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Treatment of Organics Containing from Leather Processing Unit using Electro–Oxidation – A Noval Approach

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Abstract: Electro – Oxidation of high COD wastewater generated from liming section and other leather processing unit has been treated by a novel Electro – Oxidation method from the removal of Pollutants using triple oxide coated (Coated with the oxides of lead, manganese, and tantalum) titanium electrodes. Initially a synthetic wastewater was used with and without NaCl of reaction time, concentration, and then it was applied for real leather wastewater. DC was used in the experiment with a constant current density of 0.065 A / cm^2 was attained for optimization. The optimum time, and NaCl was found to be 120 min and 1% respectively for removal of 85 % of TOC. The complete removal of total Kjeldhal nitrogen and sulphide of organics was also observed after treatment by Electro – oxidation of liming wastewater.

Key Words: Tannery, Lime water, reuse of tannery wastewater, removal of sulphide and total kjeldhal nitrogen, electro- oxidation of tannery wastewater.

Introduction

Leather sector play an important role in Indian economy. However, the generation of wastewater is the major limiting factor which reduces the potential function of the sector considerably. Hence, for the past two decades, huge research attentions have been given on the management of wastewater through treatment methods. The complex nature of the processing operations and the chemical constituents of wastewater demand more treatment innovations. Amongst the various unit operations, wastewater of soaking and liming operations need special attention. The high salt concentration along with other organics and halophilic bacteria are the major problems with soaking wastewater (soak liquor), and, high pH (>12), presence of proteineous compounds are the problems for the lime wastewater. Thus the electro – oxidation of soaking wastewater and the results are highly encouraging for the reuse of the recovered salt for the tanning sector itself.

Beam house operations (soaking, liming, deliming, bating and pickling) of tanning sector alone generates approximately 70 Mm^3 of wastewater containing approximately 0.85Mt of chemical oxygen demand and 0.07 Mt of total Kjeldhal nitrogen[1], with high concentration of sulphide ions, When this wastewater is released in to the environment it will pose severe hazard to the environment[2]. With regard to the wastewater generatedfrom liming operations, a wide range of percentage of chemicals is being employed for limingandreliming without understanding the rationale behind hair removal and opening up of fibre bundles[3].

Addition of lime increases the pH (12-13) of the material and causes osmotic swelling due to ionic imbalances built up in the matrix[4]. The hydrostatic pressure built up would enhance the splitting up of fibre bundles, separation of unwanted interfibrillary materials and easy removal of flesh[5]. Moreover, the combined action of S^{2-} and OH^- ions helps to degrade hair protein by nucleophilic displacement reaction of disulphide bonds. Calcium hydroxide acts upon[6] the hair in such a way as to produce S^- or SH^- ions. Calcium hydroxide suspensions acted upon the cystine, breaking the -S-S- linkage and produce metallic sulphides and ammonia. The portion of the collagen acted upon by the alkaline unhairing liquor yields a large proportion of its total nitrogen as ammonia. Ammonia is released from wastes mainly by decomposition of proteins[7]. Thus, the complexity of the wastewater generated from liming operations demand special attention. Conventional biological treatment methods are not efficient to reduce or remove ammonia or chemical oxygen demand[5].

In contrast, electrochemical techniques are becoming more reliable and are gaining popularity for the treatment of industrial wastewater containing ammonia[8]. The removal of undesirable organics from liquid (usually aqueous) solutions through electrochemical process is based on the selection of electrodes and potential/current conditions. [9]Abu Ghalwa and Abdel suggested that the lead oxide coated titanium electrodes are highly efficient in the treatment of wastewater containing sulphur black dye.

Based on the said efficacy of electro-oxidation process, in the present study an attempt was made on the feasibility of the electro-oxidation process for the treatment of lime liquor. A batch study was conducted with simulated lime water (synthetic lime wastewater) with various concentrations of sodium chloride concentrations. Further, the study has been extended to the real lime wastewater with optimum salt concentration. Furthermore, the treated water was examined for its reusability in other unit operations. Reduction in TOC, TKN and sulphide load have been taken as the benchmarks for efficacy of the process adopted.

Experimental:

Synthetic Lime Wastewater Preparation

Synthetic liming wastewater (SLW) was prepared by dissolving 1.2 gms of bovine serum albumin, 3.3 gms of calcium hydroxide, 14.6 gms of sodium sulphide, 15gms of wool grease and sodium chloride (5000 to 20000 mg L^{-1}) in distilled water to a volume of 2 L and characterized accordingly[10]¸ The composition was such that the characteristic of the synthetic wastewater was in congruence with that of the real-case wastewater. Important process parameters of electro-oxidation those influence the process and efficiency of pollution reduction are, pH of the wastewater, current density, salt concentration and time.

Real Lime Wastewater

The straight (real) lime sectional wastewater was collected from Tannery Division of CLRI. The samples were filtered before subjecting to electro-oxidation process and characterization.

Reactor Set up for the Treatment of Lime Liquor Using Electro-Oxidation Process

Electro-oxidation process has been carried out in a cylindrical cell of an effective capacity of 2 litres. The temperature of the reactor was maintained at 30°C using thermo regulated water bath. A titanium mesh electrode (coated with the oxides (lead, manganese, tantalum) was used as the anode and cathode. Both electrodes were cylindrical and placed concentrically as shown in Figure 1. The anode surface area was estimated to be 200 cm^2. The electric power supply was provided by the laboratory direct current power source equipped with current – voltage monitoring. For all the experiments, the current density of $0.065 A/cm^2$ was maintained. The salt concentration was varied from 0 to 20,000 mg L^{-1} with an increment of 5,000 mg L^{-1}. The electro-oxidation process time was 2 hours and the samples collected for every 30 min intervals were subjected to TOC, COD, TKN, sulphide analyses. The free chlorine (DPD) was analysed for varied salt concentrations.

Results and Discussion

Treatment of Synthetic Liming Wastewater

According to Apostolos et al[11] and Angela Anglada et al[12], electro-oxidation of samples with alkaline pH, indirectly mediated by the presence of chlorides. Hence, in the present study, salt concentration has been taken as one of the variables in addition to time. Though pH and current density are the two important variables of electro-oxidation, in the present study, these two parameters were not considered, because, (i) change in pH results with the generation of neutral salts which ultimately affect the electro-oxidation processes and (ii) the majorobjective of the study lies on the efficiency of the process at different salt concentration, hence, the current density was kept constant.

Upon electro-oxidation process in the absence of chlorides, reduction in pollutant parameters, viz., TOC, COD and TKN at 31.7±1, 57.1±1 and 45.2±2% were observed (APHA) (Table .1).

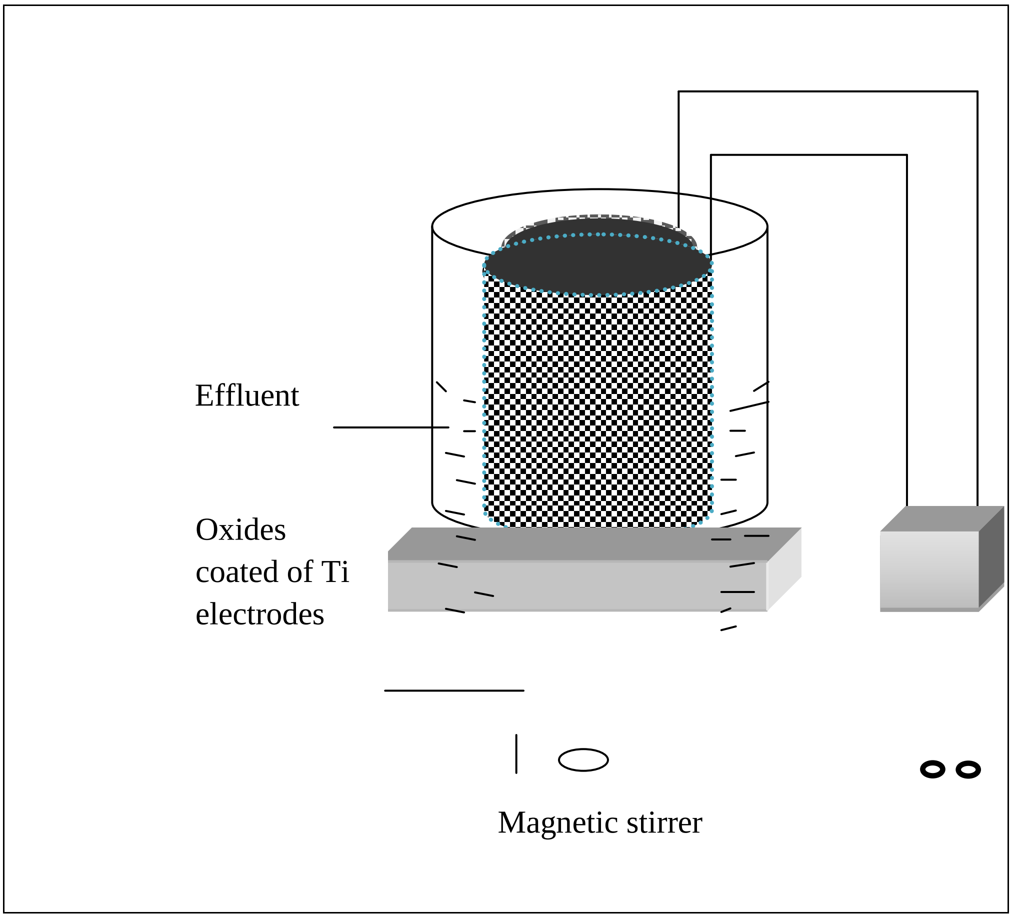


Table .1. Characteristics of synthetic lime wastewater after electro-oxidation treatment without salt

Parameter	Synthetic lime wastewater without NaCl*				
	0 min	30 min	60 min	90 min	120 min
pH	12.50±1	11.38±1	10.68±1	10.03±1	9.26±1
TOC mg/l	6126±215	5424±155	5020±120	4622±100	4184±120
% reduction of TOC	0	11.46±0.5	18.05±2	24.55±2	31.7±1
COD	22400±300	18500±350	12540±250	10010±150	9600±200
% reduction of COD	0	17.4±2	44±2	55.3±2	57.1±1
TKN mg/l	210±55	191±30	153±30	143±25	115±15
% reduction of TKN	0	9±2	27±1	31.9±1	45.2±2
Sulphide mg/l	688±120	626±30	563±25	382±20	303±20
% reduction of sulphide	0	9±4	18.1±2	44.4±1	55.9±1

*Mean ±SD

Since the percentage of reduction was not at the expected level, electro-oxidation of simulated lime wastewater in the presence of chlorides at 5000 mg L^{-1} was executed which results with 84±2, 71.3±5 and 77±2 % reduction in said pollutant parameters, TOC, COD and TKN respectively. The question on the fate of sulphide has been explained as; sulphide may oxidize to sulphite, bisulphite or sulphate according to Valeika et al[13]. Thus, in the present study, during electro-oxidation, reduction in sulphide was observed in the experiments with and without chlorides with significant difference. In the absence of chlorides, most of the sulphides are converted to sulphite/bisulphite and further transformed to sulphate with the 56% remaining sulphide concentration. Whereas, in the presence of salt, more than 90% of sulphide oxidized to sulphate, which results with the meagre percentage of sulphide in the treated water and suggested, chlorides mediated the electro-oxidation of sulphides in the simulated wastewater. With reference to the concentration of chlorides required for maximum reduction in pollutant parameters, experiments were done with 4 different salt concentrations, viz. 5000, 10000, 15000 and 20,000 mg L^{-1}. Results implied, increasing the salt concentration from 5000 mg L^{-1} to 10000 mg L^{-1} increases the percentage reduction of pollutant parameters. Additional increase in salt concentration displayed no significant change in the percentage reduction. From the results it can be understood that the oxidation of organic matter (TOC. COD) increases significantly when the salt concentration increased from 0 to 5000 mg L^{-1}is showed in Table .2. With reference to reduction of TKN versus salt concentrations, results implied, complete removal of TKN was observed with 10000 mg L^{-1} salt concentration (Table.3). The attenuation of pollution beyond 5000 ppm of salt concentration, the pollution attenuation was not incremental. This may be due to the generation of free chlorine and active chlorine that reaches a threshold. The level of free chlorine was not increased at 10000 ppm and more of salt concentration. At 15000 ppm of salt, the attenuation in TOC and COD were 86.9% and 77.6% respectively (Table .4). At 20000 ppm of salt concentration, the attenuation in TOC and COD were 87.9% and 79.8% respectively (Table .5).

Table 2. Characteristics of synthetic lime wastewater after treatment through electro-oxidation at salt concentration of 5000 mg L^{-1}

Parameter	**Synthetic lime wastewater with 5000 mg L^{-1}NaCl***				
	0 min	**30 min**	**60 min**	**90 min**	**120 min**
pH	12.5±1	11.03±1	10.08±1	9.24±1	8.10±1
TOC mg L^{-1}	6126±350	3854±120	2030±90	1442±100	980±200
% reduction of TOC	0	37±3	66.8±4	76.4±4	84±2
COD mg L^{-1}	22400±450	15242±200	11544±150	9584±200	6421±100
% reduction of COD	0	31.9±2	48.4±3	57.2±2	71.33±5
TKN mg L^{-1}	210±55	168±15	123±10	76±10	49±10
% reduction of TKN	0	20±3	41±6	64±6	77±2
Sulphide mg L^{-1}	688±120	482±100	172±80	105±76	28±4
% reduction of Sulphide	0	30±2	75±2	84.7±2	95.9±1

*mean ± SD

Table 3. Characteristics of synthetic lime wastewater after treatment through electro-oxidation at salt concentration of 10000 mg L^{-1}

Parameter	**Synthetic lime wastewater with 10000 mg L^{-1}NaCl***				
	0 min	**30 min**	**60 min**	**90 min**	**120 min**
pH	12.5±1	11.14±1	9.03±1	8.59±1	8.23±1
TOC mg L^{-1}	6126±350	3063±150	1887±200	1311±150	845±200
% reduction of TOC	0	50.2±2	69.2±2	78.6±2	86.2±2
COD mg L^{-1}	22400±450	12840±300	10000±250	8564±280	5100±350
% reduction of COD	0	42.6±2	55.3±2	61.7±2	77.2±2
TKN mg L^{-1}	210±55	126±16	71±10	BDL	BDL
% reduction of TKN	0	40±2	57.9±3	-	-
Sulphide mg L^{-1}	688±120	389±70	BDL	BDL	BDL
% reduction of sulphide	0	43.5±3	-	-	-

*Mean ±SD

Table 4. Characteristics of synthetic lime wastewater with 15000 mg L^{-1}salt concentration by electro-oxidation

Parameter	**Synthetic lime wastewater with 15000 mg L^{-1}NaCl***				
	0 min	**30 min**	**60 min**	**90 min**	**120 min**
pH	12.5±1	10.51±1	9.02±1	8.6±1	8.01±1
TOC mg L^{-1}	6126±350	2943±260	1562±200	1106±130	798±100
% reduction	0	51.9±2	74.5±4	81.9±2	86.9±1
COD mg L^{-1}	22400±450	11684±224	10256±156	9002±124	5010±86
% reduction	0	47.8±2	54.2±2	59.8±2	77.6±2
TKN mg L^{-1}	210±55	118±22	60±12	BDL	BDL
% reduction	0	68.7±2	71.4±2	-	-
Sulphide mg L^{-1}	688±120	285±36	BDL	BDL	BDL
% reduction	0	58.6±2	-	-	-

*Mean ±SD

Table 5. Characteristics of synthetic lime wastewater with 20000 mg L^{-1}salt concentration by electro-oxidation

Parameter	**Synthetic lime wastewater with 20000 mg L^{-1}NaCl***				
	0 min	**30 min**	**60 min**	**90 min**	**120 min**
pH	12.5±1	10.01±1	9.82±1	8.2±1	8.02±
TOC mg L^{-1}	6126±350	3002±120	1712±114	1200±130	741±130
% reduction	0	50.9±3	72±3	80.4±2	87.9±2
COD mg L^{-1}	22400±450	9600±212	8520±200	7984±156	4522±130
% reduction	0	57.1±2	61.96±2	64.35±3	79.8±3
TKN mg L^{-1}	210±55	110±22	BDL	BDL	BDL
% reduction	0	47.6±3	-	-	-
Sulphide mg L^{-1}	688±100	72±30	BDL	BDL	BDL
% reduction	0	89.5±3	-	-	-

*Mean ±SD

The following paragraphs summarize the role of chlorides in the electro-oxidation of proteineous lime liquor with high alkaline pH. The general chloride reaction involved in electrochemical oxidation was as follows;

Anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$(1)
Cathode: $2e^- + H_2O \longrightarrow 2OH^- + H_2$(2)
Overall: $2OH^- + Cl_2Cl^- \longrightarrow OCl^- + H_2O$ (3)

The continuous and *in situ* release of chlorine, hypochlorous acid (HClO) and hypochlorite ions (ClO^-) during electro-oxidation are strong oxidizing species[14], responsible for the reduction in organic contaminations measured in terms of TOC and COD.

Alkaline condition boosts the $Cl^- \rightarrow Cl_2 \rightarrow ClO^- \rightarrow Cl^-$ redox circulation to enhance the indirect oxidation. In the present study, an electrolyte concentration of 10000 mg L^{-1} was selected as the operating concentration despite the known toxic effects of excess chloride concentrations. Chlorine, hypochlorous acid and hypochlorite ions are strong oxidizing species and are often collectively referred as active chlorine, e.g. $ClO\cdot$, $Cl\cdot$, $OH\cdot$ and $H\cdot$. And these active chlorine present in thewastewater with pollutants in which is being reduced and lead to the recovery of chloride ions which are in turn continuously oxidized at the anode to form chlorine /hypochlorite again[15,16]. In general, nitrogenous pollutant is supposed to be eliminated mainly by a reaction with ‘‘active chlorine’’ as ammonia.Estimations on the release of chlorine with respect to salt concentration suggested, between 5000 and 10000 mg L^{-1}NaCl concentration, the threshold was reached for free chlorine as shown in Table .6.

Table 6. Characteristics of Real lime wastewater with 10000 mg L^{-1}salt concentrationby electro-oxidation

Parameter	**Real lime wastewater with 10000 mg L^{-1}NaCl***				
	0 min	**30 min**	**60 min**	**90 min**	**120 min**
pH	12.25±1	11.03±1	10.21±1	9.53±1	8.21±1
TOC mg L^{-1}	4896±340	2634±230	2022±230	1293±160	764±120
% reduction	0	46.2±1	58.7±1	73.6±2	84.4±3
COD mg L^{-1}	15328±568	9565±430	7756±300	6514±315	4394±300
% reduction	0	37.6±1	49.4±2	57.5±2	71.2±2
TKN mg L^{-1}	560±78	316±56	223±41	BDL	BDL
% reduction	0	43.5±1	60.1±2	-	-
Sulphide mg L^{-1}	374±68	235±16	BDL	BDL	BDL
% reduction	0	37.2±4	-	-	-

S*Mean ± SD

3.2. Treatment of Real Case Liming Wastewater

Based on the results obtained from synthetic lime wastewater, an experiment on real lime waste water was executed with the optimized concentration of salt as 10000 mg L^{-1} with the same current density and time intervals.

Table .7 depicts the initial pollutants concentration (mg L^{-1}) along with the concentration levels upon treatment. Similar to the reduction in pollution parameters observed for batch study experiments on simulated wastewater, significant percentage of reduction in TOC (84.4±3), COD (71.2±2) and TKN (>99) was observed for the real wastewater within 120 minutes of the treatment. These observations suggested that the pollutant in the form of proteineous matter was completely disintegrated.

Table .7. Free chlorine – synthetic lime wastewater with varied salt concentration byElectro-oxidation

Nacl concentration mg L^{-1}	**Free chlorine mg L^{-1*}**				
	0 min	**30 min**	**60 min**	**90 min**	**120 min**
5000	0	480±80	1565±220	1420±130	1875±100
10000	0	2350±220	2188±112	1875±78	1875±68
15000	0	2655±260	2198±80	1870±61	1756±55
20000	0	2746±310	2078±75	1798±90	1786±87

*Mean ±SD

With regard to the consumption of energy, results demonstrated an increase in energy consumption with an increase till 60 minutes and thereafter no proportionate increase was observed Similar to batch studies, reduction in sulphide, nitrogen and other organics observed with real wastewater may be attributed to the said release of oxidized products of chlorides[11].

FT-IR Characterization

Further FT-IR analysis (synthetic and real lime wastewater) of samples before and after treatment suggested (Fig.2 & 3), the spectra of electro-oxidation of synthetic lime wastewater displayed the prominent band at 3400 to 3350 cm^{-1} corresponding to N-H stretching vibration band, BSA exhibits an intense Amide I bond[17] centred at approximately 1650 cm^{-1}, the prominent bands (1635 – 1650 cm^{-1}). The N-H stretching vibrations and amide I bands were minimized with respect to time and after 2 hours of electro-oxidation process the peaks were absent which clearly emphasize the complete removal of proteineous molecules and correlated well with the TKN analysis of the treated water.

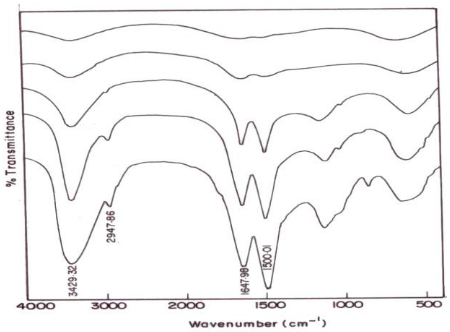


Figure .2FT-IR results of synthetic lime wastewater with 10000 mg L^{-1} by Electro- oxidation

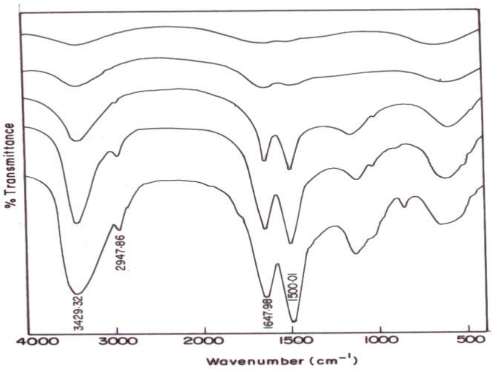


Figure 3. FT-IR results of Real lime wastewater with 10000 mg L^{-1} by Electro- oxidation

Energy Consumption

Although the study exemplify the significant reduction in pollutant parameters of simulated lime wastewater through electro-oxidation process, the answer for the question on energy requirement is necessary. Hence, calculations on energy requirement was made according to the following equation (4) and it has been calculated as 0.149 kWhm-3 per litre

$$SEC= 10^{-3}Jut \qquad (4)$$

Where, SEC is the specific energy consumption (kWhm^{-3}); t is the time needed for the removal of a given pollutant (h); J is the total current applied (A); U is the overall cell voltage (V) according to Szpyrkowicz et al[15,16].

Reuse Studies

Though the above said paragraphs demonstrated the reduction in major pollutant parameters of real lime wastewater, without studying the application or the reuse of the treated water, the whole study is incomplete. Hence, the reusability of the treated water was tested in leather processing itself and an organo-leptic property of final leather was studied to authenticate the reuse.

Table .7 depicts the characteristics of the liming wastewater after electro-oxidation and suggested the suitability for reuse in beam house operations. And the pelt obtained from the above process was subjected to tanning and the resultant tanned material was analysed for its organo-leptic properties. Four batches of study were conducted. The chrome tanned leathers - wetblue were tested by using the lime treated water (Table .8) for chrome content and shrinkage temperature. The chrome content and shrinkage temperature of the leathers limed using the treated for the first, second and third batches were comparable to that of the control leathers. The leathers were further processed into finished leathers. The finished leathers were also tested to ascertain the quality of the final leathers. It can be understood from the results (Table .9) that the quality in terms of physical characteristics such as tensile strength, tear strength and grain breaking strength of the leathers limed using the treated wastewater was much comparable to that of the control leathers.

Table .8 Reusability of treated lime wastewater

Parameter * (mg/l)	Untreated	Treated I	First reused	Treated II	Second reuse	Treated III	Third reused
TOC	4896±350	764±120	4925±525	778±225	4883±400	739±230	5012±400
COD	15328±500	4307±290	16422±575	4212±225	15836±555	4452±215	17123±455
TKN	560±75	BDL	582±100	BDL	549±80	BDL	592±155
Sulphide	374±55	BDL	359±80	BDL	388±55	BDL	362±65
Chloride	9858±375	8795±300	10112±450	8838±750	10087±415	8679±600	10183±375
Free chlorine	0	1960±250	0	1846±255	0	1933±215	0
Sulphate	608±124	2035±440	632±120	2134±500	662±100	2185±400	664±75

*Mean ±SD BDL: Below Detectable limit

Table .9(a) Chrome content and temperature of finished leather

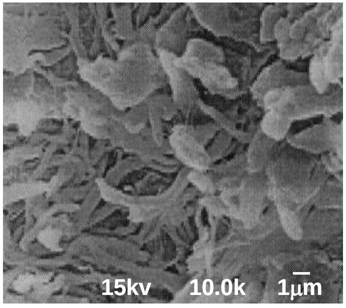
Finished leather	Control	Reuse I	Reuse II	Reuse III
Chrome content (% w/w Cr_2O_3)	2.1	2.1	2.2	1.9
Shrinkage temperature (°C)	102	102	103	102

Table .9(b) .Physical properties of finished leather

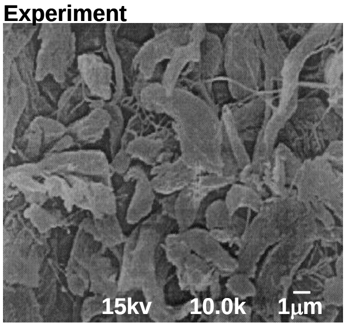
Finished leather	Control	Reuse I	Reuse II	Reuse III
Tensile strength (Kg/cm^2)	198	184	189	195
Tear strength (Kg/cm)	85	92	88	87
Grain breaking strength (Kg/cm)	98	92	98	99

SEM analysis of the finished leather of both control and experimental samples (Figure .4) suggested the compact internal structures and packing of fibrillar network in both the samples.

Control



Experiment



Conclusion

The present study emphasizes the feasibility of electro-oxidation of wastewater generated from liming process and the reusability of the treated water in leather processing by assessing the physical and organo-leptic properties of the finished leather. Based on the success on treatment of soak liquor using electro-oxidation technique, the amenability of the said technique for liming wastewater was attempted. Before proceed to the real lime wastewater, batch studies were carried out to understand the practical difficulties and efficacy of electro-oxidation process for simulated (synthetic) lime wastewater. Since, chlorides mediates the oxidation process, the whole study has been extended for with and without chlorides. Further, the optimum concentration of chlorides for the significant improvement in reduction parameters was also made. Results revealed, at 5000 mg/l chloride concentration, more than 70% reduction in pollution parameters (COD, TOC, TKN) was observed, and further increase in salt concentration results with complete disintegration of TKN. FT-IR analysis of the samples before and after treatment also coincides with the observations made on TKN concentration. Similar results were obtained for the treatment of real lime wastewater. Further, reuse of the treated water in beam house operations demonstrated no significant changes in the physical, organo-leptic properties and SEM analysis of the finished leather obtained from processing with treated water and with freshwater (control).

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