of the skins), the skins were peeled in a bath containing 400% water (T=18 to 20°C), 2% lime and 3.2% sulphide (the percentages are relative to the weight of the skins) for 48 hours.

After each cycle, the waste bath is readjusted to its initial volume using a 10-litre graduated container, then the sulphide, lime, nitrogen, DBO, DCO, MES and PH are dosed according to AFNOR methods.

The recycling of the liming baths covered 21 cycles spread over two months. Precision is needed on the conduct of the tests. Indeed, for the last we doubled the weight of the skins: 22Kg instead of 11Kg one part is lime with the bath used 20times, the other part is treated by a new liming. This methodology makes it possible to directly compare the effect of the bath on the skin.

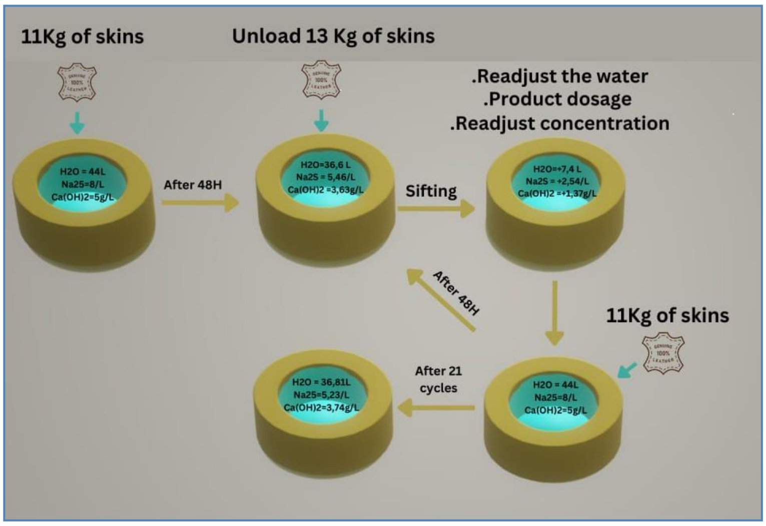


Figure 3 : Liming bath recycling diagram

Physical-mechanical and chemical controls of leathers after recycling:

In order to verify the recycling efficiency, physical-mechanical and chemical controls are carried out on our goat leather obtained. The quality of a leather is linked to its manufacturing process and the tanner must regularly know the percentages of products contained in its refinement in order to change the rate of them to: improve the qualities of the leather, meet the requirements of the standards, Physico-mechanical tests are important since the article undergoes different forms of transformation (sewing, stitching..) (AFNOR, 2003).

Thus the quality control tests of the article NAPPA clothing (mineral tanning) have focused on parts of a standard liming and parts of a liming of the last cycle. they concern: the arrow to the bursting using a flashometer, water permeability using a penetratometer, tear, seam and tensile strength using a dynamometer (DY22),chromium oxide levels, water soluble materials, extractable fats, Moisture and volatile matter according to AFNOR,2019.

RESULTS AND DISCUSSION

The liming stage waste water (2) (see Fig. 2) has a very high pH with an average of 11.85 (Table 1) and is rich in suspended solids of 1.25 g/l and an average sulphide content of 4.17 g/l. They are too high in organic matter with an average COD of 37573 mg L-1. (Folachier, 1997) and (Cooman and al., 2003) showed that liming contain the majority of organic pollution, a large proportion of suspended matter, and most importantly almost all of the toxicity. Indeed, during this stage, the skin is treated with an alkaline solution that will allow the hydrolysis of keratins (proteins that make up the epidermis and hair).

The mixed discharge (5) (see Fig. 2) collects all the effluents released by the different stages of the leather manufacturing processes. The variation in wastewater quality of the main sewer is due to the nature and variable composition of the collected effluent at the various stages of the process.

The average pH of the mixed wastewater analyzed shows a slightly basic value (Table 1). The mean COD level is significant at 10 801 mg/L. The mean BOD monitoring shows an average BOD level of 1138.5 mg/L. in addition, an average NTK concentration of 86.33 (mg L-1) was recorded. This high organic matter load is mainly due to the biogenic materials in the skins and the chemicals and organics products used. In addition to organic loading, these effluents are rich in mineral salts.

The high chloride concentration (4666 mg/l) is mainly due to the use of sodium chloride as a preservative for the skins, which is discharged with the wastewater into the river workshop especially during the hardening, re-drying and pickling stages. In addition to organic loading, these effluents are rich in mineral salts. Ramaswamy and Krishnamurthi (1980) note that if the salinity is too high, it can lead to a biochemical imbalance of the receiving medium and even have a toxic action. The electrical conductivity that reflects the ionic concentration of the medium shows an average result of 41.2 mS cm^{-1}. This important conductivity value is due to the use of a large quantities of salts during the manufacturing process.

An average sulphide concentration of 140mg/l was observed at the main sewer. The average suspended solids content of the raw wastewater analyzed is 2744 mg/l (Table 1) with an estimated average pollutant load of 825 kg carried by a volume of 300m^3/d, which explains the average turbidity value of 240 NTU.

On the other hand, Table 1 shows that the DBO_5/DCO ratio is 0.527. Thus, the liquid discharges from this industrial unit are not readily biodegradable despite the use of mechanical sieving of the effluents at the general collector. The levels of the pollutants identified in these discharges, by the measurement of the various parameters, exceed sharply the standards for the discharge of industrial effluent into a natural environment (Algerian Official Journal, 2006). Thus, from the polluting flux reported per tone of skins treated at the level of the pelage operation (Table 2), it results in valuable indications that highlight the importance of the discharge. This load, which is high in pollutants from tannery effluents, can be attributed to the non-rational use of chemicals and to organic substances released by the skin during the process. However, to ensure the penetration and reaction of these products with collagen, the reagents are added in excess and are partially used by the skin (Scholz and Lucas, 2003).

Table 1 : Characterization of liming Bath and Main sewer Wastewater

Parameter	Average value		Limit value (Algerian standard)
	Pelain bath	main collector	
Effluent volume/ton of leather and skin	5m^3	40m^3	
T (C°)	21	21.63	30
PH	11.85	9.72	6.5-8.5
Conductivity (ms cm^{-1})	25.9	41.2	-
Turbidity (NTU)	590	240	-
MES (mg L^{-1})	1251.5	2744	35
Cl^- (mg L^{-1})	2239.5	4666	
Sulphide (mg L^{-1})	4170	140	3
Total chromium (mg L^{-1})	0	53	0.5
NTK (mg L^{-1})	1015.66	86.33	30
BDO_5 (mg L^{-1}) à 20°C	1882.5	1138.5	35
CDO (mg L^{-1})	37573	10801	120
BDO_5 /DCO	0.527	0.105	-

Table 2 : Polluting charge of the pelain baths

Parameter	BDO_5	CDO	Salinity	Total Nitrogen (NTK)	Sulphide	MES
Polluting load of leather and skin (kg/tonne)	9.41	187.87	11.20	5.08	20.85	6.26
Polluting load (Kg / jour)	70.575	1409.03	84	38,1	156.38	46.95

Reactions during liming :

The reactions that occur during the liming operation are: the consumption of a proportion of sulphide, a part of lime as well as a fraction of the bath itself and the products it contains is retained in the skin due to alkaline swelling. The hair degraded, partly solubilized, is found either in suspension or in solution in the waste bath. The skins also contain a quantity of fat that also goes into the bath. hus the composition of the waste bath is more complex than the initial bath. The quantitative analysis of these components leads to the values expressed in grams per liter and in relation to the weight of the skin in tripe see Table 3. We find that there is a loss of bath of 16.81% due to its absorption by the skins. We find 72.6% of the initial value in lime and 68.25% in sodium sulphide. So why do we use such propotion if we can't consume everything? According to Money it has been shown that a minimum concentration of the reducing ion is necessary or it is inoperative. The content of this product (sulphide) in the bath cannot therefore be reduced from the 2 to 3.5% currently used. The decrease in volume and the partial disappearance of the reagents from the dry residue undeniably reflect a heavy burden of the waste bath, mainly due to organic matter present at a rate of 0.3% compared to the weight of the skin in tripe. In subsequent passes, this balance of a single use of the bath will increase. The more the same bath is reused, the more there will be overconcentration in foreign residues. We believe that this effect can in the end cause an inhibition of the action of sulphide and lime on the skins, which may cast doubt on the effectiveness of the treatment. However, only the experimental study can confirm or deny this hypothesis.

Table 3: Liming formula and waste bath analysis

Composition	initial bath		Waste bath	
	g/l	%	g/l	%
Sulphide	8	3.2	5.46	2.18
Limestone	5	2	3.63	1.45
Eau water	44	400	36.6	332.72
Nirogen total (NTK)	-	-	0.92	0.37
(MES) dry residue	13	5.2	15	6
PH	12.7	-	12.6	-

Percentages with respect to the weight of the skin in tripe.

Phisico-chemical analyses of liming baths after each cycle

Baths Readjustment after each cycle

The liming bath was recycled over 21cycles. In order to readjust the bath to its initial values (water, sulphide and lime), we determined the content of the residual pelain during each cycle. The results are shown in Figure 4.

After each cycle the bath should readjust to its initial volume. The average of the volumes of the baths to be adjusted is around 16.77% of the length of the initial baths with a range of 16.36 to 18.18%. The variation of 1.82% is due to bath handling.

The absorption of the skins and the swelling (Figure 5) justify this loss of 67.08% compared to the weight of the skins. The grafic representation (fig.n°4) of the quantities of sulphide and lime residues of the various baths according to the number of cycles shows that there are recoveries of 66.87% of sulphide and 71.50% of lime. They vary in relation to the initial quantities of 2.09 to 2.22% of the weight of sulphide skins, or 2.14% on average and 1.39 to 1.5% of the weight of lime skins, or 1.43% on average.

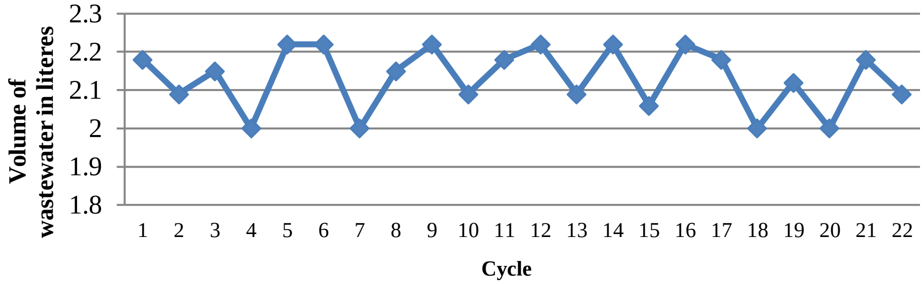
The ranges are not wide, exhaustion is relatively constant. These results show that the depletion of the liming baths is reproducible from one cycle to another, that is to say the quantities of lime sulphide and water are substantially the same from one pass to the other.

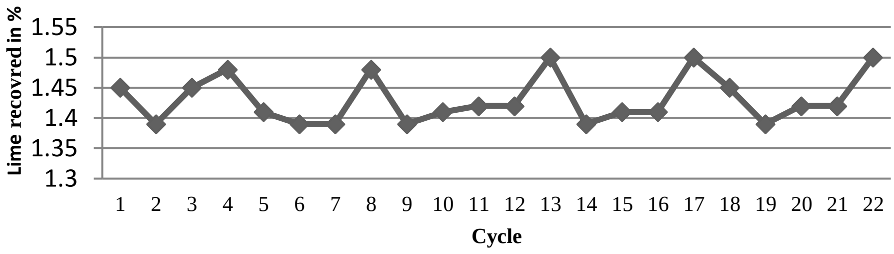
Control of nitrogen, density, PH and swelling.

We note that during the first cycles, the protein content increases rapidly until the 13th cycle see figure 5; then the curve bends sharply and the nitrogen concentration varies only very slightly and tends to stabilize. An unexpected phenomenon since after each cycle there should be an increase in the concentration close to or equal to that of the first cycle. Folachier (1997) specifies that the dissolution of the liming of the skins creates a protein content in the bath during each depilation operation. However, the risk of a constant and infinite increase in the level of protein dissolved in the waste baths as they are recycled is excluded for the following reasons: the volume of the waste liming is only 84to 86% of the initial volume each time; therefore, this loss must be compensated with clean water. In this bath will dissolve again a quantity of protein added to the first and since the concentration of nitrogen reaches these limits in the first 13 cycles then the proteins dissolve only in the volume of water added and the concentrations appear constants.

Changes in organic matter may affect the density of the waste bath. As their rate stabilizes at the 13th cycle, this density should also stabilize. This is verified perfectly from the 15th cycle and the density reaches its maximum at 5.8. The evolution of the PH of the recycled baths according to the number of cycles is shown in Figure 5. The results obtained lead us to the following explanation: PH from 12.7 to 12.4 under the influence of ammonium salt plus at least substituted in small proportion, is buffered but its value stabilizes quickly at 12.4. Swelling becomes less important when the number of cycles increases. This decline is undoubtedly due to the presence of excess substances in the bath, which causes pressure on the skin. The comparison of the two cuts of the same skin shows that the swelling and thickness are different, the half-skin treated with a new liming at a 125% weight yield, the other treated with a recycled bath at a 115% yield.

The latter absorbed 10% less bath, which justifies the difference in swelling.





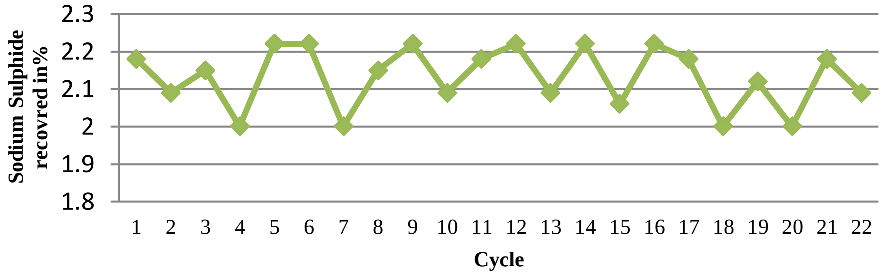
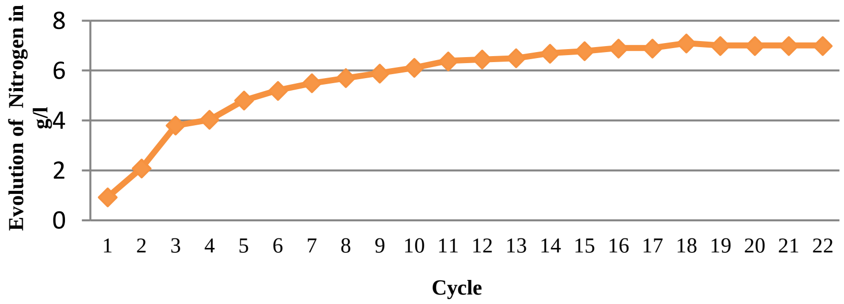


Figure 4: Water, Sulphide and lime content in waste water.



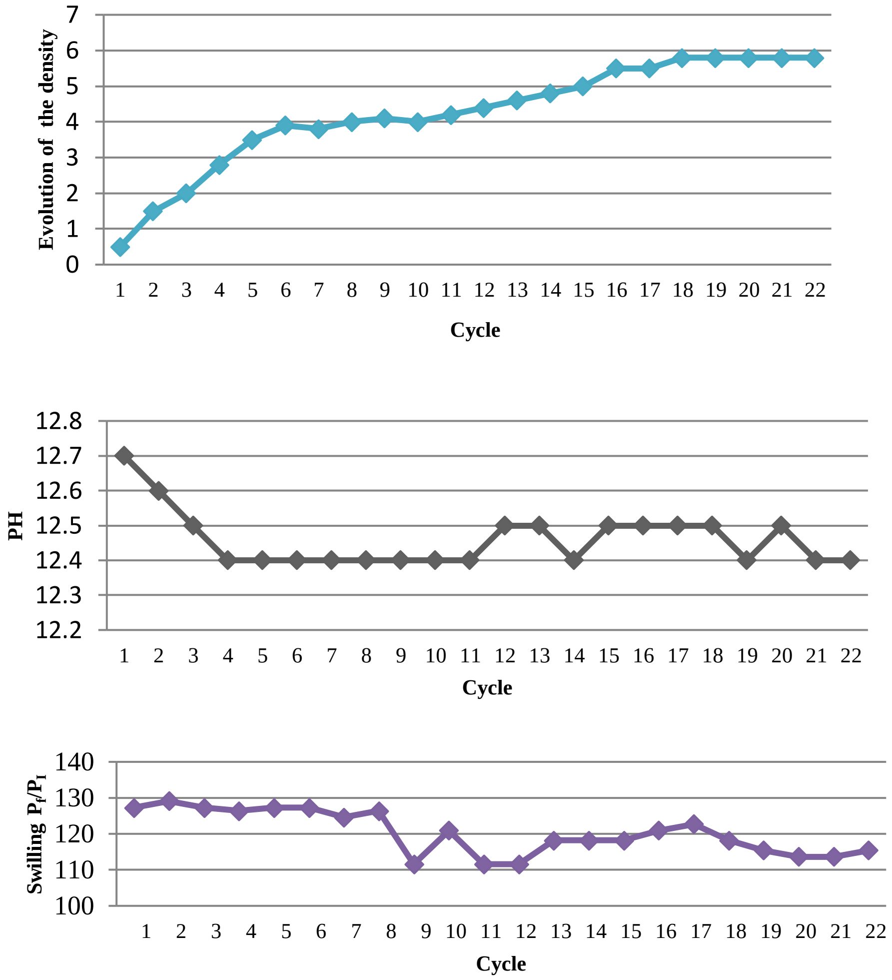


Figure n°5 : Control of Nitrogen, density, PH and swelling.
(P_I skin initial weight in kg ,P_f skin final weight in kg)

COD, BOD5 and ESM Control

Although in the light of the above results there is no theoretical reason why the recycling of liming in infinite number of times and the pollution will be clearly eliminated, but it is necessary to be realistic and to think that stops are obligatory if not what at the time of vacation or end of series. Then the release of this pollution becomes necessary.

A comparative assessment of the pollution released was carried out for one conventional process and another involving recycling for a series of 21 cycles (Table 4). According to the pollution reduction rates, the pollution caused by the liming baths has been reduced in a very significant way more than three-quarters of the COD have been reduced and almost all DBO5and ESM have been eliminated.

Table 4 : Comparative assessment of the pollution released.

Analysis	Conventionnal Pollution one bath	Comparaison		Réduction %
		Recycling Pollution Last cycle	Conventionnal Pollution 22 baths	
DCO mg/l	39577	197400	870694	77.33
DBO_5 mg/l	700	2220	15400	85.58
MES mg/l	8690	42000	191180	78.03

Verification of the efficiency of the 'liming bath recycling' process

Control of hair removal effects

In order to control hair removal, the surface condition of the leathers from the different cycles was observed with the naked eye after peeling and with a magnifying glass on blue. The flowers proved to be clean, from the first to the last cycle which reflects the effectiveness of the baths.

The epilating was performed in a perfectly constant way from the first to the last cycle. To make sure, samples were taken from the last cycle and from the new liming and for the same skin cut in symmetry. The comparison of the two passes and slices leads to a difference in swelling and thickness, but no problems with the hair removal.

Characteristics of the obtained leathers

Table 5 sums up the physic-mechanical and chemical characteristics of leathers obtained with a recycled liqueur (21 cycles) compared with a manufacturing standard. The values obtained are satisfactory and very close in both cases. The results show that the recycling of the liming baths did not affect the efficiency of the liming compared to a manufacturing standard.

Table 5 : Leather characteristics

Tests	Leather obtained with a new liming	Leather obtained with recycled lime : (21 cycles)	AFNOR standard
Flaiche at bursting (mm)	8.3	7.6	> 7
Tensile resistance DAN/mm^2	1.9	2.14	1.5 à 2
Tear resistance DAN/mm	2.3	2.5	> 3
Stitch resistance DAN/mm	10.15	10.01	8 à10
water permeability %	25.29	29.04	Time : > 20min Absorption : < 30%
Moisture and volatile matter %	17.7	17.5	>18
Volatile fats %	8.5	8.1	>8
Water soluble substances %	1.2	1.2	>1.5
Chromium oxide %	3.2	3.1	> 2.5
Difference index	0.4	0.4	0.5

CONCLUSION

This study demonstrated the feasibility and benefits of recycling liming baths in an Algerian tannery to reduce
water pollution. Analysis showed the raw tannery effluents far exceeded regulatory discharge limits for pollutants like COD, BOD, sulfides, chromium, chlorides,.. etc. A closed-loop recycling process was tested for 21reuse cycles of the liming baths. The results demonstrated that this process enabled the recovery of 66.87 % of sulfides and 71.50 % of lime, while significantly pollution loads by over 75% for COD and almost eliminating BOD and suspended solids. Furthermore, extensive physico-chemical testing showed the quality of leathers produced using the recycled baths met industry standards and specification. Technical performance was not affected. This addresses industry concerns about impacts on quality from bath reuse. in the final, liming bath recycling proved ecologically and economically viable by drastically reducing water usage and pollution, while maintaining leather quality. It should motivate broader adoption of this circular approach in tanneries. Further research can refine and optimise the process. But this study clearly validated the feasibility and merits of sustainable bath reuse to transition the sector towards closed-loop manufacturing.

REFERENCES :

Afnor (2001) La qualité de l'eau. Recueil , Environnement. Association Française de Normalisation. Paris, France.

Afnor NF EN ISO 23910, (2019), Indice de classement : G 52-005, ICS : 59.140.30

Akinola, M.O., Ekiyoyo T.A. (2006) Accumulation of lead, cadmium and chromium in some plants cultivated along the bank or river Ribila at Odo-nla area of Ikorody, Lagos state, Nigeria. J. Environ. Biol., vol.27, pp597-599

Aloy.M., Folachier A. Vulliermet B. (1976) tannerie et pollution. editon Centre Technique Du Cuir,p63 (In french).

Aloy.M., Folachier A. (1978) Les eaux residuaires de tannerie-megisserie. Waste waters from tanneries and taweries. Technique-de-l'Eau-et-de-l'Assainissement (Belgium). no.380-381 pp. 13-29.

Asaad Bashir M., Naveed M., Ahmad **Z.**, BinGao, Mustafa **A.** (2020). Combined application of biochar and sulfur regulated growth, physiological, antioxidant responses and Cr removal capacity of maize (*Zea mays* L.) in tannery. Journal of Environmental Management Volume 259, p 10051.

Cooman K., Gajardo M., Nieto J., Bornhardt C., Vida G. (2003). Tannery wastewater characterization and toxicity effects on Daphnia spp, Environmental Toxicology. vol.18, pp 45-51.

Cassano A., Drioli E., Molinari R. (1998). Intégration of ultrafiltration into unhairing and degreasing opérations. J.Soc. of Leather Technologists and Chemists., vol.82, pp130-135.

Dantas AA., Castro MCP., Talencar ME. (2004) Evaluation and optimization of chromium removal from tannery effluent by micro emulsion in the Morris extractor. J. Hazardous Mater., vol.114, pp115-122.

Folachier A. (1997) Recyclage des bains épilage pelanage chaux-sulfure. 9 th edition Techni cuir n°4, pp 66-77

Gomes M.A., Davis R.A.H, Suzuki M.S., Vitória A.P. (2017). Plant chromium uptake and transport, physiological effects and recent advances in molecular investigation. Ecotoxicology Environmental Safety. vol.140, pp 55-64.

Hooda v. (2007) Phytoremediation of toxic metals from soil and waste water. Journal of Environ Biology., vol.28, pp 367-376

Journal officiel de la république algerinne démocratique et populaire, N°26 du 23-04-(2006). Décret exécutif n°06-141 du 19 avril 2006 définissant les valeurs limites des rejets d'effluents liquides industrièl, P.27

Kanagaraj J. (2008) Recovery and reuse of chromium from chrome tanning waste water aiming towards zero discharge of pollution , Journal of Cleaner Production. vol.16, pp 1807-1813

Lofrano G., Meriç S., Zengin GE., Orhon D. (2013) Chemical and biological treatment technologies for leather tannery chemicals and wastewaters. Science of the Total Environment. Elsevier, vol.461-462, pp 265-281.

Mony C. A, Adminis U. (1974) Recyclage des liqueurs d'épilage chaux-sulfure, Partiel, Edition J.S.L.T, Vol.58, p37.

Norme NF G52-001 Cuir - Essais physiques et mécaniques - Préparation et conditionnement des échantillons Afnor Editions 2003

Ramaswamy.P Krishnamurthi V.S. (1980). water pollution by tannery effluents, editin JLCA75, pp200-206.

Rapport interne de la TAMEG n°1, 2001. Etats de la gestion des déchets rejetés.

Scholz et Lucas,Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals Water Research Volume 37, Issue 8, April 2003, Pages 1859-1867.