New Trends in Leather Waste Reduction and Its Control

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Abstract

Leather production has long been an important global industrial activity and remains traditional in several developing countries without optimizing the usage of chemicals, water etc. and controlling the leather waste production. Leather industry has gained a negative impact in society with respect to its pollution potential and this has been regarded as an inevitable consequence of that industrial activity. Therefore, it is facing severe challenges due to the increasing health and environmental regulations and restrictions.

However, it is not always possible to achieve the required discharge standards for leather industry. Thus, new technologic investments are required in leather waste treatment technologies that cost additional charges. Recently, researches and R&D work carried on this field gain a great importance to fulfill the requirements in leather waste minimization, reduction and its control. Consequently, revealing new studies and trends are playing an important role for further studies in leather waste management.

Key words: leather, pollution, environmental, waste, new studies

1 Introduction

The leather production process is composed of various chemical (conservation, soaking-softening, dehairing-liming, descaling, bating, degreasing, pickling, tanning, neutralization, dyeing, retannage, finishing) and mechanical procedures (fleshing, chipping, splitting, shaving, stretching and squeezing, tensioning, grinding) employed to transform rawhide into finished leather(Fela et al. 2011). In chemical procedures, plenty of chemical agents such as salt (NaCl), arsenic (Na_2S), lime ($Ca(OH)_2$), ammonium sulphate ($(NH_4)2SO_4$), sulphuric acid (H_2SO_4), weak organic acids, chromium (Cr_2O_3), sodium carbonate (Na_2CO_3), sodium formate, dyes, greases, tannins, cellulose-based solvents, water-based varnishes, plastic binders, pigments, non-ionic detergents, various enzymes, and natural-synthetic lubricants are commonly employed. As a result, waste leather waters contain high levels of salt, organic matters, inorganic matters, dissolved and suspended solids, ammonia, organic nitrogen, sulphur, chromium and many other toxic substances(Kılıç et al. 2009).

As leather processing industry produces lots of waste solids, fluids and gases, it is classified as one of the top polluting industries. During the production of 1000 kg of rawhide, almost 730 kg solid wastes are produced, in other words, only 270 kg of the rawhide can be yielded into the useful product. Processing 1 ton of rawhide requires the use of 20-80 tons of water, with a resulting waste water output of 30-50 tons. Such water masses are pollutant and should be treated. The reason underlying the stink released is volatile compounds that are decay products of the rawhide as well as ammonia, hydrogen sulphur, hydrocarbons, amines

and aldehydes resulting from chemicals employed in leather production(Fela et al. 2011; Öztürk 2008).

Current treatment methods are generally ineffective in treating leather waste waters containing highly polluting components up to the level prescribed in discharge criteria. Therefore, need to different waste reduction methods has appeared. The present study discusses various methods recently employed in this field within the leather industry. Such novel methods offer a more environment-friendly process for leather production, and are of critical nature for their prospective contribution to efforts aimed at building a background for future studies.

2 Waste Issue Faced By The Leather Industry

During leather production, procedures from soaking up to bating produce 60-70% of the total pollution load. However, it is 90% if this process is extended to cover tanning. On the other hand, various acids, alkalis and salts used for pH regulation grow pollution parameters such as the chemical oxygen demand (COD) of waste water, total dissolved solids (TDS), chlorine, sulphate and other minerals(Aravindhan et al. 2007). Table 1 shows pollution loads generated during the processing of various rawhides.

Table 1: Pollution values from tannery processes under conditions of good practice (IUE-6,2008)

Values per tone of raw hide	Water(m^3/t)	COD(kg/t)	BOD_5(kg/t)	S.S(kg/t)	Cr^{3+}(kg/t)	S^{2-}(kg/t)	TKN(kg/t)	Cl^-(kg/t)	SO_4^{2-}(kg/t)	Grease (kg/t)	TDS(kg/t)
Bovine Salted Raw Hide Process											
Beamhouse(soaking to bating)	7-25	120-160	40-60	70-120		2-9	9-14	120-150	5-20	5-8	200-300
Tanning	1-3	10-20	3-7	5-10	2-5		0-1	20-60	30-50	1-2	60-120
Post Tanning	4-8	15-40	5-15	10-20	1-2		1-2	5-10	10-40	3-8	40-100
Finishing	0-1	0-10	0-4	0-5							
Total	12-37	145-230	48-86	85-155	3-7	2-9	10-17	145-220	45-110	9-18	300-520
Pig Skin											
Beamhouse	23-49	120-272	46-98	62-110		3-7	11-17	57-197	4-15	30-67	120-300
Tanning	2-5	10-18	3-6	4-8	2-4		0-1	20-37	26-45	1	40-120
Dyeing	5-10	10-25	3-9	8-15	1-2		1-2	3-6	10-40	3	20-80
Finishing	2-5	0-5	0-2	0-2							
Total	32-69	140-320	52-115	70-135	3-6	3-7	12-30	80-240	40-100	34-71	180-500
Values in litres or grammer per skin	Water(l/skin)	COD(g/skin)	BOD_5(g/skin)	S.S(g/skin)	Cr^{3+}(g/skin)	S^{2-}(g/skin)	TKN(g/skin)	Cl^-(g/skin)	SO_4^{2-}(g/skin)	Grease(g/skin)	TDS(g/skin)
Sheepskins(wet-salted)											
Beamhouse	65-150	250-600	100-260	150-300		6-20	15-30	150-400	5-40		
Degreasing-Tanning	30-100	50-300	20-100	15-30	8-12		4-10	40-200	30-50	40-150	
Post Tanning	15-35	30-100	15-35	10-20	1-3		2-4	20-40	10-20		
Finishing	0-10	0-5	0-2	0-2							
Total	110-265	330-1005	135-397	175-352	9-15	6-20	21-44	210-640	45-110	40-150	
Wool-on Sheepskin											
Beamhouse	160-240	550-1100	150-1000	100	-	-	16	400			600
Tanning	40-70	150-300	45-250	15	15	-	2	460		40-150	650
Dyeing	75-100	80	25-50	80	5	-	3	50			270
Finishing	-	-	-	-	-	-	-	-			
Total	275-410	780-1500	220-1300	195	20	-	21	910		40-150	1520

As high amount of water is employed during each phase of leather processing, a considerable amount of waste fluids occurs. However, chemicals employed are not fully absorbed by leather, and and almost 50% mix with water(Fela et al. 2011).

Dehairing-liming procedures eventually generate pollution loads of biological oxygen demand at a rate of almost 84%, chemical oxygen demand of almost 75% and total suspended

solids of almost 92%. While lime employed in this procedure creates lime, sodium sulphur poses hazards for the environment as well as the treatment plant itself. Ammonium salts used in the next descaling step for lime removal leads to the release of ammonia gas(Aravindhan et al. 2007).

Salt employed for protection in the conservation process, and for prevention of acid swelling during pickling increases the total dissolved solid amount of waste water. During the traditional chromium tanning process, chromium uptake by the leather occurs merely at a rate of 50-70% while the remaining part is mixed into the waste water. In case of a chromium content of 10-100 ppm particularly in sandy soil, micro-organism population and CO_2 content in soil is reduced. International standards for discharge prescribe an upper limit of 2 ppm for chromium content in waterways. On the other hand, it is known that, trivalent chromium may easily be transformed into hexavalent chromium even in the presence of mild oxidants. Chromium +6 is carcinogenic and causes fish death even at a level as low as 0.2 ppm, and poses great risk for disposal through landfill (Aravindhan et al. 2007; Sahu et al. 2009; Yılmaz 2011).

Standards prescribed on pollutant loads for the leather industry by the Regulation for the Control of Water Pollution published in the Official Gazette no 25687 of 31 December 2004 are shown in Table 2.

Table 2: Waste water discharge standards to receiving environment of leather industry(Şanlı 2006)

Parameter	**Unit**	**Composite Sample(2 hour)**	**Composite Sample (24 hour)**
COD	mg/l	300	200
Suspenden Solid	mg/l	125	-
TKN	mg/l	20	15
Grease	mg/l	30	20
Sulphur(S^{-2})	mg/l	2	1
Chrome(Cr^{+6})	mg/l	0.5	0.3
Total Chrome	mg/l	3	2
Fish Bio-Test (ZSF)		4	4
pH		6-9	6-9

Table 3 further shows limit values applying to various pollution parameters permitted for ground and sewer waters in France, Italy and India.

Table 3: Discharge limits for treated tannery effluents in France, Italy and India(UNIDO 2002)

Parameter	Unit	France		Italy		India	
		Surface	Sewer	Surface	Sewer	Surface	Sewer
pH	-	6.5-8.5	6.5-8.5	5.5-9.5	5.5-9.5	5.5-9.0	5.5-9.0
COD	mg/l	125	2000	160	500	250	-
BOD_5	mg/l	30	800	40	250	30	350
Suspended Solids	mg/l	35	600	40-80	200	100	100
Ammonia Nitrogen(as NH_3)	mg/l	-		15	30	50	50
TKN	mg/l					100	
Nitrate Nitrogen(as N)	mg/l	-		20		-	
Total nitrogen in sensitive areas	mg/l	30-15	150			-	
Sulphide(S^{2-})	mg/l			1	2	2	-
Cr^{+6}	mg/l	0.1	0.1	0.2	0.2	0.10	2.0
Cr^{+3}	mg/l	1.5	1.5	-	4.0	-	-
Total Cr	mg/l	-		2.0	4.0	2	2
Iron+Aluminium	mg/l	5	5			-	
Phenol index	mg/l	0.3				1[1]	5[1]
AOX	mg/l	1.0	1.0			-	
Cl^-	mg/l	***		1200*	1200	**	**
SO_4^{2-}	mg/l	***		1000*	1000	1000	1000
Al	mg/l	-	-	1.0	2.0	-	-
Fe	mg/l	-	-	2.0	4.0	-	-

[1]As phenolic compounds (as $C_6 H_5 OH$). *,**,***:Discharge limits have different from territorially

3 Some Recent Initiatives Launched For Reducing Leather Waste

Traditional treatment systems are typically far from achieving intended discharge standards for the leather industry. Therefore, need to different waste reduction methods supplementary to or independent from such systems has appeared. Table 4 shows capacities of methods applied in the leather industry for the treatment of various pollution loads.

Table 4: Typical performance for tannery waste water treatment(IUE-5 2008)

Parameter	COD		BOD_5		Suspended Soli		Chrome	Sulfide		N(kjeldahl)		Sludge Production
	%	mg/l	%	mg/l	%	mg/l	mg/l	%	mg/l	%	mg/l	kg DS/ton rawhide
PRETREATMENT												
Grease removal(dissolved air flotation)	20-40											
Sulfide oxidation(liming and rinsin liquors)	10								10			
Chromium precipitation							2-10					
PRIMARY TREATMENT												
Mixing + Sedimentation	25-35		25-35		50-70		20-30			25-35		80
Mixing + Chemical treatment + Sedimentation	50-65		50-65		80-90		2-5		2-10	40-50		150-200
Mixing + Chemical treatment + Flotation	55-75		55-75		80-95		2-5		2-5	40-50		150-200
BIOLOGICAL TREATMENT												
Primary or chemical + Extended aeration	85-95	200-400	90-97	20-60	90-98	20-50	<1		<1	50	150	70-150(1)
Primary or chemical + Extended aeration with nitrification. and denitrificat	85-95	200-400	90-97	20-60	90-98	20-50	<1		<1	80-90	30-60	130-150(1)
Primary or chemical + Aerated facultative Lagoons	80-90	300-500	85-95	60-100	85-90	80-120	<1		<1	50	80	100-140
Anaerobic treatment (lagoon or UASB)	65-75	500-700	60-70	150-200	50-80	100-120	<2	0		20-30		60-100
Membrane biological reactor (MBR)	80-95	160-500	97-100	5-50	100	0	<0.5	99	<0.5			
Constructed wetlands (after primary treat.)	70-80	300-400	85-95	60-100								

(1)Without chemical treatment, UASB = upflow anaerobic sludge blanket

Waste reduction initiatives may be defined as the set of phases including the application of advanced methods in wastewater treatment, modifying or substituting current toxic and polluting chemicals with those having inferior environmental impact, full consumption of chemicals employed, modifications in steps performed during the production cycle, and recycling and recovery of chemicals. While each of these procedures may be conducted as a stand-alone initiative, also multiple steps may be involved within the same procedure.

Wastes of the leather industry are typically treated by means of physical, chemical and biological treatment methods. There are various initiatives adopting different methods due to the problems faced in the set-up of such treatment systems and achievement of discharge criteria. In some recent studies, various researches have surveyed the capability of advanced treatment methods such as electrochemical oxidation, membrane separation methods (nanofiltration, ultrafiltration, reverse osmosis, electrodialysis, etc.) and ion-exchange resins to treat the wastes of the leather industry.

Electrooxidation as an electrochemical treatment method is the system where insoluble electrodes are used to remove unintended matters by oxidization through O_2 and H_2 gases formed by these electrodes. In electrooxidation, anode plays an active role. Parameters that determine the capability of the process are the catalytic activity of the anode, current, temperature, pH and diffusion rate of oxidants. This is a highly preferred method for effective removal and less sludge formation(İlhan et al. 2007).

A membrane may be defined as barriers that selectively undertake the separation process. Separation is realized by the impulsive force formed by either or a combination of pressure difference, concentration (chemical potential) difference, electrical potential difference and temperature difference. Separation is supervised by porous membranes based on size, shape and load separation, and by non-porous membranes based on sorption and the diffusion pattern. Membrane performance is determined by selectiveness and flux parameters. The membrane has 3 major functions, namely purification, concentration and fractioning, which are what make this method widely applied in the industry. A membrane separation system separates an inflow into two sub-flows namely permeate and retentate. Permeate is the portion of the fluid passing through the semi-permeable membrane. And retentate flow constitutes the portion retained by the membrane. The membrane may have a thickness varying between the micron level and the millimetre level. Major membrane processes are Microfiltration (MF), Nanofiltration (NF), Reverse Osmosis (RO), Ultrafiltration (UF) and Electrodialysis (ED). Method of separation in MF, UF and NF is similar and based on the molecular sieving principle. Since pore size is quite small in RO membranes, separation mechanism relies upon the thermal motion of the chains making up of the membrane. However, in ED, the electrical potential difference is employed as the impulsive force to separate ions from aqueous solutions (Salt and Dinçer 2006).

Ion exchange process is based on the principle of removing unwanted anions and cations in wastewater. Cations are displaced by hydrogen or sodium whereas anions are displaced by hydroxyl ions. Ion exchange resins are composed of functional groups bound to organic and inorganic matters. Ion exchange resins employed in the treatment of wastewaters are synthetic resins produced through the polymerization of organic matters into rough three dimensional structures. The ion exchange capacity of the resin is determined by the number of functional groups in the resin unit mass. If ion exchange resins are exchanging positive ions,

then they are called cationic; if they are exchanging negative ions, then they are called anionic. Cation exchange resins contain acidic functional groups such as sulphonic acids whereas anion exchange resins contain basic functional groups such as amines. Reactions depend on chemical equilibrium and occur with the replacement of one ion by the other(Hughes 2004).

One study where the capacity to treat salt-containing wastewaters of the leather industry by electrooxidation was researched has revealed that wastewater with a salt concentration of 30 g/l could effectively be treated with a current density of 0,012A/cm^2 at ph 9 for 120 minutes at a total cost of USD 1,13 by consuming 0,3 kWh electrical power per 1m^3 of saline. Removal of organic pollution is estimated to be the reduction in TKN and COD in wastewater. Treated water was reused in the pickling process, yielding leather of standard quality(Sundarapandiyan et al. 2010).

In one study where chromium and sulphate recovery was researched, 99% of chromium and 97% of sulphate was retained by membrane particles of 2,5 inch in diameter applied at a pH range of 2-11. Such recovered sulphate and chrome were reused in the tanning process. Researchers suggest that, despite the study is useful in terms of water and chemical saving and less discharge of chromium and sulphate to the receiving medium, nanofiltration cost is high(Aleixandre et al. 2011).

In one study targeting to treat the wastewaters of the greasing process, waters containing greasing wastes were first subjected to gravitational precipitation followed by nanofiltration and reverse osmosis for treatment. In such study, commercial iron sulphate and calcium oxide were employed for coagulation. For the nanofiltration and reverse osmosis procedures, organic composite membranes in a molecular weight up to 400 and coated with thin polyamide film were used. Lubricants employed in greasing should not be discharged to the outer environment as they would likely obstruct the sewer. Amount of greasing wastewater produced during the daily processing of 3500 kg rawhide is 10,000 l. Pressurized membrane procedures are quite suitable for the removal of grease from wastewater. At the end of this study, it is observed that, dissolved solid wastes could successfully be removed by means of the nanofiltration and reverse osmosis methods(Prabhavathy and De 2010).

There is a research where wastewaters from the dehairing procedure were treated by nanofiltration and then the impacts induced by the reuse of filtrate on leather quality were studied. It is observed that membranes retain only 35% of the chemical oxygen demand, yet achieve the recycling of protein at a rate as high as 90%. Therefore, we may reasonably infer that UF separation is suitable primarily for organic substances involved in dehairing. It is suggested that recycled chemicals may be reused in leather processing without sacrificing standard leather quality(Roca et al. 2010).

There is a study in the literature where a novel ion-exchange resin was employed in an effort to remove from wastewater and then recover chromium. Such resin has a cationic nature together with excellent physical, chemical and thermal stability, favourable ion exchange rate and high variation capacity. And it is suitable for removing heavy metals from wastewater. 92% of chromium could be removed from a solution containing 500-ppm Cr(III) in 15 minutes. Once treated with resin, the solution diluted down to 458 ppm yielded 95% chromium, which was then rinsed with sulphuric acid to recover 93% of chromium in a single step. Thus, such resin has proven its effectiveness in the treatment of chromium from wastewater and further in recovery(Sahu et al. 2009).

In one study, wastewater produced after one whole cycle of a tanyard including all processes ranging from rawhide up to finishing was treated with traditional treatment system, and subjected to further treatment by means of photo-electro oxidation (PEO) for 24 hours followed by combined PEO-ED (Electrodialysis) for 36 hours. The PEO-ED method allows to obtain water of a quality quite comparable to supply water. Such system has proven to have an ammonium nitrogen and chromium removal efficiency of 100%. On the other hand, also a successful colour and odour removal could be achieved as well. Finally, the treatment method obtained by combining the PEO and ED procedures proved a higher effectiveness compared to the traditional treatment method(Rodrigues et al. 2008).

In one study, Cr(VI) removal from different depths of soil contaminated by Cr(VI) by employing zero-valent iron of nano size (nZVI) was performed. In this study, soil samples with pre-determined Cr(VI) content were treated with nZVI solutions at different concentrations. It was observed after these procedures that, by employing 0,10 g/L nZVI, a Cr(VI) removal below the permitted limit could be achieved in 120 minutes(Shing et al. 2012).

In one study where polyethylene glycol (PEG) of a molecular weight of 200 applied at a rate of 3% by leather weight was employed in conservation instead of salt, it was observed that such material ensured conservation at desired leather quality standards, and that it reduced biological oxygen demand (BOD), chemical oxygen demand, chlorine amount and total dissolved solids load of wastewater from the soaking process by 71%, 34%, 99% and 93% respectively. It further yields a significant chemical saving as it has reduced the amount of chemicals employed in this procedure by 92,5%. Researchers suggest that, the cost of the method is just USD 6/goat leather higher than picked wet conservation(Kannan et al. 2010).

Liu et al. used sodium silicate and enzyme instead of lime in leathers treated with dehairing. This way, pollution due to lime in wastewater could be prevented while desired fibre stretch could be achieved in the leather with conserved mechanical properties and hydrothermal stability. Chemical oxygen demand and total solid load of wastewater could substantially be reduced. Furthermore, as no ammonium salt is employed in lime removal, ammonia emission and the resulting pollution is also reduced(Liu et al. 2009).

Finally, there is a study in the literature where the impact of procedures including dehairing by means of enzymes, fibre stretch with sodium hydroxide (NaOH), pickling and chromium tanning without basification on the reduction of pollution and cost were surveyed. In this study, an effective dehairing and fibre stretch could be achieved, and chemical oxygen demand and total solid amount could be decreased by 67% and 78% respectively. Furthermore, it is observed that, compared to traditional methods, amount of chromium was decreased from 81 ppm to 32 ppm in the composite bath. It is suggested that the amount of water used decreased, and water output as well as the procedure time were reduced as certain steps were omitted. Compared to the traditional method in terms of cost, a total saving of USD 14 per each metric ton of sheep leather is achieved(Aravindhan et al,2007).

4 Conclusion

Environmental awareness evolving and growing on global scale requires the adoption of various limitations or additional procedures in all industrial lines including the leather industry. Inefficacy of traditional waste reduction methods in achieving evolving standard limits requires to explore different processes. Recent implementation of advanced treatment methods (electrooxidation, membrane separation, ion-exchange resins, etc.) to meet these requirements drive studies as regards the use of alternatives to toxic chemicals that grow the pollution load. Insight into these studies is critical as achievements yielded by them would constitute a reference for future researches and foster more environment-friendly leather processing.

References

1) Fela, K., Ciurova, W. K., Konopka, M., Wozny, Z., 2011, Present and Prospevtive Leather Industry Waste Disposal, Polish Journal of Chemical Technology, 13(3), 53-55p.
2) Kılıç, Y. M., Mert, K. B., Kestioğlu, K., 2009, Deri Atık Sularının Arıtımında Kimyasal Arıtma ve Adsorbsiyon Yöntemlerinin Uygulanması, Fırat Üniversitesi Fen Bilimleri Dergisi, 21(2), 95-101p.
3) Öztürk, M., 2008, Deri Sanayinde Kromun Geri Kazanılması ve Üretimde Tekrar Kullanılması,http://www.mozturk.net/Upload//deri%20sana[1].pdf, accessed:01.05.2012
4) Aravindhan R., Saravanabhavan S., Thanikaivelan P., Raghava Rao J., Unni Nair B., 2007, A chemo-enzymatic pathway leads towards zero discharge tanning, Journal of Cleaner Production (15)1217-1227p.
5) IUE-6; Typical pollution values related to conventional tannery processes, Document on Recent Developmants in Cleaner Production and Environment Protection in World Leather Sector, October 2008.
6) Sahu S.K., Meshram P., Pandey B.D.; Kumar V., Mankhand T.R. ,2009, Removal of chromium(III) by cation exchange resin, Indion 790 for tannery waste treatment, Hydrometallurgy ,99 ,170–174p.
7) Yılmaz B., 2011, Deri Atıkları ve Değerlendirilmesi Yayınlanmamış Ders Notları.
8) Şanlı, N., 2006, Deri Sanayi Atık Sularının Kimyasal Koagülasyon ve Elektrokoagülasyonla Arıtımı, Gebze İleri teknoloji Enstitüsü Mühendislik ve Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi.
9) UNIDO; Introduction to treatment of tannery effluents, Vienna 2011.
10) IUE-5; Typical performance for tannery wastewater treatment, Document on Recent Developmants in Cleaner Production and Environment Protection in World Leather Sector, October 2008.
11) İlhan F., KURT U., Apaydı Ö., Arslankaya E., Gönüllü M.T., 2007, Elektrokimyasal arıtım ve uygulamaları:Katı Atık Sızıntı Suyu Çalışması, AB Sürecinde Türkiye'de Katı Atık Yönetimi ve Çevre Sorunları Sempozyumu.
12) Salt Y., Dinçer S., 2006, An option for special separation operations: Membrane Processes, Journal of Engineering and Natural Sciences Mühendislik ve Fen Bilimleri Dergisi, 1-23p.
13) Hughes L., 2004, Ion exchance resins: Unique solutions to formulation problems,Pharmaceutical Technology,20-25p.
14) Sundarapandiyan, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S., Saravanan, P., 2010, Electrochemical oxidation and reuse of tannery saline wastewater, Journal of Hazardous Materials 180 , 197-203p.

15) Aleixandre, M.V.G., Roca J.A.M., Pia, A.B., 2011, Reducing Sulfates Concentration in the Tannery Effluent by Applying Pollution Prevention Techniques and Nanofiltration, Journal of Cleaner Production 19 , 91-98p.

16) Prabhavathy, C., De, S., 2010, Treatment of fatliquoring effluent from a tannery using membrane separation process: Experimental and modeling, Journal of Hazardous Materials ,176 ,434–443p.

17) Roca, J.A.M., Aleixandre, M.V.G., Garcia, J. L. , Pia, A.B.,2010, Purification of Tannery Effluents by Ultrafiltration in View of Permeate Reuse, Separation and Purification Technology 70 , 296–301p.

18) Rodrigues M.A.S., Amado F.D.R., Xavier J.L.N., Streit K.F., Bernardes A.M., Ferreira J.Z., 2008, Application of photoelectrochemicaleelectrodialysis treatment for the recovery and reuse of water from tannery effluents, Journal of Cleaner Production 16 ,605-611p.

19) Singh R., Misra V., Singh R. P., 2012, Removal of Cr(VI) by Nanoscale Zero-valent Iron (nZVI)From Soil Contaminated with Tannery Wastes, Bull Environ Contam Toxicol ,88,210–214p.

20) Kanan K.C., Kumar M.P., Rao J. R., Nair B. U., 2010, A novel approach towards preservation of skins, Jalca,105, 360-369p.

21) Liu Y.,Fan H., Zhang X., Peng B., Shi B., An environment-friendly lime free liming process based on sodium silicate, http://www.aaqtic.org.ar/congresos/china2009/download/2-2/2-71.pdf ,accessed: 21.09.2012.