Electrochemical Oxidation and Reuse of Pickling Wastewater from Tanneries

by

Sundarapandiyan S, Rajeswari G, Saravanan P*, Dhanaselvan M C K, Ramalingam S and Chandrababu N K

Central Leather Research Institute

Adyar, Chennai, India 600 020

Abstract

Reuse of pickling wastewater after treating it electrochemically has been studied. Pickling wastewater has been neutralised to pH 7.0 and subjected to electrooxidation. Electrooxidation has been carried out using graphite electrodes at a current density of 0.012 A/cm^2 for 2 hrs. Pickling wastewater has been analysed prior to and after the treatment. Treated wastewater has been reused and the cycle continued for seven times. The pickled pelts were chrome tanned and further converted into crust leathers. Shrinkage temperature, chromium uptake and chromium distribution of wetblue were tested. Crust leathers were tested for physical characteristics. Characteristics of treated pickling wastewater indicated that electrooxidation reduced the pollution load in terms of COD and TKN significantly. Results indicated that the recycling did not influence the characteristics of wetblue and crust leathers.

Resumen

La reutilización de los residuales del baño del piquelado luego de tratarlos electroquímicamente se ha investigado. Los residuales del baño de piquelado se han neutralizado hasta pH 7.0 y sometidos a oxidación electrolítica. La oxidación se efectuó durante dos horas por medio de electrodos de grafito bajo una densidad de corriente de 0,012 A/cm^2. El desperdicio del baño del piquelado se analizó antes y después del tratamiento. Baños tratados se reutilizaron y reciclaron siete veces. Las pieles piqueladas fueron curtidas al cromo y convertidas a crostas. Temperatura de contracción, contenido y distribución del cromo en el cuero "wet-blue" fueron determinados. Las características físicas de las crostas fueron determinadas. Las características de los baños del piquelado indicaron que la oxidación electrolítica redujo la carga contaminante en términos de DQO y "TKN" [se refiere al nitrógeno orgánico por método Kjeldahl] significativamente. Los resultados indican que el reciclado no afectó las características del cuero en "wet-blue" y crosta.

Introduction

Leather manufacturing is associated with the generation of huge volume of wastewater. Among different waste streams, saline waste streams pose greater problems. In many countries such as India, Australia and Italy, management of waste streams with high TDS and chloride level is a serious issue. Techniques such as ultrafilteration[1], reverse osmosis[2] and electro-dialysis[3] have been studied for the treatment of waste streams with high TDS. These methods are not only cost intensive but generate rejects.

Recycling can be a promising option for the management of pickling wastewater. Direct reuse of pickling wastewater without treatment may be detrimental. The protein matter and fat present in the pickling wastewater may interfere with chrome tanning process since the pickle bath is predominantly used for the chrome tanning. High natural fat content or free fatty acid in the chrome tanning bath form stains of insoluble fat soaps[4]. Similarly presence of high amount of protein may lead to patches on tanned leathers. Appropriate and effective method of removal or reduction of the organic pollutants in pickling wastewater would facilitate continuous recycling of pickling wastewater.

Electrochemical methods have been used effectively for water purification. Nevertheless electrochemical methods have not yet attracted adequate attention for wastewater treatment[5]. Treatment of landfill leachate by indirect electrochemical oxidation was reported. Leachate with a BOD/COD ratio of 0.2 and chloride level of 2500 mg/l was used. Reduction of pollution load was attributed to the oxidation by chlorine and hypochlorite produced[6]. Tannery wastewater was treated using Ti/Pt and Ti/Pt/Ir electrodes for the removal of ammonium salts. It is reported that electrochemical treatment was suitable for the final polishing of tannery wastewater and an alternate step for biological nitrification and denitrification[7]. In another work tannery wastewater after secondary clarification was treated using Ti/Pt, Ti/Mno_2 anodes and Ti cathodes[8]. Treatment of composite wastewater from tannery was carried out using Ti/Pt anode and SS 304 cathode. It was concluded that electrooxidation was not economically viable for the treatment of composite wastewater from tanneries[9].

* Corresponding Author - e-mail address: dermagroup@yahoo.co.in, Telephone and fax: 91 + 44 + 24915730
Manuscript received April 23, 2007, accepted for publication March 17, 2008

It is clear that electrochemical treatment may not be viable for the treatment of composite wastewater. But it may be a suitable option for the treatment of sectional waste streams. In this study, pickling wastewater has been treated following electrooxidation process. From previous investigations, it is evident that moderate alkaline to neutral conditions are very much suitable for carrying out electro-oxidation in chloride environment[10, 11]. Electrooxidation has been carried out after neutralizing the pickling wastewater to pH 7.0. Treatment has been carried out for two hours at a current density of 0.012 A/cm^2. Treated wastewater has been reused for pickling of subsequent batches for seven times. Quality of wet blue and the crust leathers were tested.

MATERIALS AND METHODS

Electrooxidation

Electrooxidation cell of 2 litre capacity has been used in this work. Graphite electrodes were used both as anode and cathode. They are cylindrical with a diameter of 2.54 cm and a length of 13 cm. The distance between the adjacent electrodes was 1 cm. The electric power supply was provided by laboratory D.C power source equipped with current – voltage monitoring and of maximum output of 60 A.

Chemicals

The chemicals that were used for leather manufacturing process were of commercial grade. Relugan RE, Basyntan DI and Lipoderm Liquor FB1 were obtained from BASF (India) Limited.

Chemical oxygen demand

Standard procedure as reported by American public health association was followed for the determination of COD[12]. Open reflux method as given in the standard procedure has been followed. According to this procedure, most types of organic matter are oxidized by a boiling mixture of chromic and sulphuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable matter is calculated in terms of oxygen equivalent. Keep ratios of reagent weights, volumes, and strengths constant when sample volumes other than 50 mL are used. The standard 2 hour reflux time may be reduced if it has been shown that a shorter period yields the same results. Some samples with very low COD or with highly heterogeneous solids content may need to be analyzed in replicate to yield the most reliable data. Results are further enhanced by reacting a maximum quantity of dichromate, provided that some residual dichromate remains.

Total Kjeldahl nitrogen

TKN was also estimated following the standard procedure as reported by American public health association[12]. According to this procedure, in the presence of H_2SO_4, potassium sulfate (K_2SO_4), and cupric sulfate ($CuSO_4$) catalyst, amino nitrogen of many organic materials is converted to ammonium. Free ammonia also is converted to ammonium. After addition of base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulphuric acid. The ammonia may be determined colorimetrically, by ammonia-selective electrode, or by titration with a standard mineral acid. In this present study, method of titration was followed.

Chloride content

Standard procedure as per American public health association was followed for the determination of chloride[12]. According to this procedure, Silver nitrate reacts with chloride ions to form silver chloride, slightly soluble with precipitate. The completion of reaction is indicated when all the chlorides get precipitated. Free silver ions react with chromate to form silver chromate of reddish brown colour.

Leather manufacturing process

The following process of leather manufacturing was followed in the present study.

Wet salted Indian goatskins were taken for these experiments. The skins were desalted and soaked twice, using 300% of water on the weight of the skins. Paste liming was carried out with the lime-sulphide paste (water 15%, Lime 10% and sodium sulphide 2.5%). Paste was applied on the flesh sides of the skins and piled for six hours. The skins were unhaired. Unhaired pelts were relimed in paddle using 300% water and 5% lime for 2 days. Flesh was removed after reliming. The fleshed pelt weight was noted and the subsequent chemical offer was on the basis of pelt weight. The fleshed pelts were washed with 200% water in drum for 20 minutes. Then deliming was carried using 150% water and 1% Ammonium chloride in drum for 40 minutes. The delimed pelts were washed with 200% water in drum for 20 minutes. Pelts were then pickled using 100% water and 10% common salt in drum. After treating the pelts for 10 minutes in saline water, 1% hydrochloric acid diluted with 10% water was administered in three feeds. After first and second feeds, drum was run for 15 minutes and after the third feed it was run for 30 minutes. The pH of the cross section of the pelt was ensured to be 3.0.

Chrome tanning was carried out in 50% (by volume) of the pickle liquor. Pickled pelts were treated with 8% basic chromium sulphate (BCS). After running the tanning drum for 45 minutes, 50% water was offered and the drum was run for 40 minutes. Then basification was carried out using 1% sodium formate and 1% sodium bicarbonate. The weight of the tanned materials was noted down and the offer of chemicals from this point onwards was based on the tanned leather weight.

Wet blue materials were washed with 100% water and 0.2% acetic acid for 30 minutes. Rechrome tanning was carried out using 100% water and 5% BCS and the retanning process was carried out for 40 minutes. Basification was carried out using 1% sodium formate and 1% sodium bicarbonate. Leathers were then washed using 150% water for 20 minutes and neutralised using 1% sodium formate and 1% sodium bicarbonate. After neutralisation the leathers were once again washed using 150% water. Leathers were retanned and fatliquored by offering 2% Relugan RE, 2% Basyntan DI and 2% Lipoderm Liquor FB1 with 100% water and the drum was run for 45 minutes. Fixing was carried out using 1% formic acid. Acid was diluted with 10% water. Acid solution was offered in three feeds. After the first and second feeds drum was run for 15 minutes and after the third feed drum was run for 30 minutes. The crust leathers were piled for a night and next day they were sammed and set. Then the leathers were hooked for drying under shade. The dried crusts were staked.

Chromium content of wet blue

Samples were cut from butt portion as per the official procedure IUC 2 and the chrome content was analyzed as per IUC 8 of IULTCS methods. For assessing layer wise chromium distribution, samples were taken from the butt portion and then the samples were split into three layers. Chromium content of these layers was estimated. For the assessment of area wise distribution of chromium, samples were cut as per IUC 2 from different areas[13].

Physical testing methods

Sampling for physical testing of leather was done as per IUC 2. Leathers were tested for tensile strength, tongue tear strength, grain bursting strength and shrinkage temperature following the procedures IUP 6, IUP 8, IUP 12 and IUP 16 respectively[13].

RESULTS

Reuse experiments were carried out using Indian goatskins. Four wet salted goatskins were taken per batch. Pickling of first batch was performed as given above and the wastewater was collected. Half of the volume of pickling wastewater was filtered to remove gross suspended matters using a cloth filter. The wastewater was them neutralized to pH 7.0 using NaOH and electrochemically oxidised with a current density of 0.012 A/cm^2 for 2 hours. The remaining pickling wastewater was used for carrying out chrome tanning. The treated wastewater was used for pickling of the second batch. Chloride content of the treated pickling wastewater was analyzed to estimate the amount of salt to be replenished during reuse.

For reuse of pickling liquor, necessary volume of water and required level of salt were supplemented to make 100% water and 10% salt. The specific gravity was maintained at 8^0Be. In similar manner, reuse was carried out for seven batches. Details of water and salt supplementation are presented in Table I. Characteristics of the pickling wastewater are given in Table II. Average reduction in COD and TKN was found to be 85.25% and 88.38% respectively. The characteristics of pickling wastewater after treatment in all the seven experimental cases are found to be similar without significant variation. Also the characteristics of pickling wastewater in the case of experiments are similar to that of the control.

To ascertain the possible impact of the reuse on the quality of wet blue made, chrome uptake and distribution were assessed. Results of chrome content of the leathers are given in Table III. Layer wise and area wise distribution of chromium was also assessed.

TABLE I
Supplementation details

Batch	Weight of pelt (kg)	Fresh water added (l)	Volume of wastewater for reuse (l)	Salt content of treated liquor used for reuse (g/l of NaCl)	Total salt content of treated liquor used for reuse (g)	Salt replenished (g)
Control	4.0	4	---	---	---	400
Reuse 1	4.0	2	2	58.5	117	283
Reuse 2	4.0	2	2	52.9	106	294
Reuse 3	4.0	2	2	62.6	125	275
Reuse 4	4.0	2	2	56.0	112	228
Reuse 5	4.0	2	2	58.5	117	283
Reuse 6	4.0	2	2	59.0	118	282
Reuse 7	4.0	2	2	56.5	113	287

TABLE II
Wastewater characteristics

Batch		Parameter	
		COD (mg/l)	TKN (mg/l)
Control	Pickling wastewater prior to treatment	3448	215
	Pickling wastewater after treatment	552	20
	Reduction (%)	84	91
Reuse 1	Pickling wastewater prior to treatment	3210	228
	Pickling wastewater after treatment	482	32
	Reduction (%)	86	87
Reuse 2	Pickling wastewater prior to treatment	3680	210
	Pickling wastewater after treatment	516	28
	Reduction (%)	87	86
Reuse 3	Pickling wastewater prior to treatment	3420	208
	Pickling wastewater after treatment	489	26
	Reduction (%)	86	88
Reuse 4	Pickling wastewater prior to treatment	3300	220
	Pickling wastewater after treatment	470	24
	Reduction (%)	82	89
Reuse 5	Pickling wastewater prior to treatment	3280	210
	Pickling wastewater after treatment	490	22
	Reduction (%)	85	90
Reuse 6	Pickling wastewater prior to treatment	3400	228
	Pickling wastewater after treatment	465	28
	Reduction (%)	86	88
Reuse 7	Pickling wastewater prior to treatment	3300	210
	Pickling wastewater after treatment	470	26
	Reduction (%)	86	88

TABLE III
Chrome content of wet blue

Batch	Chrome content (% w/w of Cr2O3)				
	Piece 1	Piece 2	Piece 3	Piece 4	Mean
Control	2.26	2.19	2.20	2.19	2.21
Reuse 1	2.15	2.08	1.84	1.85	1.98
Reuse 2	2.19	2.15	2.20	2.10	2.16
Reuse 3	2.18	2.24	2.16	2.22	2.20
Reuse 4	2.17	2.12	2.12	2.15	2.12
Reuse 5	2.12	2.16	2.20	2.12	2.14
Reuse 6	2.14	2.07	2.14	2.22	2.22
Reuse 7	2.17	2.12	2.18	2.18	2.12
Mean of mean					2.14
S.D					0.09

TABLE IV
Layer wise distribution of Chrome

Batch	Chrome content* (% w/w of Cr2O3)				
	Shoulder	Belly	Butt	Mean	S.D
Control	2.32	1.95	2.27	2.18	0.20
Reuse 1	2.12	1.93	1.67	1.90	0.23
Reuse 2	2.13	2.22	2.06	2.14	0.08
Reuse 3	2.23	2.22	2.16	2.20	0.04
Reuse 4	2.08	2.11	2.12	2.10	0.02
Reuse 5	2.17	2.19	2.18	2.18	0.01
Reuse 6	2.19	2.18	2.20	2.19	0.01
Reuse 7	2.11	2.13	2.20	2.15	0.03

* Values are the average chrome content of particular area of four pieces in an experiment

TABLE V
Area wise distribution of Chrome

Batch	Chrome content* (% w/w of Cr2O3)				
	Top	Middle	Bottom	Mean	S.D
Control	2.17	2.21	2.15	2.18	0.031
Reuse 1	1.97	1.95	1.99	1.97	0.020
Reuse 2	2.12	2.17	2.14	2.14	0.025
Reuse 3	2.22	2.17	2.20	2.20	0.025
Reuse 4	2.14	2.17	2.11	2.14	0.030
Reuse 5	2.20	2.16	2.15	2.17	0.026

* Values are the average chrome content of particular layer of four pieces in an experiment

TABLE VI
Physical Characteristics of Leather

Batch	Parameter*			
	Tensile strength (kg/cm^2)	Tongue tear strength (kg/cm)	Grain bursting strength (kg/cm)	Shrinkage temperature (^{0} C)
Control	240	54	82	102
Reuse 1	220	56	87	103
Reuse 2	224	52	85	102
Reuse 3	238	56	92	102
Reuse 4	228	52	88	102
Reuse 5	220	52	86	103
Reuse 6	225	54	90	103
Reuse 7	234	56	82	102
Mean	228.6	54.0	86.5	102.4
S.D	7.83	1.85	3.55	0.52

* Values are the average of characteristics of four pieces in each experiment

For assessing area wise distribution, chromium content in samples cut from areas namely shoulder, belly and butt was analyzed. Results are presented in Table III and IV. Results of physical properties such as shrinkage temperature, tensile strength, tongue tear strength and grain bursting strength of the crust leathers were are presented in Table VI. Physical properties of the leathers obtained through reuse experiments were akin to those of control leathers.

DISCUSSION

Reduction of COD and TKN of pickling wastewater can be attributed to the formation of chlorine and hypochlorite. Salt present in the wastewater facilitated the formation of chlorine and hypochlorite and ultimately favoured oxidation of organic matter. In a study of electrooxidation of saline wastewater, the reduction in chloride and generation of chlorine were monitored. It was reported that the concentration of chlorides was reduced by 34% in first 10 minutes and was stabilized at this concentration. Similarly chlorine level was increased during the first 10 minutes and was stabilized through out the process for two hours. This is indicative of the existence of the theoretical cycle of chlorides-chlorine-chlorides[9]. Hence the release of chlorine from the electrooxidation process may not be significant as the chlorine formed during the process is converted back into chlorides. Major proportion of the chlorine generated is utilized for the oxidation of pollutants. Many radicals of short life such as OH^-, $O^-$and $ClOH^-$ may also contribute to the oxidation of organic matter[9,14]. In this present work, the average reduction in COD and TKN were found to be 85.25% and 88.34% respectively. Reduction in COD and TKN indicates that protein and fat present in the pickling wastewater were oxidized substantially.

There was no much variation in the quality of the pickling wastewater. Hence it could be inferred that the electrochemical treatment carried out and the conditions chosen could result with adequate treatment of the pickling wastewater to render the same suitable for continuous reuse. Chrome content of the leathers produced from reuse experiments was on par with that of the control leathers. Area wise and layer wise distribution of chromium of the recycle experiment cases in comparison with control case show that there was no significant influence on chromium distribution due to recycling. Also it is clear that continuation of reuse did not cause significant impact on chrome content and distribution. The physical testing data of the crust leathers also support this inference. As there is no appreciable change in the quality of wastewater, chromium uptake, chromium distribution and quality of crust leathers for seven reuses, it can be enunciated that this system of electrochemical treatment and reuse is an effective solution for the management of pickling wastewater.

It can be concluded that the system is not only benevolent in reducing water consumption but a sustained solution for the management of pickling wastewater.

CONCLUSIONS

The following are the conclusions derived from this present work.

- Electrooxidation of pickling wastewater with a current density of 0.012 A/cm^2 for 2 hours could bring about significant reduction of organic pollutants.
- Electrooxidation of pickling wastewater and its reuse for seven batches do not have significant influence on the quality of wet blue in terms of chrome uptake and distribution.
- Reuse of electrooxidized pickle liquor continuously for seven batches does not render the cruse leathers with quality non-compliance.
- Hence electrooxidation and reuse of pickling wastewater is a viable solution for the management of pickling wastewater.

ACKNOWLEDGEMENT

It is acknowledged herewith that this project has been carried out under the network project (SMM 10) of Council of Scientific Industrial Research, India. The authors thank profoundly Dr Bhaskar Raju, Scientist, National Metallurgical Laboratory, for his support.

REFERENCES

1. Ana Maria Brites Alves, Maria Norberta de Pinho.; Ultrafiltration for colour removal of tannery dyeing wastewaters. *Desalination* **130,** 147-154, 2000.
2. Cassano, R., Molinari, R., Romano, M., Drioli, E., Treatment of aqueous effluents of the leather industry by membrane processes: A review. *Journal of Membrane Science*. **181,** 111-126, 2001.
3. Raghava Rao, J., Prasad, BGS., Narashimhan, V., Ramasami, T., Shah, PR., Khan, A.A.; Electrodialysis in the recovery and reuse of chromium industrial effluents. *Journal of Membrane Science*. **46,** 215-214, 1989.
4. Gerhard John.; Possible defects in Leather production, p.66, 1997.
5. Grimm, J., Bessarabov, D., Sanderson, R.; Review of electro assisted methods for water purification. *Desalination* **115,** 285-294, 1998.
6. Li-Choung Chiang., Juu-En Chang.; Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. *Wat. Res.* **29,** 671-678, 1995.
7. Lida Szpyrkowicz., Jeremi Naumczyk., Francesco Zilio-Grandi.; Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes. *Wat. Res.* **29,** 517-524, 1995.
8. Rao, N. N., Somasekar, K. M., Kau, S. N., Szpyrkowicz. L.; Electrochemical oxidation of tannery wastewater. *J. Chem. Technol. Biotechnol.* **76,** 1124-1131, 2001.
9. Apostolos, G., Vlyssides, Cleanthes, J., Israilides; Detoxification of tannery waste liquors with an electrochemical system. *Env. Pollution.* **97,** 147-152, 1997.
10. Apostolos, G., Vlyssides., Cleanthes, J., Israilides., Loizidou, M., Karvouni, G., Mourafeti, V.; Electrochemical treatment of vinasse from beet molasses. *Proceedings of the 2nd Specialised Conference on Pretreatment of Industrial Wastewaters.* IAWQ, Athens, **522-529,** 1996.
11. Wilk, I.J., Altmann, R.S., Berrg, J.D.; Antimicrobial activity of electrolyzed saline solutions. *The Science of the Total Environment*. **63,** 191-197.
12. APHA-AWWA-WPCF. *Standard methods for the examination of water and wastewater,* American public health association, 17th Edition; Washington, D C, 1989.
13. *Official method of analysis*. The society of leather technologists and chemists (IULTCS), Northampton, 1996.
14. Apostolos, G., Vlyssides., Loizidou, M., Karlis, P.K,. Zorpas, A.A., Papaioannou, D., Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode. *Journal of Hazardous materials*. **B70,** 41-52, 1997.