

ADVANCED TREATMENT OF BIOLOGICALLY PRETREATED TANNERY EFFLUENT BY ELECTRO FLOATATION TECHNIQUE

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Abstract – In the present work, electro floatation treatment of tannery effluent was used for reduction of COD by addition of surfactant as well as flocculent was investigated. The influence of critical parameters such as current density, electrode material, pH, addition of surfactant and flocculent on the reduction of COD have been discussed. Maximum degradation was found to be at the current density of 0.15 A/cm² at pH of 6. Stable electrodes such as commercial Titanium coated with Ru or Ir oxides was not significantly reducing the effluent Chemical Oxygen Demand (COD) compared to soluble anodes such as Fe/Al/Mn. Additionally, coagulation of suspended solids was sighted under the presence of Fe and Al electrodes and further addition of Tween 20 (surfactant) and FeCl₃ (flocculent) enhances the COD removal from tannery effluent. Under these experimental conditions approximately 72.2% of COD removal and 90% of total solids removal was achieved. This observation intends the potential role of the mentioned critical parameters in the treatment of the tannery effluent. This technique has also been noticed for an effective elimination of color as well as previously utilized bacterial consortium from the treated tannery effluent.

INTRODUCTION

Tannery effluent consists of mixture of organic and inorganic chemicals as well as biogenic stuff made up of hides that are not biodegradable. Direct disposal of this toxic effluent with high dosage of metal compounds started accumulating in the soil over years and spoil the fertility of the soil and diminish the surface and ground water (Mohtashami and Shang, 2019). Thus the tannery effluent produces an extensive threat to the ecology and environment by their waste streams. Generally, industries use the typical effluent treatment technologies such as physiochemical techniques followed by biological treatment but still unable to reduce the COD and chloride levels to acceptable safe levels (Pouet and Grasmick, 1995). The possible harmful environmental impact of the chemicals present in tannery effluent was widely established (Lin and Peng, 1994; Emamjomeh and Sivakumar., 2009; Bhaskar Raju *et al.*, 2008; Sivakumar *et al.*, 2005).

The existing conventional tannery effluent

pretreatment includes sedimentation, coagulation/flocculation. Secondary and tertiary treatment techniques are also been practiced for efficient removal of total suspended solids and additional de-nitrification process is followed for the removal of high nitrogen content in the effluent (Mohan *et al.*, 2001; Costa *et al.*, 2008). But separation of low density colloidal particles by the above methods is inadequate and removal of animal fats and proteins in the effluent can also be partially separated by floatation in a simple and quick manner (Sahu *et al.*, 2014). Electro floatation for elimination of dissolved solids and metal ions was studied by Wang and team (Wang *et al.*, 2009). According to this technique, fine bubbles are required to float the suspended particles from the pre treated effluent and these fine bubbles in the range of 20 – 100 µm can be generated through electrolysis of water (Sarkar *et al.*, 2010). The electrodes are aligned at the bottom of the electrolytic tank containing tannery effluent. During electrolysis, electric current is passes between the electrodes to produce hydrogen and oxygen gases in their atomic state and impart

significant changes in the suspended particles in the effluent (Zaroual *et al.*, 2006). As this effect exists only for short duration, surfactants (collectors) have been added to afford hydrophobic nature to the mineral particles that are to be floated from the effluent (Chaturvedi, 2013). The foam was then skimmed off from the tank using skimmer.

In this paper, the influence of critical parameters such as current density, electrode material, pH, addition of surfactant and flocculent on the reduction of COD have been discussed. The number and size of the fine bubbles produced for floatation depends upon the current density. The selection of electrode material determines the nature of suspended particles to be eliminated from the effluent. The performance of electrolysis is influenced by the pH of the medium and further enhancement of electro floatation process was done by addition of surfactant and flocculent.

MATERIALS AND METHODS

Sample

Waste water effluent used in the study was collected from commercial tannery plant, Chennai, India. The effluent was pretreated according to our previous studies.

Electro floatation cell

The dimension of the cell used in this study measures 15cm × 15cm × 15cm fabricated with Plexiglas material. The volume of the cell is around 3m³ and the cell lip was provided on the front side for scooping of the floated floc materials. The designed EF cell consists of set of electrodes with the length of 12 cm and diameter 0.6cm with an inter electrode distance of 2 mm arranged parallel to each other in order to minimize the ohmic loss. Spacers were also provided to prevent short circuiting. The power was supplied to electrodes through DC power supply unit (0-40 V, 0-15A) and the treated effluent was finally collected by peristaltic pump at different time intervals.

Experimentation

The pretreated effluent sample was loaded into the EF cell and the pH was adjusted. The respective anode and cathode materials were connected to the terminals of DC power supply unit fitted with ammeter and voltmeter. During the experiment, the effect of different electrodes (static and soluble) in the removal of suspended particles were

investigated with varying current densities ranging from 0.025A/cm², 0.05 A/cm², 0.1 A/cm² to 0.15 A/cm². The pH range was also varied from 3 to 10 by supplying the optimal current density for 1 h. The effect of addition of surfactant Tween 20 and the chemical flocculent FeCl₃ in the reduction of COD of tannery waste effluent was also examined.

RESULTS AND DISCUSSION

Effect of electrodes

Table 1 shows the influence of electrode materials on the elimination of suspended solids from the tannery effluent. The results shows that effective separation of suspended solids occurred in the metal electrodes in the presence of Fe, Al and Mn rather than the titanium electrodes in which partial separation takes place. The observation of Karishma and co-workers evident the high particle-bubble collision rate only under the same order of the particles and bubbles (Karishma *et al.*, 2014). The current density and pH of the electrolytic cells determines the bubble size and so optimized. Moreover, the performance of EF cell is found to be attributed with coagulation of colloidal solids present in the soluble anodes with respective metal ions rather than stable titanium anodes (Aoudj *et al.*, 2015).

Table 1. Influence of electrode material on the removal of COD

Cathode	Anode	COD removal (%)
Fe	Al	60.8
Al	Fe	62
Mn	Al	52.5
Fe	Mn	57.55
Al	Mn	50.14
Mn	Fe	55.2
Ti	Ti/Ru	54.6
Ti	Ti/Ir	58.25

This is mainly due to the influence of formation of aqueous oxy-hydroxy species from metal ions that interacts with adjacent hydroxyl molecules and undergoes the well-known process of polymerization (Mouedhen *et al.*, 2008). Aqueous solutions of iron form different species include FeOH₂⁺, Fe(OH)₂⁺, Fe(OH)₃, and Fe(OH)₄⁻. Similarly Al and Mnelectrodes also reported to possess charged poly-nuclear metal hydroxyl complexes that act as a good coagulant to adsorb the suspended colloidal solids from the effluent to form

a coagulum that could be easily skimmed off (Nanseu-Njiki *et al.*, 2009). Such reactions were not observed in case of use of commercial insoluble titanium electrodes coated with hydroxides of Ru/Ir.

Effect of current density

The current density plays a critical role in influencing the efficiency of electro floatation process. It is also observed that the rate of COD reduction increased in a non-linear fashion (Fig. 1) because of the controlled diffusion process. Fig. 2 represents the effect of current density in the reduction of COD level in the tannery effluent. The graph shows that the COD removal efficiency increases from 62% to 64.8% as the current density increases. In batch experiments, it is evident that the magnitude of current density significantly affects the efficiency total solid removal from the effluent. This also reaches its maximum at the same current density after 1 h of EF. This is mainly associated by direct oxidation of organic matters on electrode or indirect oxidation through reactive (oxy-hydroxy) species or elimination of residues by gas bubbles (Murugananthan *et al.*, 2004).

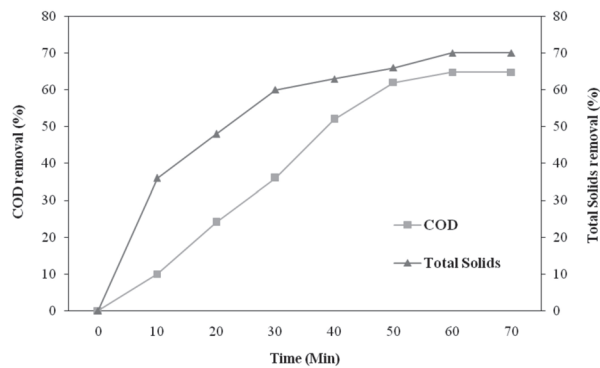


Fig. 1. Influence of current density in the removal of COD and TS

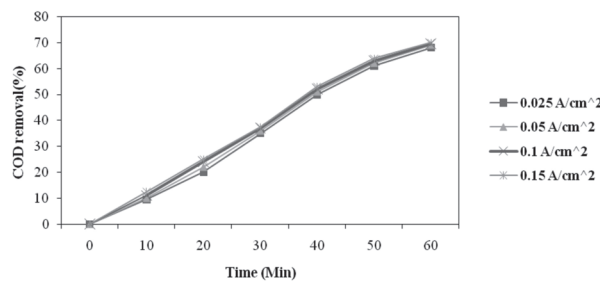


Fig. 2. Influence of different current density in COD removal

Effect of pH

It was apparent that pH plays a significant role in

the COD removal efficiency during the process of electro floatation. To explore the influence of pH, the effluent sample was adjusted to required pH by HCl or NaOH. The batch experiments were done at varied pH from 2 to 10 at 0.15 A/cm² for 1 h. From Fig. 3, it was evident that the efficiency of total solid removal as well as COD reduction decreased below pH 3 and above pH 9 and found similar to the findings of Gomathi Priya *et al.* (2011). This may due to the different reactions like hydrolysis and reduction of ferrous ions from the ferrous electrodes that forms mononuclear or ploy nuclear ferrous complexes and aided in the coagulation of pollutant matters from the effluent. Thus according to our findings, the pH of our experiment was fixed as 6.

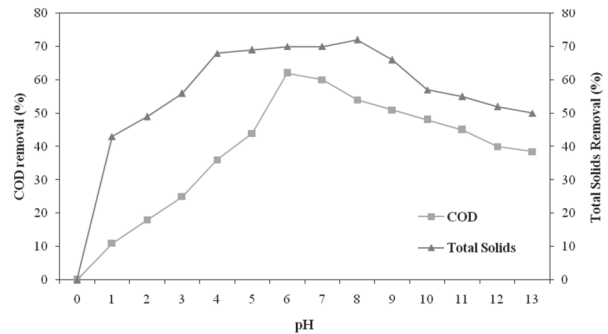


Fig. 3. Influence of pH in the removal of COD and TS

Effect of Surfactant

In general, addition of surfactants during EF transmits hydrophobic characteristics to mineral matters so that it aids in the floatation of particles and can easily separate from other pollutants in the effluent (Gunatilake, 2015). Thus the total solid as well as COD removal efficiency was enhanced by the addition of Tween 20, the widely available cost effective surfactant. Fig. 4 shows the efficiency of COD reduction was also improved from 60 to 67.2% due to the presence of surfactant at the current density of 0.15 A/cm² and Fig.5 shows that the

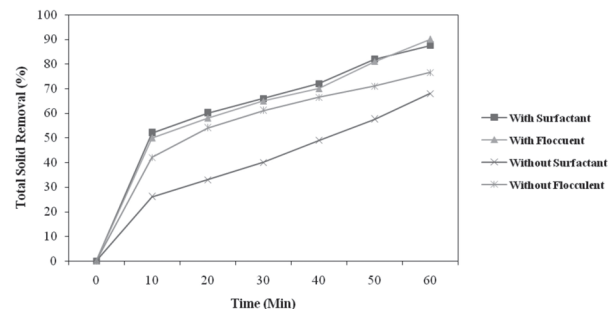


Fig. 4. Influence of Surfactant (Tween 20) and Flocculent (FeCl₃) in the removal of TS

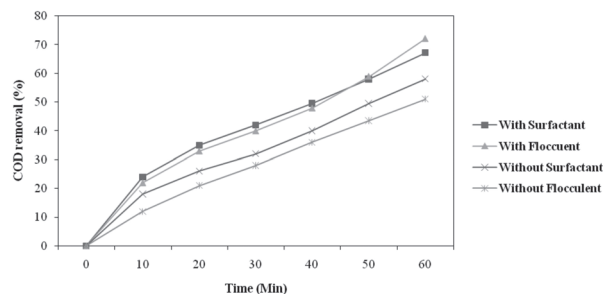


Fig. 5. Influence of Surfactant (Tween 20) and Flocculent (FeCl_3) in the removal of COD

removal of total solids during the EF process is enhanced from 82% to 87.5% after the addition of Tween 20. By the end of the reaction, these surfactant molecules get removed as low density colloidal particles with the bubbles and could be separated easily.

Effect of flocculent

The cheaper and familiar chemical flocculent FeCl_3 was used for the efficient removal of TS and COD in this study. FeCl_3 was known to be a high molecular weight polymer that having property of forming bridges between the dispersed solid matters in the effluent and the metal ions of the flocculent results in the coagulation of organic suspended matters and forms larger flocs. This could be easily separated by the bubbles during the EF process and can be washed out through the lip of the EF cell. Fig. 5 evident the enhancement of EF process in separating the total solids from 87% to 90% and the COD removal efficiency increases from 67% to 72.2% due to the addition of flocculent in the EF cell at the current density of 0.15 A/cm^2 (Fig. 4). The COD removal is enhanced also due to the oxidation of organic residues during electrolysis under the presence of strong oxidizing agents such as oxygen in the gas bubbles and chlorine molecules in the FeCl_3 flocculent (Grimm *et al.*, 1998).

Disinfection effect on the effluent

The treated effluent was observed for bacterial colonies by standard plate count method after subjecting to EF process. The presence of bacterial consortium in the effluent was eliminated up to 98.55% due to the disinfection mechanism. This involves oxidation and precipitation with $\text{Fe}(\text{OH})_3$ species. Additionally the chlorine ions also contributes to the disinfection function of the treated effluent

CONCLUSION

Electro floatation technique is found to be highly efficient for the reduction of COD as well as removal of total solids and bacterial consortium from the tannery effluent. Using of soluble metal electrodes such as Fe anode enhances the COD removal efficiency up to 64.8% and total solids up to 82%. The addition of surfactant enhanced the COD removal efficiency up to 67.2% at the current density of 0.15 A/cm^2 and total solids up to 87.5%. The presence of flocculent FeCl_3 further improved the COD removal efficiency up to 72.2% at the current density of 0.15 A/cm^2 and total solids up to 90% and eliminates to the extent of 98.55% of bacterial consortium from the effluent.

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Compliance with Ethical Standards

Conflict of interest

There are no conflicts of interest to declare.

REFERENCES

- Aoudj, S., Khelifa, A., Drouiche, N. and Djamel, M. 2015. Simultaneous removal of chromium (VI) and fluoride by electrocoagulation electroflotation: application of a hybrid Fe-Al anode. *Chem Eng J.* 267 : 153–162.
- Bhaskar Raju, G., Thalamadai Karupppiah, M., Latha, S.S., Parvathi, S. and Prabhakar, S. 2008. Treatment of wastewater from synthetic textile industry by electrocoagulation and electrooxidation. *Chem. Eng. J.* 144 : 51-58.
- Chaturvedi, S.I. 2013. Electrocoagulation: a novel waste water treatment method. *Int J Modern Eng Res.* 3(1) : 93-100.
- Costa, C.R., Botta, C.M.R., Espindola, E.L.G. and Olivi, P. 2008. Electrochemical treatment of tannery wastewater using DSA electrodes. *J. Hazard. Mater.* 153 : 616-627.
- Emamjomeh, M.M. and Sivakumar, M. 2009. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *J Environ Manage.* 90 (5) : 1663–1679.
- Grimm, J., Bessarabov, D. and Sanderson, R. 1998. Review of electro assisted methods for water purification. *Desalination.* 115 : 285–294.
- Gunatilake, S.K. 2015. Methods of removing heavy metals from industrial wastewater. *J Multi Discip Eng Sci Stud.* 1(1) : 234–241.
- Karishma, C., Vyas, M. and Mehta, M. 2014. Feasibility study of electrocoagulation as a treatment method for textile industry wastewater. *Int J EngSci Res Technol.* 3 (2) : 847–852.

- Lin, S.H. and Peng, C.F. 1994. Treatment of textile wastewater by electrochemical method. *Water Res.* 28 : 277–282.
- Mohan, N., Balasubramanian, N. and Ahmed Basha, C. 2001. Electrochemical oxidation of textile wastewater and its reuse. *J. Hazard. Mater.* 147 : 644–651.
- Mohtashami, R. and Shang, J.Q. 2019. Electroflotation for Treatment of Industrial Wastewaters: A Focused Review. *Environ. Process.* 6 : 325–353.
- Mouedhen, G., Feki, M., Wery, M.D.P. and Ayedi, H.F. 2008. Behavior of aluminum electrodes in electrocoagulation process. *J. Hazard Mater.* 150 : 124–135.
- Murugananthan, M., Raju, G.B. and Prabhakar, S. 2004. Separation of pollutants from tannery effluents by electro flotation. *Sep Purif.* 40 : 69–75.
- Nanseu-Njiki, C.P., Tchamango, S.R., Ngom, P.C., Darchen, A. and Ngameni, E. 2009. Mercury(II) removal from water by electrocoagulation using aluminium and iron electrodes. *J. Hazard. Mater.* 168 : 1430–1436.
- Pouet, M.F. and Grasmick, A. 1995. Urban wastewater treatment by electrocoagulation and flotation. *Water Sci. Technol.* 31 : 275.
- Priya, P.G., Ramamurthi, V. and Anand, P. 2011. Degradation Studies of Tannery Effluents using Electro Flotation Technique. *J. ChemEng Process Technol.* 2 : 104.
- Sahu, O., Mazumdar, B. and Chaudhari, P.K. 2014. Treatment of wastewater by electrocoagulation: a review. *Environ Sci Pollut Res.* 21 : 2397–2413.
- Sarkar, M.S., Evans, G.M. and Donne, S.W. 2010. Bubble size measurement in electroflotation. *Miner. Eng.* 23: 1058–1065.
- Sivakumar, V., John Sundar, V., Rangasamy, T., Muralidharan, C. and Swaminathan, G. 2005. Management of total dissolved solids in tanning process through improved techniques. *J. Clean. Prod.* 13: 699–703.
- Wang, C.T., Chou, W.L. and Kuo, Y.M. 2009. Removal of COD from laundry wastewater by electrocoagulation/electroflotation. *J. Hazard. Mater.* 164 : 81–86.
- Zaroual, Z., Azzi, M., Saib, N. and Chaïnet, E. 2006. Contribution to the study of electrocoagulation mechanism in basic textile effluent. *J. Hazard. Mater.* 131:73–78.
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