

**Research Article** 

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# Degradation Studies of Tannery Effluents using Electro Flotation Technique

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## Abstract

This study reveals that the treatment of tannery effluent samples by electro flotation. In this system, the various parameters like effect of pH, current density, COD, total solids, addition of surfactant and flocculent were investigated. It was found that maximum degradation was at the current density of 0.14A/cm<sup>2</sup> and at a pH of 6.0. Under the same experimental conditions the removal efficiency of chemical oxygen demand (COD) and total solids were found to be approximately 66.3% and 80% respectively. The current density was the most significant factor in the suspended solids elimination by the addition of surfactant and flocculent concentration. The addition of surfactant increases the COD removal and it also enhances the total solids removal. The flocculent also enhanced electro flotation and this technique was found to be effective in removing total solids and reducing COD from tannery effluents. These results intend an important role of these parameters in electrochemical process for removing tannery effluents.

**Keywords:** Electro flotation; Flocculent; Surfactant; Chemical oxygen demand; Tannery effluent

# Introduction

Industrialization has its effect on environment by causing pollution, among which water pollution is contributed by the industries, the nature of effluents from industries are varied and is industry specific. Especially the leather industry has been facing a major threat regarding the ecological problems caused by their waste streams [1]. In tanneries the conversion of the raw hide into leather necessitate different mechanical and chemical treatments e.g. soaking, liming, deliming, bathing, pickling, skin degreasing and tanning, etc. The low efficiency of the chemical operations generates large quantities of effluents like 30 -35 L kg<sup>-1</sup> of raw materials processed [2]. The commonly used technology for effluent treatment was physicochemical followed by units of biological treatment, and activated sludge or aerated lagoon systems [3]. Generally these conventional treatments are unable to reduce all of the polluting parameters like COD, chlorides, sulphates and ammonia [4,5]. The tanning of hides and skins to convert them into leather has been an important activity.

The tannery effluent is a mixture of biogenic matter and large variety of organic and inorganic chemicals. These may contains high concentrations of chlorides, aliphatic sulphonates, sulfates, aromatic and aliphatic ethoxylates, sulfonated poly-phenols, acrylic acid condensates, fatty acids, dyes, proteins, soluble carbohydrates and Na<sub>2</sub>S. Conventional physio-chemical treatment of tannery effluents consists of pretreatment, coagulation/flocculation, sedimentation and sludge handling. In addition to chemical coagulation treatment, secondary and tertiary treatment methods such as biological filters, activated sludge etc. are being practiced. If nitrogen content is high, an additional step involving de nitrification is essential. The fats and proteins are partially hydrophobic they can be easily separated by floatation rather than sedimentation. Separation by flotation is relatively simple and faster compared to the other process. Hence removal of such pollutants by floatation could be more appropriate. Water treatments based on the electro flotation technique have been recently proved to circumvent most of these problems, while being also economically attractive [6-8,8-12]. In this work industrial effluent was carried out using electro floatation.

Electro flotation is a process of removing dispersed particles from liquid using gas bubbles. The gas bubbles are obtained through the

electrolysis of water, which produces hydrogen and oxygen gas. The electrodes are arranged at the bottom of a tank filled with the solution containing the dispersed solids. During the electro flotation process, current is passed through the electrodes and producing bubbles of hydrogen and oxygen gas. Where the bubbles float on the tank may colloid with particles suspended in the water. Adhere to them and float them to the surface of the water. Dispersed foam was skimmed off the surface of the tank with a bladed transport system or skimmer.

## Overall process of electro flotation

The basic principle of such process lies on water electrolysis subsequently. It may be determined among other variables on pH and temperature. The electrochemical reactions at the cathode and the anode are hydrogen evolution and oxygen evolution respectively.

#### At Anode:

$Fe_{(s)} \rightarrow$	Fe 2+ +2e	(	1)	
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Fe (aq) +2OH <sup>-</sup> (aq)	Fe (OH) $_{2(s)}$	(2	)
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At Cathode:

$$2 H_2O + 2^{e_-} \rightarrow H_2 + 2OH_{(aq)}^-$$
 (3)

Overall:

$$Fe_{(S)} + 2H_2O_{(I)} \rightarrow Fe(OH)_{2(S)} + H_{2(g)}$$
 (4)

The protonated water shows to be equivalent in both consumption and generation of positively charged species. Half reaction (first reaction) is proposed to be achieved in the anode while the second

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at the cathode. From the literature [13] the author has performed a complete analysis about the experimental consequences of producing gas through electrolysis.

One of the gases (oxygen or hydrogen) is preferably used to perform the electro flotation, the aqueous speciation will change. The current density influences directly the number and size of bubbles [14]. If the current density is significantly low, both convective and diffusive mechanisms lead to gas to be dissolved and there may not even a bubble to occur. The latter will happen even at high current density which represents a waste of energy. Besides, this problem comes in addition to the inherent chemical irreversibility of both electrode reactions which set the voltage applied be significant. From the process point of view, during gas nucleation, other mechanisms start to work such as bubble coalescence. This mechanism makes bubbles to coarse and produce bubbles of larger size decreasing the bubbling surface available and inevitably an inefficient global process.

# Materials and Methods

The tannery effluents were collected from KAS leathers, Erode, Tamil Nadu in India. These effluents were taken in a way to respect the standards of sampling and were stored in the cold storage before experimental works were started. The characterization of the effluent was carried out. The electrolytic cell is comprised of a sheet of mild steel as anode and a sheet of stainless steel as cathode each having the dimensions of 7.5cm X 4cm with the porosity of 0.5mm in both the electrodes. The Triton –X and the FeCl<sub>3</sub> was added as surfactant and flocculent during the experiment. The electrodes were connected to a digital DC regulated power supply unit (0-30V, 0-12A). A peristaltic pump was used to take away the treated effluent at different time intervals.

The number of colony forming units can be found using equation (5)

No. of colony forming units (CFU) (Per ml of sample) = No. of colonies X Dilution factor of the plate counted. (5)

# **Experimental procedure**

The electro flotation was carried out in an electrolytic cell having the capacity of one liter effluent solution. The distance between the electrodes maintained was 1.5cm. Before the experiment the electrodes were washed with diluted hydrochloric acid to remove surface grease, rust, oil and other impurities on the steel surfaces and then dried. The effluent was taken in the electrolytic cell and electro flotation was carried out at different time intervals. During the electro flotation reaction the effluents were taken out and analyzed for COD and Total Solids content. The various effects of the surfactant Triton -X (0.1ml/100ml) and the flocculent FeCl<sub>3</sub> (0.5g/L) during the experiment were also discussed.

# Results

# Effect of current density

To carry out the optimum current density to the removal percentage of COD of tannery waste water was represented in Figure 1. The experiments were conducted using the tannery waste water at pH of 6. During the experiment, the current densities ranging from 0.035A/ $Cm^2$ , 0.07 A/ $Cm^2$ , 0.105 A/ $Cm^2$  to 0.14 A/ $Cm^2$  were adjusted. The current density significantly affects the efficiency of electro flotation. It showed that the COD removal efficiency was increased with increasing the current density 63% to 65.9%. The rate of reduction of COD increases with different current densities but the increase is not linear then it may be concluded that the process is controlled by diffusion.

In electro flotation, COD reduction is associated with three factors,

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- 1. Direct oxidation of organic residue on electrode
- 2. Removal of material particles by gas bubbles
- 3. Indirect oxidation through reactive species

During the electro flotation batch experiments, the magnitude of the current density had a significant effect on COD and the total solids removal. The total solids removal efficiency was increased with increasing the current passed through the electrodes. The removal rate of COD assumed to be obeying first order kinetics; hence the rate equation is given as [15]

$$\frac{d(COD)}{dt} = -K(COD) \tag{6}$$

The rate constant was calculated for all the current density and using the above equation the K was calculated for each value of current density and at each time interval and averaged.

From the Figure 1 it was observed that the total solids removal was reached maximum at the same current density after 60 minutes of electro flotation. The raw effluent was subjected to electro flotation and was observed for bacterial colonies by standard plate count method. The major part of the procedure deals with a series of successive dilutions of the tannery waste water in sterile bottle with sterile water. The diluted waste water samples of before and after electro flotation was taken. Then it was poured into Petri dishes containing nutrient agar. The numbers of colonies were counted after incubation for 48 hours at 37°C. The disinfection involves two mechanisms like due to oxidation and precipitation with Fe (OH)<sub>3</sub>.

The chlorides ions present in the effluent also contribute disinfection. i.e. in electro flotation the anodic oxidation causes chloride ions to form hypo chlorites ions which could be used as disinfectant.

It was observed at the crude sample after series of dilution had contained 7200000 (approximately) that is 72 prominent colonies. Bacteria of mixed culture per ml. after subjecting to electro flotation for various time intervals from 5-60 minutes at 0.14 A/Cm<sup>2</sup> of current density the colonies were found to be eliminated to the extent of 86.6% shown in the Figure 1.

# Effect of pH

It has been found that the influence of pH is an important parameter for the performance of the electrochemical process [16,17]. In the electro flotation process the pH of the solution is known to play an important role in the removal efficiency of pollutants. To examine the pH on the tannery effluent was adjusted to the desired pH with diluted sodium hydroxide or hydrochloric acid. The experiments were conducted for pH ranges from 3 to 10 by keeping the current density constant at 0.035A/Cm<sup>2</sup> for the same electro flotation time of 60 minutes. The experiment results shows in Figure 2, and it was observed that the total solids removal efficiency and COD decreased for pH below 4 and above 9, this is due to an extent of the reduction of  $Fe^{3+}$  is favored. At the pH range of 5-9, hydrolysis and reduction takes place and it forms mononuclear or poly nuclear ferrous complexes as Fe (OH) <sub>3</sub>, Fe (OH) <sup>+</sup>. Which are effective pollutants but at high pH solutions that dominant species was Fe  $(OH)_{4}^{-}$  which does not coagulate with the pollutants [18]. From this result it may be concluded that the pH of the experiment was further followed at 6.

# Effect of surfactant

Total solids were removed using electro flotation and the process

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was further enhanced by adding the surfactant Triton –X. In the Figure 3, it was observed that the addition of surfactants enhances the total solids removal. In the process of electro flotation alone the removal percentage was found to be 66% but when this process was improved with surfactant and the removal percentage of total solids has been reached to 78%. From the same Figure, it may be concluded that, an addition of surfactant initially increases the COD value due to the release of a new organic compound in the waste water. During electro flotation, these surfactants also gets removed along with the low density colloidal particles by formation of surfactant – particulate - bubble composite and reduction of COD removal percentage is slightly decreased when surfactant is used in normal electro flotation process the removal percentage was 71% when surfactants are added the value

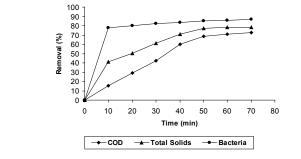


Figure 1: Effect of current density as a function of electrolysis time on COD, Total solids and Bacteria removal percentage.

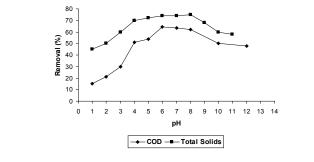


Figure 2: Effect of pH on COD and Total solids removal.

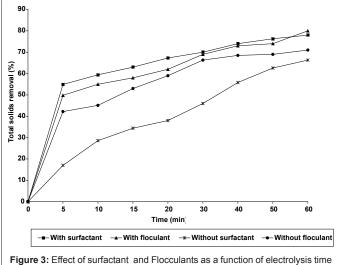
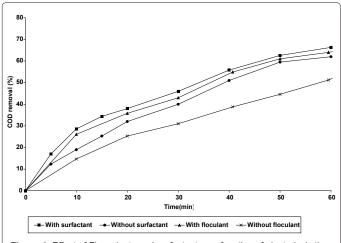
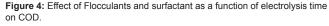
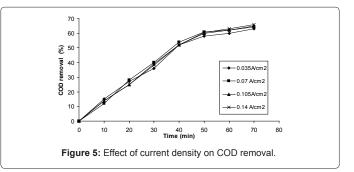


Figure 3: Effect of surfactant and Flocculants as a function of electrolysis time on Total solids removal.



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## Effect of flocculating agent

The well known flocculating agent known as FeCl<sub>3</sub> was added to the waste water and its effect in removal of total solids and COD has been studied. FeCl<sub>3</sub> was used in most of the tannery waste water treatment due to its efficiency and low cost [19]. The flocculating agents are polymers of high molecular weight; they have property to be adsorbed with solid –liquid or liquid –liquid interface which allows the aggregation of the colloidal particles by formation of bridges between the dispersed particles. The metal ions present in the coagulant causes coagulation of the colloidal organic matter and the suspended solids resulting in the formation of rather larger particles (flocs) which are attached to the surface of the gas bubbles and are collected at the top of the electro flotation bath [20].

The removal efficiency of Total Solids has been increased up to 80% within 60 minutes of electro flotation at the current density of 0.14A/ Cm<sup>2</sup>. The COD removal percentage has also been increased up to 64% with the addition of FeCl<sub>3</sub> this is explained by the oxidation of dissolved organic substance due to the presence of both fine oxygen bubbles and the chlorine as a strong oxidizing agent in the medium. The Chlorine was the oxidation product in the secondary electrochemical anodic reaction during electrolysis [21]. From the Figure 4, it was found that Total Solids removal efficiency and COD removal efficiency increased with the addition of flocculent to the electro flotation unit.

#### Discussion

Tannery effluent samples were treated by electro flotation technique

and found to be effective for the removal of total solids and COD using mild steel as anode and stainless steel sheet as cathode. During the process the increase in removal of total solids and COD was found to be increasing with the different applied current densities. The addition of surfactant increases the COD removal as well as it increases the total solids removal from 66.3% to78%. The flocculants FeCl<sub>3</sub> enhanced electro flotation was found to be more effective in removing Total solids and COD from tannery effluent. After the electro flotation process COD removal was reached to about 66% and pathogenic bacteria could be eliminated to the extent of 86.6%

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