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# FEASIBILITY STUDIES ON PERFORMANCE IMPROVEMENT FOR TANNERY EFFLUENT THROUGH CHEMICAL OXIDATION- BIOLOGICAL TREATMENT

**[1]S. Dhinakaran, A. Navaneethagopalakrishnan**
[1]AVIT,Chennai,
[2]Centre for envirionmental studies, Anna university, Chennai
***Corresponding author: Email: dhinaa13@gmail.com**

**ABSTRACT**

Leather industries use very broad spectrum of chemicals covering inorganic, natural organic and synthetic organic compounds during the manufacture of leather. The transformation of the raw hide into leather products involves several processing steps consuming considerable amounts of water influence, BDI ratio of the raw effluent is about 0.23-0.25. Even After physicochemical treatment it shows the low biodegradability improvement. For this reason, more efficient methods advanced oxidation processes have been proposed to improve the biodegradability.

Among the AOPs, the most widely used technique is solar Fenton process are the most promising technologies for the treatment of tannery waste water. In this study, an attempt was made to assess the feasibility of enhancing the biodegradability of tannery effluent using solar Fenton oxidation process and to study the effect of operating variables viz, pH, concentration of $H_2O_2$, dosage of $Fe^{2+}$ and solar exposure contact time on biodegradability and to study the extent of Biodegradation of solar Fenton treated tannery effluent by anaerobic biological process. The raw tannery wastewater from an industry, located near Chennai was characterized for pH, BOD, COD, TDS, and TSS. The wastewater has very low biodegradability measured in terms of biodegradability index (BDI), was 0.24;COD recalcitrant( $COD_R$) and biorefractory index(BRI) was 3195 and 0.76 respectively. So there is need to improve the biodegradability by solar Fenton process.

A laboratory scale study on the biodegradation by solar Fenton process was carried out in a 2L capacity of glass tray of size 16x8x8cm. 500ml of raw effluent was taken in a glass tray. Each experiment was conducted by keeping any two variables constant and varying the third one. The treated sample were analysed for biodegradability in terms of biodegradability index (BDI), COD recalcitrant( $COD_R$) and biorefractory index(BRI). From the biodegradability studies the maximum percent increase in (BDI) was found at $H_2O_2$ 20g/L , $Fe^{2+}$ 0.5g/L, pH 3, solar exposure contact time 15 min and liquid depth 1.5 cm. When the experiments were conducted at optimal conditions, the increase in BDI was 81%, the reduction in $COD_R$ and BRI were 50% and 25%. The feasibility of further degradation of solar Fenton treated tannery wastewater by biological process (anaerobic process) was studied in batch mode. The solar Fenton treated sample with inoculums gave maximum amount of biogas production was added at the rate of 0.28 $m^3$/day was 412ml and also gave 79% of COD removal. The overall performance of the combined photochemical and biological treatment for COD removal was 85%.From the above concluded that feasibility on enhancement of biodegradability of tannery wastewater, using solar Fenton process was attended and found to be effective for this wastewater.

## METHODOLOGY

**General:** Solar Fenton process has been reported to treat various industrial wastewaters. In this study, the feasibility of improving the biodegradability of tannery effluent by using solar Fenton oxidation was investigated. Further extent of Biodegradation by the subsequent biological treatment by anaerobic process was also studied. The materials used and the methodology adopted for the study is discussed in this chapter.

**Experimental Methodology for Solar Fenton Process:** The tannery wastewater was characterized by high BOD and COD. A laboratory scale study on the biodegradation by solar Fenton process was carried out in a 2L capacity of glass tray of size 16x8x8cm. 500mL of raw effluent was taken in a glass tray, liquid depth maintained about 1.5cm and mixtures of optimum dosage of Fenton reagents were added. To study the various effects viz., pH, dosage of $Fe^{2+}$, concentration of $H_2O_2$ and contact time, are optimized by varying the concentration of one variable at a time and maintaining the concentration of other variables at constant value. The treated samples were analysed for BOD and COD. Treatment efficiency in terms of Biodegradability index (BDI), COD recalcitrant ($COD_R$) and Biorefractory index (BRI) were evaluated.

**Preparation of Stock Solution:** Fenton reagent was prepared using ferrous sulphate ($FeSO_4.7H_2O$) and hydrogen peroxide ($H_2O_2$). Ferrous sulphate ($FeSO_4.7H_2O$), sulphuric acid, hydrogen peroxide and all other chemicals were used. The stock solution of potassium dichromate, sulphuric acid reagent, calcium chloride, ferric chloride, magnesium sulphate, sodium azide, phosphate buffer sodium hydroxide and indicator solution were prepared for various physiochemical analysis viz.BOD, COD etc.0.1N sulphuric acid and 0.1N sodium hydroxide solution was used for adjusting the pH of tannery wastewater throughout the study.

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## RESULTS AND DISCUSSION

**Characterisation of raw tannery effluent:** The experiments were done as per procedure given section 3.5. Samples were collected at various time intervals and analysed for BOD and COD. The treated samples were analysed for BOD and COD and then BDI, $COD_R$ and BRI were evaluated. The photo treated wastewater was neutralised by NaoH solution and it was allowed to investigate the extent of Biodegradatability by using anaerobic process. The further biodegradation of tannery wastewater was studied and the results of the study are presented and discussed below.

The raw tannery wastewater was collected from a CETP near Chennai and analysed for pH, BOD, COD and TDS as per standard methods. The wastewater has very low biodegradability measured in terms of Biodegradability index (BDI) was 0.24; COD recalcitrant ($COD_R$) and Biorefractory index (BRI) were 3195 and 0.76 respectively.

**Table.1.Characterization of raw tannery effluent**

| Parameters | Trial 1 | Trial 2 | Average |
|---|---|---|---|
| pH | 6.1 | 5.9 | 6 |
| BOD | 980 | 1030 | 1005 |
| COD | 4180 | 4220 | 4192 |
| TDS | 7200 | 7600 | 7400 |
| BDI | 0.234 | 0.244 | 0.24 |
| $COD_R$ | 3200 | 3190 | 3195 |
| BRI | 0.76 | 0.75 | 0.76 |

All values are in mg/L except pH, BDI, $COD_R$, BRI The raw tannery wastewater has acidic pH and hence the application of Fenton process to the wastewater is easy and it has high TDS concentration. Moreover it has low biodegradability due to the presence of non biodegradable organics present in the wastewater.

**Treatment of tannery waste water by solar fenton process:** The effect of various operating variables to attain biodegradability, such as dosage of $H_2O_2$, dosage of $Fe^{2+}$, effect of pH and solar exposure time were studied as per the procedure described in section 3.5.To study the effect of said parameters the volume of wastewater was taken 500ml in to a 2L capacity of tray and the results were furnished and discussed here under.

**Studies on the Effect of concentration of $H_2O_2$ on biodegradability of tannery effluent:** The effect of concentration of $H_2O_2$ was studied by keeping the dosages of 5, 10, 15, 20, 25, 30 g/L. The dosage of $Fe^{2+}$ (0.25g/L) and pH 5 was maintained at constant level. The treated samples were analysed for BOD and COD and then improvement of biodegradability was analysed in terms of the percentage increase in biodegradability index (BDI), percentage reduction in COD recalcitrant ($COD_R$), and decrease in percentage of Biorefractory index (BRI) In this study, the optimum dosage of $H_2O_2$ on biodegradability was found out at 20g/L. The maximum amount of biodegradability index (BDI) was 58.6, Percentage reduction in ($COD_R$) was 58.3 and decrease in percentage (BRI) 17.1 was measured at 20g/L After that the biodegradability index was gradually reduced in the dosages of 25,30g/L. Hence the optimum dosage of $H_2O_2$ on biodegradability of tannery wastewater was found 20g/L.

**Studies on the Effect of concentration of $Fe^{2+}$ on biodegradability of tannery effluent:** The effect of $Fe^{2+}$ on biodegradability was studied by varying the dosages of 0.125, 0.25, 0.375, 0.5, 0.75, 1 g/L. The optimum dosage of $H_2O_2$ (20g/L) and pH 5 was maintained at constant level. The treated samples were analysed in terms of the percentage increase in biodegradability index (BDI), percentage reduction in COD recalcitrant ($COD_R$), and decrease in percentage of Biorefractory index (BRI).The procedure was repeated for various dosages of $Fe^{2+}$. In this study, the optimum dosage of $Fe^{2+}$ on biodegradability of tannery wastewater was found at 0.5g/L. The maximum percent increase in BDI was 69.3, percentage reduction in $COD_R$ was 57.8 and percentage decrease in BRI was 21.3 measured at 0.5g/l. After that it was decreased in the dosages of 0.75 and 1 g/L. Hence the optimum dosage of $Fe^{2+}$ on biodegradability was found at 0.5g/L.

**Studies on the Effect of concentration of solar exposure time on biodegradability of tannery effluent:** To study the effect of solar exposure time on biodegradability of tannery wastewater, the parameters viz, $H_2O_2$ was 20g/L and $Fe^{2+}$ was 0.5g/L was taken. The treated samples were analysed for BOD and COD and then improvement of Biodegradability in terms of the percentage increase in biodegradability index (BDI), percentage reduction in COD recalcitrant ($COD_R$), and decrease in percentage of Biorefractory index (BRI) were evaluated. Biodegradability was analysed for 5,10,15,20,30,45,60 mins. In this study, the optimum solar exposure time on biodegradability was observed at 15 min. The maximum percent increase in BDI was 71.4, percentage reduction in $COD_R$ was 64 and percentage decrease in BRI 46 was measured at 15 min. With longer reaction time, there would not be more increase in biodegradability. A slow decrease of biodegradability was observed after 60min.

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**Studies on the Effect of pH on biodegradability of tannery effluent:** In this study, the optimum pH on biodegradability of tannery wastewater was found at 3. The maximum percentage increase in BDI was 81, percentage reduction in $COD_R$ was 50 and percentage decrease in BRI was 25.So optimum pH was found to be 3 which indicate that at this pH rate of solar Fenton oxidation of organic matter is greater than that of rate of formation of intermediates. This might be due to the generation of Fe $(OH)^{2+}$ which is generating the hydroxyl radicals in the acidic pH of 2-5 (Rubert and Bauer 1997) and hence the maximum efficiency on biodegradability was more in acidic pH. The efficiency was decreased in pH 6 and above.

**Analysis of biodegradability of tannery wastewater:** It was observed that the the raw tannery effluent had low biodegradability in terms of Biodegradability index (BDI) 0.24; COD recalcitrant ($COD_R$) and Biorefractory index (BRI) were 3195 and 0.76 respectively. An increase was observed in the biodegradability by using solar Fenton process by the optimum operating variables viz, $H_2O_2$ 20g/L, $Fe^{2+}$ 0.5g/L, pH 3 and 15 min solar exposure time. It was observed that the maximum percent increase in BDI was 81, percentage reduction in $COD_R$ was 50 and percentage decrease in BRI was 25.Evaporation losses after 60 min ranged from 2-3%.Therefore the results were not affected by this evaporation. Chamorro (2001) concluded that the Fenton treatment eliminates the toxic substances and increases the biodegradability of the treated wastewater.

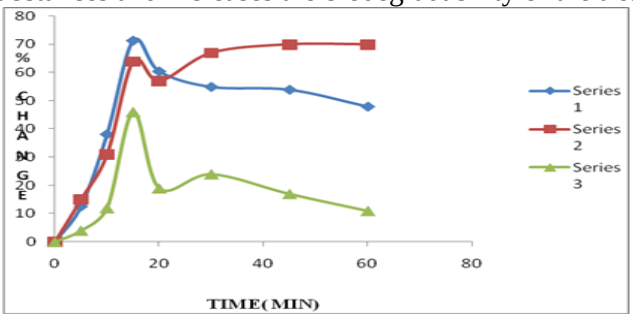


**Fig 3.1 Effect of solar exposure time on biodegradability of tannery wastewater**

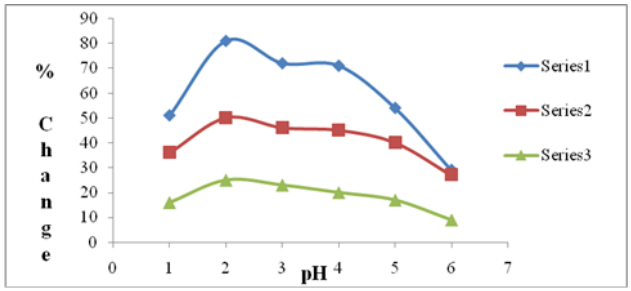


**Fig. 3.2 Effect of pH on biodegradability of tannery wastewater Series 1= BDI Series 2=CODR Series 3=B**

**Biogas Production:** The rate of production of biogas in anaerobic process was found to be increase at higher for solar Fenton treated sample with inoculums in the volume ratio of 1:0.5:0.5.The biogas produced at the rate of $0.28m^3$/day was added . The amount of biogas produced in mL was measured 412 mL, At the same time COD removal efficiency was observed 79%. When compared with solar Fenton treated effluent with inoculums biogas production is more than 53% than that of raw effluent.

**Table.2.Characteristics of tannery effluent after anaerobic process**

| Effluent | Condition | COD(mg/L) | | % COD removal | pH | | Biogas Production(ml) | VFA (mg/L) |
|---|---|---|---|---|---|---|---|---|
| | | Initial | Final | | Influent | effluent | | |
| Raw effluent | With inoculums | 4140 | 1324 | 68 | 7.1 | 7.6 | 194 | 95 |
| Solar Fenton treated sample | With inoculums | 2798 | 584 | 79 | 7.2 | 7.4 | 412 | 158 |
| Raw effluent | Without inoculums | 4140 | 1822 | 56 | 7.2 | 7.5 | 98 | 41 |
| Solar Fenton treated sample | Without inoculums | 2798 | 1119 | 62 | 7.2 | 7.5 | 142 | 74 |
| Seed sludge | - | - | - | - | - | - | 38 | 17 |

## CONCLUSIONS

The following conclusions are drawn from the study, it was found that solar Fenton oxidation can greatly enhance the biodegradability of typical tannery wastewater. The biodegradability of raw tannery wastewater increases after solar Fenton process and the wastewater was found to be bio-compatible. The maximum efficiency on biodegradability was achieved in the dosages of $H_2O_2$ 20g/L and $Fe^{2+}$ 0.5g/L. The maximum increase in percent BDI was 81%, the reduction in $COD_R$ and BRI were 50% and 25%, when tannery wastewater treated at pH 3 for solar exposure time 15 min. It could be recommended that solar Fenton oxidation treatment can be placed before biological treatment to convert the non biodegradable organic pollutants, present in the tannery wastewater. The feasibility of further degradation of solar Fenton treated tannery wastewater by biological process (anaerobic process) was studied. The solar Fenton treated sample with inoculums produced maximum amount of biogas was measured 412 ml and COD removal efficiency was 79%. Solar Fenton treated sample with inoculums produced biogas 52% more than that of raw effluent produced. At the same time COD removal efficiency was 14% more than that of raw effluent with inoculums COD removal efficiency.

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**REFERENCES**

Ali. S.A. James. R.B. and Stephen R.C., (1996), 'The use of iron in advanced oxidation processes with biological treatment', PKP open Harvester, pp.1-4.

Al-Kdasi. A.A., Idris. A., Saed. K., and Guan C.T., (2005), 'Treatment of textile wastewater by advanced oxidation processes-A review', Global Nest: The international journal, vol.6, pp. 222-230.

Badawy. M.I.,and Ali. M.E.M.,(2006), 'Fenton's per oxidation and coagulation processes for the treatment of combined industrial and domestic wastewater', Hazardous Materials, Vol.136, pp. 961–966.

Beltrán. J., Torregros., Dominguez. J.R. and Peres. J.A., (2001) 'Kinetic model for phenolic compound oxidation by Fenton's reagent'. Chemosphere Vol.45, pp, 85–90.

Chamarro. E., Marco A. And Esplugas S. (2000) 'Use of Fenton reagent to improve organic chemical biodegradability' water research vol.35 pp.1047-1051.

Dantas. T. L. P., Jose. H. J. and Moreira. (2003).'Fenton and Photo Fenton oxidation of tannery wastewater', Acta Scientiarum. Tech., Vol.25, pp.91-95.

Dogruel. S., Genceli. E., Babuna. F. and Orhon. D., (2004), 'Ozonation of Non biodegradable Organics in Tannery Wastewater', Environmental Science technology, Vol. 39, pp. 1705–1715.

Durai. G and Rajasimman. M (2011). 'Biological Treatment of Tannery Wastewater - A Review'. Journal of Environmental Science and Technology, vol.4 pp.1-17.

Ghaly.M.Y., Haertel.G., Mayer.R. and Haseneder. R., (2001), 'Photochemical oxidation of p-chlorophenol by UV/$H_2O_2$ and photo-Fenton process, a comparative study', Waste Management, Vol. 21, pp. 41–47.

Ghiziaine. K., Nihal. O., Kacem. E.K., (2003), 'Degradation of herbicides by Fenton reaction', Environmental chemistry, Vol. II, pp.1-2.

Guedes. A.M.F.M., Madeira. G.L.M.P., Boaventuraa. R.A.R. and Costa C.A.V., (2003), 'Fenton oxidation of cork cooking Wastewater overall kinetic analysis', Water Resources, Vol.37, pp.3061– 3069.

Gulkaya. I., Surucu. G.A. and Dilek. F.B., (2006), 'Importance $H_2O_2/Fe^{2+}$ Ratio in Fenton's treatment of a carpet dyeing wastewater', Hazard Mater, Vol.136, pp.763–769.

Isil A.B. and Ferhan C. (1999). 'Treatability of Kraft Bleaching wastewater by Bio-chemical Photocatalytic oxidation' journal of water science tech vol.40 pp.281-288.

Karthikeyan. S., Titus. A., Gnanamani. A., Mandal. A.B. and Sekaran. G., (2011), 'Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes', Desalination, Vol. 281, pp.438–445.

Kennedy. L.J., Das. K. M. and Sekaran. G., (2004), 'Integrated biological and catalytic oxidation of organic/inorganic in tannery wastewater by rice husk based mesoporous activated carbon Bacillus sp', Environmental science Technology.Vol.42, pp. 2399–2407.

Kurniwan. B.G., Lee. D.S., Kang N and Yoon (2009), 'Characteristics of p-chlorophenol oxidation by Fenton's reagent', Water Resources, Vol. 33, pp.2110–2118.

Kurt. U., Apaydin. O., Gonullu. M.T, (2007),'Reduction of COD in wastewater from an organized Tannery industrial region by Electro Fenton process', Hazardous Materials Vol. 143, pp. 33–40.

Lefebvre. O.N., Vasudevan. M., Torrijos.K., Thanasekaran and Moletta.R, (2006), 'Anaerobic digestion of tannery soaks liquor with an aerobic post-treatment', Water Resources, Vol. 4, pp. 1492-1500.

Lopez. A., Ricco. R. and Rozzi. A., (1999), 'Textile wastewater Reuse: Ozonation of membrane concentrated secondary effluent', water science technology, Vol.40, pp.99-105.

Miroslaw K., Marcin D., Adrina D. And Marcin Z. (2004) 'Chemical oxyzen demand reduction of various wastewater types using magnetic field-assisted Fenton reduction 'Journal of water environment research vol.76 pp.301-309.

Modenes. A.N.,(2012), 'Performance evaluation of an integrated photo- Fenton Electro coagulation process applied to pollutant removal from tannery effluent in batch system', Chemical Engineering ,Vol.197, pp.1–9.