

TREATMENT OF TANNERY WASTEWATER BY ELECTROCOAGULATION

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ABSTRACT

Treatment of tannery effluent is a challenging task as it is a biogenic matter of hides and a large variety of organic and inorganic chemicals. The objective of the present work is to study the application of electro-coagulation technique in the treatment of tannery effluent. The experiments were carried out in an electrochemical reactor using sacrificial electrodes, iron as anode and aluminum as cathode in a continuous process. Operating parameters such as current density and electrolysis time were studied for maximum Chemical Oxygen Demand (COD) reduction, Biochemical Oxygen Demand (BOD) reduction, Total Dissolved Solids reduction (TDS) and Chromium removal. Other relevant parameter such as power consumption for COD removal was also evaluated. The higher flow rate resulted in improved COD, BOD, TDS and chromium removal. The applied current density was also found to significantly influence the reduction of COD, BOD, TDS and chromium removal.

Keywords: electrocoagulation, COD, BOD, Chromium, TDS, current density.

INTRODUCTION

The tannery effluent is a mixture of biogenic matter of hides and a large variety of organic and inorganic chemicals. It usually contains high concentrations of chlorides, aliphatic sulfonates, sulfates, aromatic and aliphatic ethoxylates, sulfonated polyphenols, acrylic acid condensates, fatty acids, dyes, proteins, soluble carbohydrates, sodium sulfide and inorganic like chromium. The potential environmental impact of the chemicals used in tannery operations is well known.

Conventional physico-chemical treatments of tannery effluents consist of pretreatment, flocculation, sedimentation and sludge handling.

Chemical coagulation has been used for decades to destabilize colloidal suspensions and to effect pre-

cipitation of soluble metal species as well as other inorganic species from aqueous streams, thereby permitting their removal through sedimentation or filtration. Alum, lime, and/or polymers have been the chemical coagulants used.

These processes, however, tend to generate large volumes of sludge with a high bound-water content which can slow down filtration operation and are also difficult to dewater. These treatment processes also tend to increase the total dissolved solids content of the effluent, making it unacceptable for reuse in industrial applications.

Conventional chromium removal methods include adsorption, chemical precipitation, biological degradation, ion exchange, etc. For the adsorption process, adsorbents investigated include bioadsorbent [1-3], red

mud, phosphate treated sawdust, $\text{Fe}^{3+}/\text{Cr}^{3+}$ hydroxide and activated carbon. The major disadvantages of the adsorption process are the regeneration of the spent adsorbent and subsequent treatment of the backwash water.

Chemical precipitation usually employs the following four major steps. The Cr^{6+} is first reduced to less toxic and less soluble Cr^{3+} and the Cr^{3+} ions is then precipitated as $\text{Cr}(\text{OH})_3$ at high pH. In the third stage the insoluble metal hydroxide is settled. Finally the sludge is dewatered and disposed properly [3]. As the particle size of sludge produced in the process is relatively small and difficult to settle completely, a filtration process is necessary after sedimentation. Alternative technique like foam flotation has been used in which surfactant is added to increase the contact between the flocs and the bubbles. When the concentration of Cr^{6+} is low, ion exchange is usually adopted. The main shortcoming of this process is the high cost of the resins.

Of late, an electrochemical technique called *electro-coagulation* has attracted significant attention for chromium removal process due to its operational simplicity. This technique uses an electrocoagulation cell in which iron anodes dissolve and produce Fe^{2+} . This newly produced Fe^{2+} directly reduces Cr^{6+} to Cr^{3+} leading to the precipitation of $\text{Cr}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. This process does not require the addition of chemicals due to the oxidation and reduction reactions which take place. This influences the reduction of COD and BOD. Therefore, the maintenance and operation of the system is simple. Power consumption is also expected to be low. The present investigation is aimed at studying the effectiveness of electrocoagulation technique.

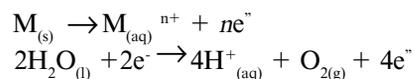
THEORY OF ELECTROCOAGULATION

The electrocoagulation (EC) process depends on responses of water contaminants to strong electric fields and electrically induced oxidation and reduction reactions. Electrocoagulation technique utilizes direct current to cause sacrificial electrode ions to remove undesirable contaminants either by chemical reaction and precipitation or by causing colloidal materials to coalesce and then they are removed by electrolytic flotation. In an electrocoagulation process the coagulating of ions are produced 'in situ' and it involves three successive stages:

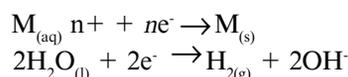
- Formation of coagulants by electrolytic oxidation of the 'sacrificial electrode';
- Destabilization of the contaminants, particulate suspension and breaking of emulsions;
- Aggregation of the destabilized phases to form flocs.

When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. The electrochemical reactions with metal M as anode may be summarized as follows:

- *At the anode:*

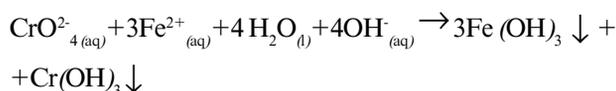
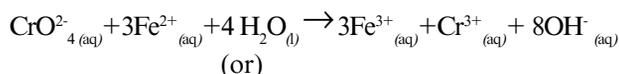


- *At the cathode:*

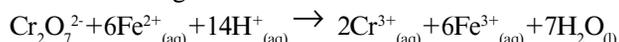


If iron or aluminum electrodes are used, the generated $\text{Fe}_{(aq)}^{3+}$ or $\text{Al}_{(aq)}^{3+}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, Al^{3+} ions on hydrolysis may generate $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Al}(\text{H}_2\text{O})_4(\text{OH})^{2+}$ and the hydrolysis products may form many monomeric and polymeric species such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})^{4+}$, $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_{18}(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$ over a wide pH range. Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, $\text{Fe}(\text{OH})_3$ and polymeric hydroxy complexes, namely: $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})^{2+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$ depending on the pH of the aqueous medium. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials.

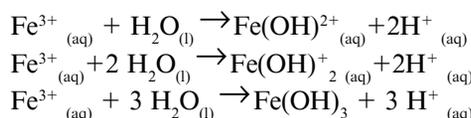
Wastewater containing Cr^{6+} (CrO_4^{2-}) ions can be removed by this electrocoagulation technique using iron as the sacrificial anode. The ferrous ion (Fe^{2+}) generated by electro oxidation of the iron anode can reduce Cr^{6+} to Cr^{3+} under alkaline conditions and is itself oxidized to ferric (Fe^{3+}) ion according to:



The $\text{Cr}^{3+}(\text{aq})$ ion is then precipitated as $\text{Cr}(\text{OH})_3(\text{s})$ by raising the pH of the solution. The $\text{Fe}^{2+}(\text{aq})$ ions can also reduce $\text{Cr}_2\text{O}_7^{2-}$ under acidic conditions according to the following reaction:



The H_2 produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation. However, the Fe^{3+} ions may undergo hydration and depending on the pH of the solution. $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_3$ species may be present under acidic conditions. The reactions involved are:



Under alkaline conditions, $\text{Fe}(\text{OH})_6^-$ and $\text{Fe}(\text{OH})_4^-$ ions may be present. It is therefore, quite apparent that EC of both anionic and cationic species is possible by using an iron plate/rod as a sacrificial electrode.

EXPERIMENTAL

Samples used in this study were collected from the tank of a Common Effluent Treatment Plant (CETP). The typical characteristics of these samples are presented in Table 1.

Table 1. Characteristics of tannery effluent.

S. No	Parameters	Value
1	COD (ppm)	3200
2	BOD (ppm)	1250
3	Total Dissolved solids (mg/l)	6700
4	Suspended solids (mg/l)	1300
5	Total Solids (mg/l)	8000
6	Chromium (ppm)	40
7	pH	6.8
8	colour	dark brown

Electrocoagulation unit

An electrocoagulation cell measuring 20 cm diameter and 15 cm height fabricated out of Perspex material was used in the present study. The effective volume of the cell is about 6.5 liters. Electrodes used are iron and aluminum plates of 100 mm in length, 100 mm in width and 2 mm in thickness. The effective area of electrode is 100 cm². Here iron is used as anode and aluminum as cathode. The feed was recirculated by using a pump as shown schematically in Fig.1.

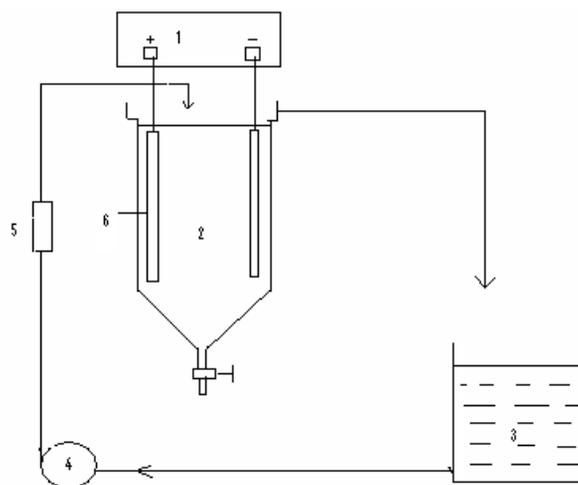


Fig. 1. Schematic diagram of the system.

(1- D.C. power supply; 2- electrocoagulation tank; 3- feed tank; 4 – pump; 5 – rotameter; 6 - electrodes (anode: iron; cathode: aluminum).

Experimentation

The tannery effluent from the feed tank is pumped into the reactor tank. The anode and cathode were connected to the respective terminals of the DC rectifier. Electric power was supplied by a stabilized power source through the DC rectifier fitted with ammeter and voltmeter. The effluent from outlet of the system is again recirculated into reactor. The sludge is removed from the bottom opening of the reactor. The current (I) was varied from 1 to 5 A and the electrical potential (E) was varied between 4 and 20 V. The efficiency of the electrochemical reactor was studied at various conditions such as different current densities and volumetric flow rates.

The effluent was treated at three different current densities, viz., 15, 20 and 25 mA/cm². The flow rates of liquid into the reactor were 2 lpm, 4 lpm, 6 lpm and 8 lpm. The flow rate of the effluent was measured by using calibrated rotameter. The duration of

electrolysis was 4 hours. Samples were collected every 1 hour. The pH was maintained between 6 and 7. The pH of solution was adjusted by using 1:5 (volume) sulfuric acid solution. The buffer solution used in adjusting the pH in the coagulation unit was prepared by mixing 0.2 M NaOH and 0.1 M Na₂CO₃ with distilled water.

Analysis

Standard methods prescribed by American Public Health Association [4] were adopted for quantitative estimation of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), chromium, total solids, suspended solids and total dissolved solids (TDS).

RESULTS AND DISCUSSION

In the present investigation the operating parameters such as flow rate, current density and electrolysis time were varied to explore their effect on COD, BOD, TDS and chromium removal. The results showed that the reduction of COD, BOD, TDS and the removal of chromium were higher at higher charge input and electrolysis time.

The effect of current density on the reduction of COD, BOD and TDS and the removal of chromium were studied by conducting experiments at different current densities, viz., 15, 20, 25 mA/cm². The current density is defined as the ratio of current input to the electrolytic cell to the surface area of the electrode. The current supplied to the electrochemical reactor is usually expressed in terms of current density. The pH was maintained between 6 and 7. Figs 2, 3, 4, 5 and 6 show

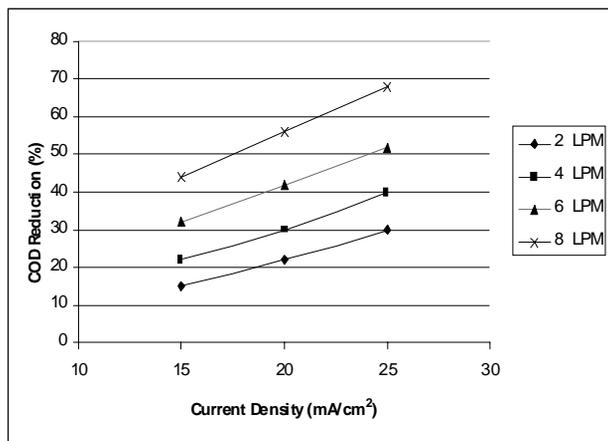


Fig. 2. Effect of current density on COD reduction.

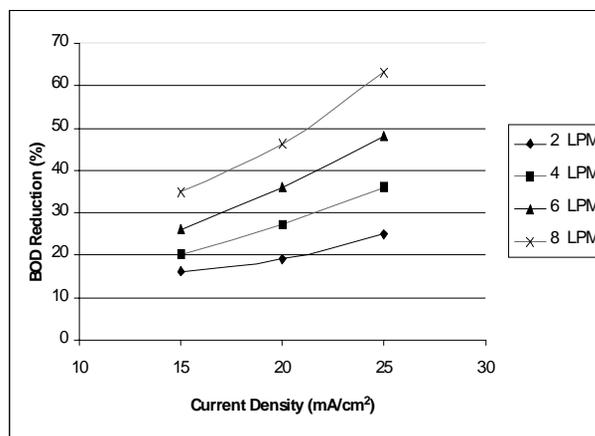


Fig. 3. Effect of current density on BOD reduction.

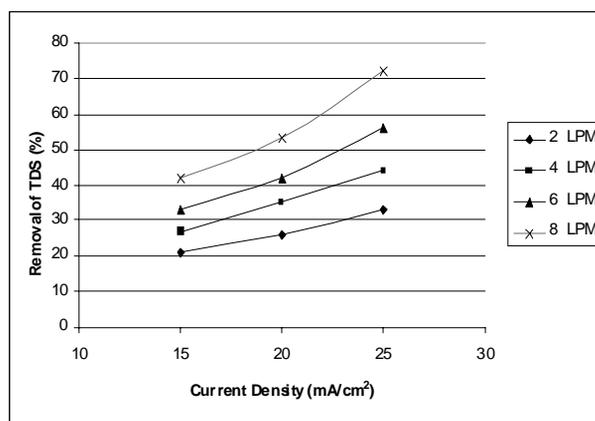


Fig. 4. Effect of current density on Total dissolved solids removal

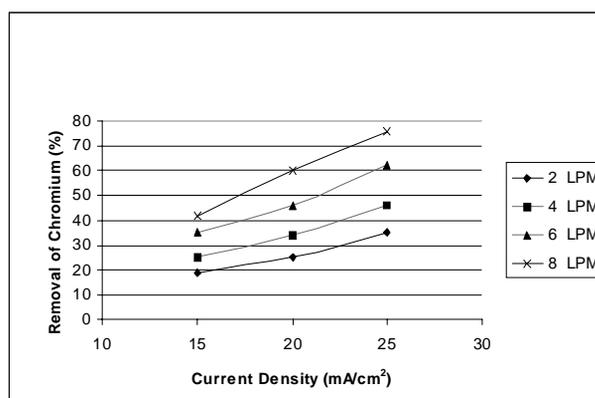


Fig. 5. Effect of current density on Chromium removal (raw effluent).

the effect of current density on the removal of COD, BOD, TDS and chromium. The results showed that the current density influences the COD reduction and increased current density increases the reduction of COD and BOD. This is due to the oxidation and reduction reactions which take place in the reactor.

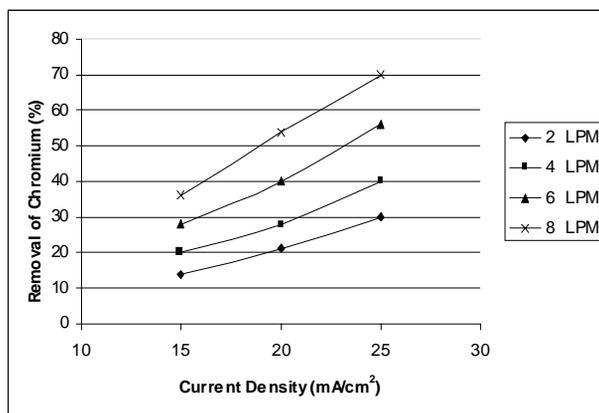


Fig. 6. Effect of current density on Chromium removal (synthetic effluent).

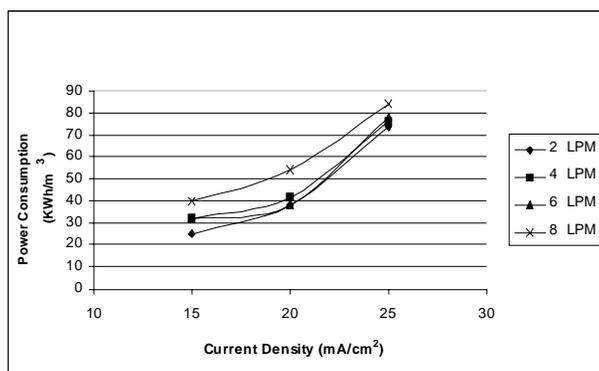


Fig. 7. Effect of current density on power Consumption.

The gas evolved at the electrodes namely oxygen and hydrogen also influence the reduction of COD and BOD. The hydrogen gas liberated at cathode also helps to float the contaminants. This influences the removal of TDS. The removal of chromium is influenced by the formation of oxy-hydroxy species in aqueous solutions. The hydroxy species thus formed have a pronounced tendency to undergo polymerization due to interaction between hydroxyl groups of adjacent molecules. The polymerized complex molecules act as coagulants which help in the removal of chromium.

To study the effect of the flow rate on the reduction of COD, BOD and TDS and the removal of chromium experiments were conducted at four different flow rates viz., 2 lpm, 4 lpm, 6 lpm, and 8 lpm. Figures 2, 3, 4, 5 and 6 show that the flow rate of effluent into the reactor remarkably affected the reduction of COD, BOD, TDS and chromium. Higher flow rates showed significant reduction and this is due to the increased produc-

tion of oxidants and coagulants. During the process at higher flow rates, the dissolution of iron metal into ions increases. This in turn influences the increase of coagulants and hence an increase in the oxidation process. The removal of chromium in synthetic effluent is more than that in raw effluent for the same operating conditions like current density, flow rate and electrolysis time. This is due to the non interference of other compounds like organic salts which are present in the raw effluent. Hence, the amount of coagulants is more while processing synthetic effluent.

The energy consumption in the process can be written as

$$E = (U_t * I_t) / (1000 * Q)$$

where,

U_t is the total electrolysis voltage (V),

I_t the total electrolysis current (A),

Q volumetric flow rate (m³/h).

Fig. 7 shows that the power consumption for COD removal increases with increase in the current density. As the power consumption increases oxidation rate increases resulting in more coagulant formation and hence better percentage of COD reduction.

The results also showed that the flow rate of effluent into the reactor also significantly influenced the power consumption. The higher power consumption leads to higher operating cost, and lower current density may increase the electrolysis time. Therefore, the operation of the electrochemical reactor has to be optimized for current density and flow rate to reduce the operating cost of the process. From the experimental parameters studied, the optimum current density and flow rate were found to be 20 mA/cm² and 6 lpm.

CONCLUSIONS

From the results obtained it can be concluded that the electrocoagulation can be effectively used for the treatment of tannery wastewater. The electrocoagulation of tannery wastewater by generation of polymerized complex molecules and liberation of oxygen and hydrogen gas at the electrodes significantly reduce the COD, BOD, TDS and chromium. The optimum operating conditions arrived at by considering maximum COD reduction and less power consumption were 6 lpm and 20 mA/cm² for the flow rate and current density, respectively. The in-

crease in flow rate and current density significantly increased the reduction of COD, BOD, TDS and chromium.

REFERENCES

1. A.I. Rapoport, O.A. Muter, Biosorption of hexavalent chromium by yeasts, *Process Biochem.*, **30**, 2, 1995, 145-149.
2. J.M. Tobin, J.C. Roux, Mucor biosorbent for chromium removal from tanning effluent, *Water Res.*, **32**, 5, 1998, 1407-1416.
3. D. Kratochvil, P. Pimentel, B. Volesky, Biosorption of chromium(III) by Sargassum, *Environ. Sci. Technol.*, **32**, 1998, 2693-2698
4. S Lenore Clesceri, E Arnold Greenberg, D Andrew Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, DC, 1992.
5. X. Chen, G.C. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, *Sep. Purif. Technol.*, **19**, 2000, 65-76.
6. N. Balasubramanian, K. Madhavan, Arsenic removal from industrial effluent through electrocoagulation, *Chem. Eng. Technol.*, **24**, 2001, 519-521.
7. T.H. Kim, C. Park, E. Shin, S. Kim, Decolorization of disperse and reactive dyes by continuous electrocoagulation process, *Desalination*, **150**, 2002, 165-175.
8. M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J. Haz. Mat.*, **B100**, 2003, 163-178.
9. Feng Shen, Xueming Chen, Ping Gao, Guohua Chen, Electrochemical removal of fluoride ions from industrial wastewater, *Separation and Purification Technology*, **58**, 2003, 987-993.
10. Mohammad Y.A. Mollah, Paul Morkovsky, Jewel A.G. Gomes, Mehmet Kesmez, Jose Parga, David L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, *J. Haz. Mat.*, **B 114**, 2004, 199-210.
11. Guohua Chen, Electrochemical technologies in wastewater treatment, *Separation and Purification Technology*, **38**, 2004, 11-14.
12. Ping Gao, Xueming Chen, Feng Shen, Guohua Chen, Removal of chromium(VI) from wastewater by combined electrocoagulation-electroflotation without a filter, *Separation and Purification Technology*, **43**, 2005, 117-123.
13. Sahset Irdemez, Nuhi Demircioglu, Yalcın S'Evki Yildiz, Zuleyha Bingul, The effects of current density and phosphate concentration on phosphate removal from wastewater by electrocoagulation using aluminum and iron plate electrodes, *Separation and Purification Technology*, in print, accepted 10 April 2006.
14. Mohamed Khemis, Jean-Pierre Leclerc, Gaelle Tanguy, Gerard Valentin, Francois Lapique, Treatment of industrial liquid wastes by electrocoagulation: Experimental investigations and an overall interpretation model, *Chemical Engineering Science*, **61**, 2006, 3602-3609.
15. M.F. Pouet, A. Grasmick, Urban wastewater treatment by electrocoagulation and flotation, *Water Science Technology*, **31**, 1995, 275-283.