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Decolourisation of Tannery Effluent by Electrochemical Oxidation

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***Abstract*— Tannery effluents are of large-scale environmental concern because they colour and diminish the quality of water bodies into which they are released. The wastewater is highly coloured and viscous due to dyestuff and suspended solids respectively. Sodium is the only major cation due to high consumption of sodium salts in processing units, chloride is the major anion found in the wastewater, the concentrations of bicarbonate, and sulphate and nitrate are also high. Electrochemical oxidation for a tannery wastewater collected from Common Effluent Treatment Plant investigated using Palladium based triple oxide coated Titanium as an anode and Stainless Steel as a Cathode. Several batch experiments run in a laboratory-scale and characteristics were analyzed at different time intervals, for a total period of 180 min. The results were reported in terms of percentage removal of Chemical Oxygen Demand (COD), Colour, pH, Total Dissolved Solids (TDS), Electrical conductivity, Chlorides and Sulphates for current density of 20V and different pH. For the pH and Contact time decolourised the Secondary Treated Effluent and RO rejects and Other Pollutants also get reduced.**

I. INTRODUCTION

The waste water discharged from industries such as textile, leather, dye manufacturing units have been of a major environment concern for many years, due to its refractory nature colour, toxicity and high level of COD and BOD. Tannery industries use a large number of chemicals (i.e., natural and synthetic tanning agents, surfactants, salts, etc.) for the treatment of skins and consequently produce large quantities of effluents which have to be purified before being discharged into the environment. Since tannery wastewater contains both organic compounds, mainly tannins that are polyphenol molecules and inorganic compounds such as ammonia, sulphides, and chlorides the combination of physicochemical primary treatments (e.g., coagulation, flocculation, sedimentation, or precipitation) and secondary biological processes do not always meet the legal limits for waste discharge. During process of retanning, dyeing, and fat-liquoring to impart special properties to the leather, increase penetration of tanning solution, replenish oils in the hides, and impart colour to the leather and its effluents are BOD, COD, chromium, Vegetable Tans, Syntans, Dyes, Fat.The establishment and enforcement of limits for the discharge and disposal of toxic and hazardous materials has required the development of advanced technologies to effectively treat a variety of gaseous and liquid effluents, solid waste and sludge. Conventionally effluents containing organics are treated with adsorption, biological oxidation, coagulation, etc. Though the conventional methods have individual advantages, they are lacking of effectiveness if applied individually. Due to the large variability of the composition of tannery wastewater, most of the traditional methods are becoming inadequate. As environmental regulations become stringent, new and novel processes for efficient treatment of various kinds of wastewater at relatively 2 low operating cost are needed. In this context, researchers are trying various alternative processes, such as electrochemical technique, wet oxidation, ionization, photo catalytic method for the degradation of organic compounds. Among these advanced oxidation processes, the electro chemical treatment has been receiving greater attention in recent years due to its unique features, such as versatility, energy efficiency, automation and cost effectiveness.

The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorption step. Basically, two different processes occur at the anode. On anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously (indirect electrolysis). In direct electrolysis, the rate of oxidation depends on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis.

II. METHODOLOGY

The decolourisation studies conducted at the Unit Operations and Process Engineering Laboratory of the Centre for Environmental Studies, Anna University. Secondary treated tannery effluent and RO rejects from the Tannery Common Effluent Treatment Plant at Pallavaram used for the studies. First step was to collect the samples of secondary treated effluent and RO rejects from the CETP for characterization. Immediately after collection, the sample preserved and analyzed for Colour, pH, TDS, Electrical conductivity, BOD, COD, Chlorides and Sulphates in the Analytical laboratory of Centre for Environmental studies, Anna University.

A. Methodology for Effluent Characterisation

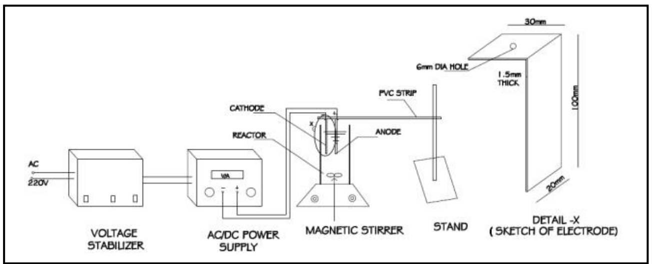
Colour Spectrometry in the visible region was used as the method for measurement of colour. This method of colour measurement involves in measurement of absorbance at wavelengths of 436 nm, 525 nm and 620 nm, in the case of tannery effluents. The measurements are expressed as absorption coefficient. Colour measurements were made at a temperature of 27^{0}C and a path of 1 cm.

For Secondary effluent and RO reject solution the calibration curves plotted by measuring absorbance of the solutions with known concentrations at the wavelengths of maximum absorption. The absorbance spectrum was recorded using UV-VIS Spectrophotometer. It observed during initial studies that the variation of pH has no significant effect on absorbance; all the colour measurements are done at the original pH of the solution. pH measurements are done using digital pH meter. Conductivity was measured by using digital conductivity meter. And the COD was determined by the waste water analysis standards.

B. *Experimental Setup and Procedure*

The material use for the Electrochemical Oxidation studies included the bench scale parallel plate single compartment type batch reactor with Palladium based triple oxide coated titanium metal dimensionally stable anode and stainless steel cathode, DC regulated power supply, magnetic stirrer, thermometer and stop watch.

Figure 1 Experimental setup for Electrochemical Oxidation and setup.



A glass beaker of 500mL capacity with 85mm diameter and 120mm depth used as the reactor. Simple parallel plate electrode system was adopted for the study. 500mL waste water effluents to use in each experiment. The electrodes are 100mm long, 20mm wide and 1.5mm thick. The electrodes were fixed with a PVC base and immersed in the reactor to a depth of 75mm so that the wet area of each electrode is 2 x 2 x 7.5 = 30 cm². The spacing between the electrodes are 10mm, throughout the study. The anode electrode was connecting to the positive terminal and the cathode to the negative terminal of the DC power supply of capacity 0 – 2A. The reactor contents were mixed using a magnetic stirrer. The conductivity of water waste effluent was raised to 45,000 µS / cm by adding NaCl (20,000 mg / L) and Na_2CO_3 (10,000 mg / L).

500mL of sample was filled in the reactor. The pH was adjusted as required. The magnetic stirrer, DC power supply and stopwatch was switched on and the residual colours at the specified time intervals measured. The studies were repeated for various pH at a current of 2A, during decolourisation by electrochemical oxidation treatment to determine COD reduction also.

First characterisation of the secondary treated and RO rejects of tannery effluent from pallavaram CETP carried out. And pH was adjusted as to various ranges like 6, 7 and 8 and the magnetic stirrer was used to stir the sample for electrochemical oxidation treatment. 10V, 20V and 30V current was applied to the reactor to maintain the oxidation reaction and reaction time taken as 2, 10, 15, 30, 60, 120, 150, 180, 210 and 240mins. During the electrochemical oxidation treatment, the water waste get mineralised and decolourisation of the sample will follow. Then the performance measurements are analysed for the parameters of colour, pH, TDS, BOD, COD, Electrical conductivity, chlorides and Sulphates. Tannery effluent were analysed for Colour, pH, Conductivity, TDS, BOD, COD, Chlorides and Sulphates.

Table 1 Tannery effluent parameters and its method / instruments used.

S.No	Parameter	Analysing Method
1.	Colour	Spectrophotometry
2.	pH	Using pH meter
3.	Electrical Conductivity	Using conductivity meter
4.	TDS	Oven drying method
5.	BOD, COD, Chlorides	Titrimetry
6.	Sulphates	Spectrophotometry

I. RESULTS AND DISCUSSION

A. *Characteristics of Secondary Effluent and RO reject from CETP*

The secondary treated effluents and RO rejects characteristics are analysed, and their results are shown in the table 2

Table 2 Characteristics of Secondary Treated Effluent and RO Reject

S.No	Parameters		Secondary treated effluent Initial Average values	RO Reject Initial Average values
1.	colour	436 nm	1.239	1.939
		525 nm	0.891	1.867
		620 nm	0.624	1.827
2.	pH		7.45	8.2
3.	EC (µs/cm)		11.19	32.5
4.	TDS (mg / L)		6000	24000
5.	BOD (mg / L)		81	214
6.	COD (mg / L)		1476	3085
7.	Sulphates (mg / L)		3160	7912
8.	Chlorides (mg / L)		1049	3347

Secondary treated effluent and Reverse Osmosis Reject Samples are collected four times from Pallavaram CETP. And their Characteristics were analysed and Average values are calculated. Ground water is used in tannery cleaning process so that the Chlorides value is lower compare with Sulphate value.

B. *Electrochemical Oxidation of Secondary Treated Effluent*

Decolourisation of secondary treated effluent treated by electrochemical oxidation process for 10V, 20V and 30V at pH 7 and pH 6 with different time intervals.

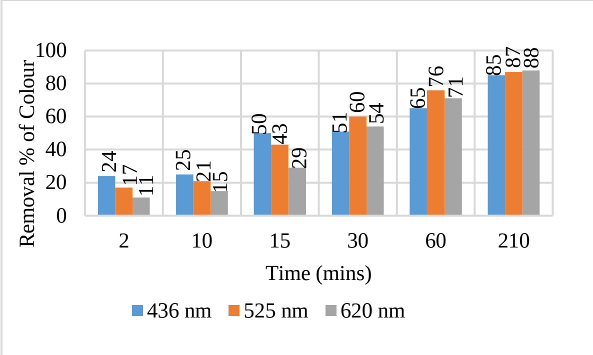


Figure 2 Effect of Contact time on Colour removal efficiency

Infer from the treated effluent Colour was 87% removed after 210mins and the other parameters like EC, TDS, BOD, COD, Sulphates and Chlorides also reduced. In this process taken a time interval of Electrochemical oxidation process is 2mins, 10mins, 15mins, 30mins, 60mins and 210mins and the Current density is 10V. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 8.8%, 30%, 62%, 85%, 33% and 22% respectively. The effect of pH on the decolourisation percentage of secondary treated tannery effluent during the electrochemical oxidation for different time intervals with a current density 10V is presented.

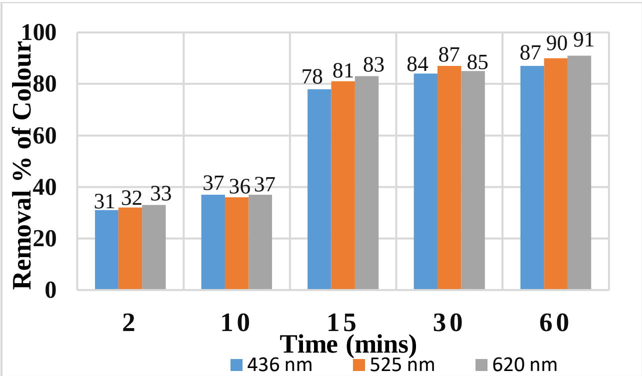


Figure 3 Effect of Contact time on Colour removal efficiency

Colour was 91% removed after 60mins and the other parameters like EC, TDS, BOD, COD, Sulphates and Chlorides also reduced. In this process taken a time interval of Electrochemical oxidation process is 2mins, 10mins, 15mins, 30mins, 60mins and the Current density is 20V. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 7.9%, 33%, 63%, 92%, 31% and 29% respectively.

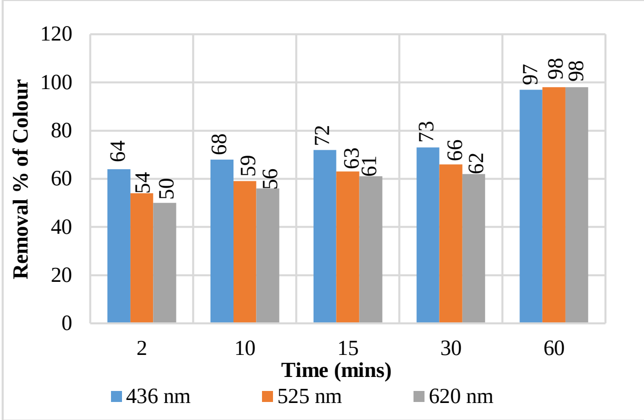


Figure 4 Effect of Contact time on Colour removal efficiency

Infer from the treatment process Colour was 91% removed after 60mins and the other parameters like EC, TDS, BOD, COD, Sulphates and Chlorides also reduced. In this process taken a time interval of Electrochemical oxidation process is 2mins, 10mins, 15mins, 30mins, 60mins and the Current density is 30V. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 10.6%, 30%, 47%, 91%, 62% and 57% respectively. The effect of pH on the decolourisation percentage of secondary treated tannery effluent during the electrochemical oxidation for different time intervals with a current density 20V and 30V.

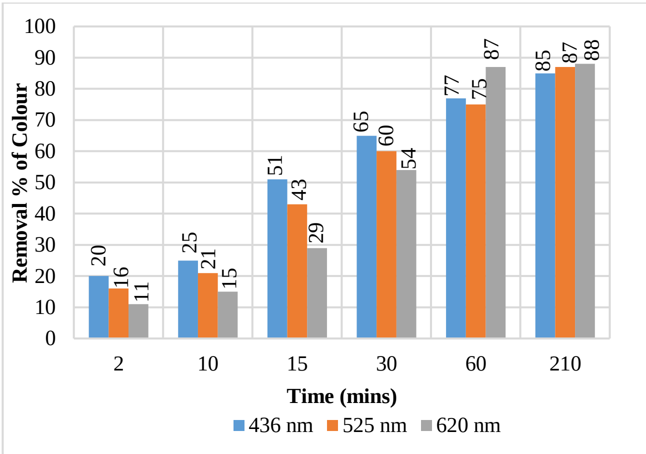


Figure 5 Effect of Contact time on Colour removal efficiency

From this pH decreases gives the decolourisation efficiency range of 88% at 240mins with 10V in secondary treated effluent. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 13.6%, 28%, 57%, 92%, 49% and 13% respectively. The effect of pH on the decolourisation percentage of secondary treated tannery effluent during the electrochemical oxidation process for different time intervals with a current density 10V.

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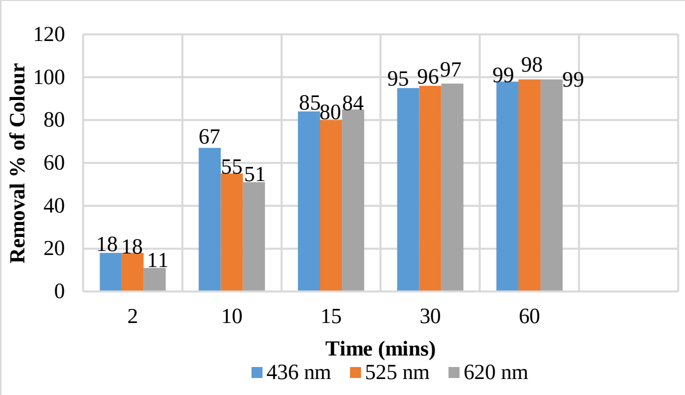

Figure 6 Effect of Contact time on Colour removal efficiency

From treated effluent gives decolourisation efficiency range of 99% at 120mins with 20V in secondary treated effluent. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 22.4%, 33%, 55%, 89%, 58% and 14% respectively.

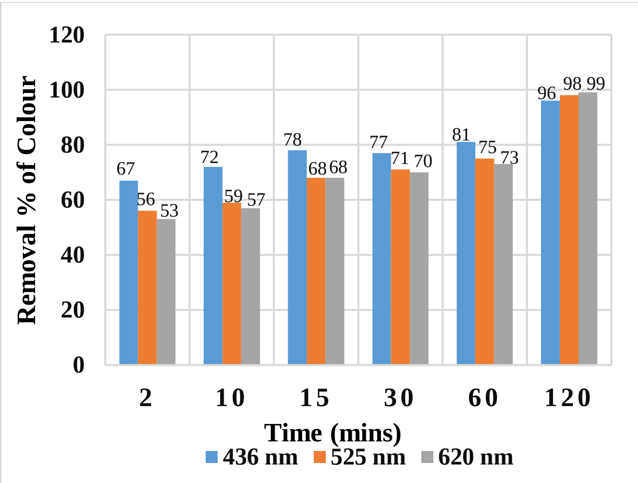

Figure 7 Effect of Contact time on Colour removal efficiency

From treated effluent gives the decolourisation efficiency range of 99% at 60mins with 30V in secondary treated effluent. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 12%, 28%, 48%, 87%, 55% and 13% respectively. The effect of pH on the decolourisation percentage of secondary treated tannery effluent during the electrochemical oxidation process for different time intervals with a current density 20V and 30V

The result shows that the optimum efficiency of colour removal is 99% for time interval of 60mins with current density is 30V at pH 6. The rate of Colour removal increases with increases the current density and decreases the pH range. Figure 8 gives the raw and decolourised secondary treated effluent.

Figure 8 Raw and decolourised secondary treated effluent

C. *Electrochemical Oxidation of Reverse Osmosis Reject*

Decolourisation of reverse osmosis reject treated by electrochemical oxidation process for 10V, 20V and 30V at pH 8 and pH 7 with different time intervals and its characteristics are characterised.

The effect of pH 8 on the decolourisation of Reverse Osmosis reject during the electrochemical oxidation with different time interval with different current density of 10V, 20V and 30V.

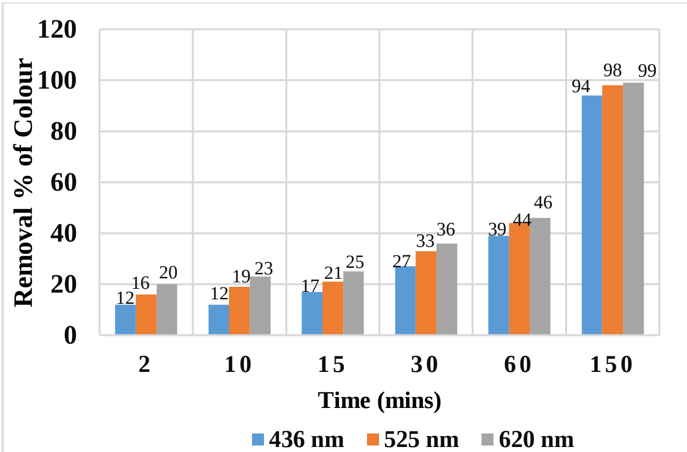

Figure 9 Effect of Contact time on Colour removal efficiency

Infer from the treated effluent gives Colour was 99% removed after 150mins and the other parameters like EC, TDS, BOD, COD, Sulphates and Chlorides also reduced. In this process taken a time interval of Electrochemical oxidation process is 2mins, 10mins, 15mins, 30mins, 60mins and 210mins and the Current density is 10V. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 5.8%, 6%, 38%, 84%, 40% and 68% respectively. The effect of pH on the decolourisation percentage of RO reject during the electrochemical oxidation for different time intervals with a current density 10V.

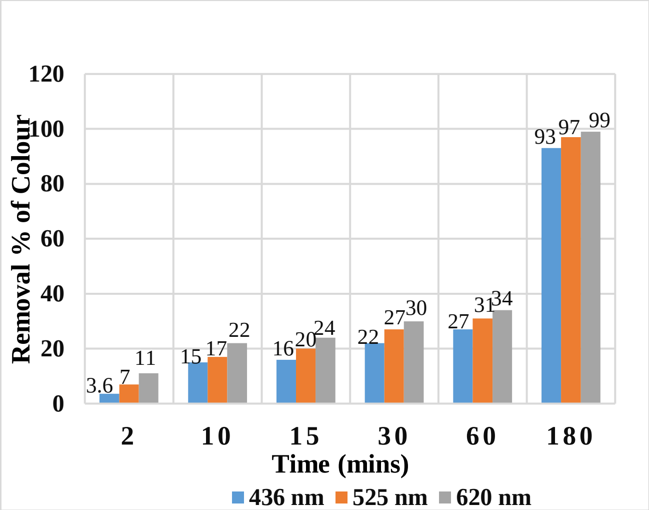

Figure 10 Effect of Contact time on Colour removal efficiency

From treated effluent Colour was 99% removed after 60mins with the Current density 20V and the other parameters like EC, TDS, BOD, COD, Sulphates and Chlorides also reduced. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 13%, 13%, 74%, 87%, 21% and 21% respectively.

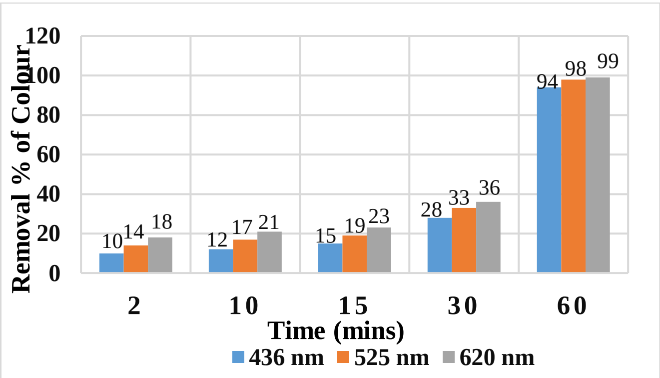

Figure 11 Effect of Contact time on Colour removal efficiency

Infer from treated effluent Colour was 99% removed after 60mins with the current density 30V and the other parameters like EC, TDS, BOD, COD, Sulphates and Chlorides also reduced. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 11.7%, 7%, 55%, 81%, 31% and 41% respectively. The effect of pH on the decolourisation percentage of RO Reject during the electrochemical oxidation for different time intervals with a current density 20V and 30V.

From this pH decreases gives the decolourisation efficiency range of 98% at 150mins with 10V in RO Reject. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 6%, 6.2%, 39%, 74%, 32% and 65% respectively. The effect of pH on the decolourisation percentage of RO reject during the electrochemical oxidation for different time intervals with a current density 10V.

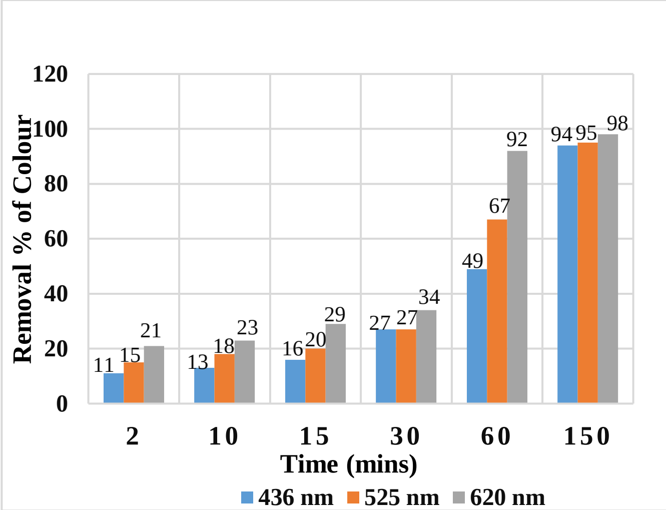

Figure 12 Effect of Contact time on Colour removal efficiency

From this pH decreases from 8 to 7 gives the decolourisation efficiency range of 98% at 120mins with 20V in RO reject. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 5%, 17.5%, 32%, 87%, 26% and 46% respectively.

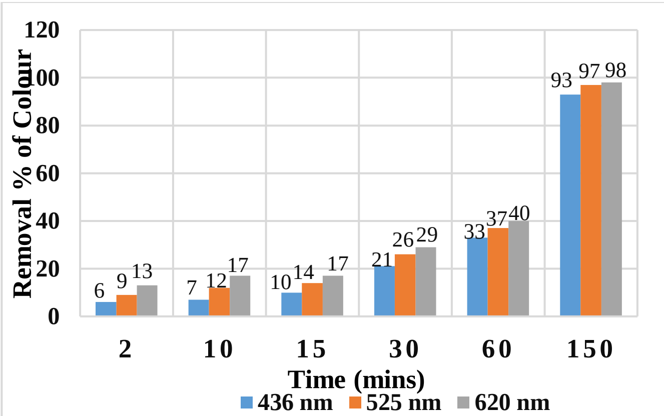

Figure 13 Effect of Contact time on Colour removal efficiency

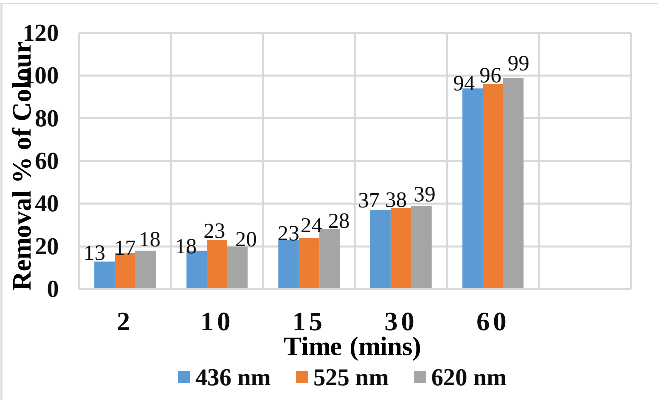

Figure 14 Effect of Contact time on Colour removal efficiency

From this pH decreases gives the decolourisation efficiency range of 99% at 60mins with 30V in RO reject. The effective Percentage removal of EC, TDS, BOD, COD, sulphates and chlorides were 9.8%, 8%, 66%, 82%, 32% and

67% respectively. The effect of pH on the decolourisation percentage of RO reject during the electrochemical oxidation for different time intervals with a current density 20V and 30V.

The result shows that the optimum efficiency of colour removal is 99% for time interval of 60mins with current density is 30V. The rate of Colour removal increases with increases the current density and decreases the pH range. Figure 15 gives the raw and decolourised Reverse Osmosis Reject.

Figure 15 Raw and decolourised Reverse Osmosis Reject

Effect of Contact Time

Experiments were carried out to evaluate the influence of contact time on removal efficiency of Colour. The contact times 2, 10, 15, 30, 60, 120, 150 and 180, 210, 240mins were considered for study. Based on the observations the following inferences have been drawn between the colour removal efficiency and contact time. Maximum removal efficiency for steady contact time of 30mins and minimum removal efficiency contact time of 2mins has been recorded. Same trends have been observed for all conditions of experimentation carried out.

Effect Of Voltage

The effect of voltage on Colour removal efficiency has been studied in the present experiment. 10, 20 and 30V were considered for the study. The following inferences were 1) the linear increase in Colour removal efficiency with increase in voltage. 2) Minimum and maximum removal efficiency has been observed at voltage of 10V and 30V respectively. 3) The similar trends have been observed from the observations of all conditions of experimentation. . Figure 4.15 & 4.16 gives removal of other parameters like BOD, COD, TDS, Chlorides and Sulphates at pH 6 and 7 with current density of 30V for Secondary treated effluent and Reverse Osmosis reject.

Effect of pH

pH viz,. 6 and 7 were considered for the study to evaluate the effect of pH on the Colour removal efficiency. Based on the observations, the following inferences were 1) pH has the direct influence on the Colour removal efficiency. 2) The removal efficiency for the pH 6 is significantly more than that of pH 7 for Secondary treated effluent and the removal efficiency for the pH 7 is significantly more than that of pH 8 for RO reject same trend was continued in all the conditions of experimentation.

Removal Effieciency of COD

COD decreases with increasing electrolysis time. The trend of COD reduction with electrolysis time vary for the current densities of 10V, 20V and 30V adopted in the present investigation. Also rate of COD reduction increases with decreasing pH ranges. COD reduction for different pH ranges varying like 6, 7 and 8. Optimum COD reduction increased a minimum pH range of 6.

Removal Efficiency of TDS

The results of experimentation carried out for tannery water waste using two electrodes. TDS removal efficiency increases with increase in contact time and decrease in pH.

TDS mainly contain various minerals in the water but does not include gas and colloidal material. The presence of solid particles is effective in electrical conductivity and is directly associated with specific conductivity, but this relationship is not linear. Thus TDS can be measured faster by using the conduct metery devices, evaporation and distillation techniques, electro gravimetery, ion exchange and reverse osmosis methods can be used for removing particles from solution. In this study the effect of the electrochemical process on removal of particles from the water soluble of effluent of reduced resin were investigated. As it can be seen in figure 15, this process had no significant effect on the removed of TDS. The maximum reduction was about 28% and 8% for secondary treated effluent and RO reject which is related to the time of 60mins and 60mins and pH range 7 and 6. In the voltage of 30 V, as previously mentioned, because the effluent samples boil, some water evaporated from effluent samples, thus by increasing the time (from 2 to 30mins), the concentration of dissolved solids is increased too (Solomon et al. 2014).

II. CONCLUSION

The percentage of colour removal efficiency calculated for different nm like 436nm, 525nm and 620nm. The highest removal efficiency of colour 99 % for optimum conditions of variables viz,. pH = 6 and contact time at 60mins at 30V have been recorded for Secondary Treated effluent.

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The highest removal efficiency of 99 % for optimum conditions of variables viz,. pH = 7 and contact time at 60mins have been recorded for Reverse Osmosis Reject.

The effective percentage removal of TDS, BOD, COD, Chlorides and Sulphates were 28%, 48%, 87%, 13% and 55% respectively for Secondary Treated effluent.

The effective percentage removal of TDS, BOD, COD, Chlorides and Sulphates were 8%, 66%, 82%, 67% and 32% respectively for RO reject.

REFERENCES

[1.] Allen, S. J., Murray, M., Brown, P., and Flynn, O- (1994) 'Peat as an adsorbent fordyestuffs and metals in wastewater', *Resources, Conservation and Recycling, 11, pp. 25-39.*

[2.] Adernoroti, C. M. A., Ukponrnwan, D. O., and Omode, A.A.(1992) 'Studies of textile effluent discharges in Nigeria', *International Journal of Environmental Studies, 39, pp. 291-296*

[3.] Carlos A. Martınez-Huitle and Sergio Ferro, July (2006) 'Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes'

[4.] Cooper, P. (1993) 'Removing color from dyehouse wastewaters - a critical review of technology available', *Journal of the Society of Dyers and Colorists,* 109(3), pp. 97-100.

[5.] Errami . M., (2013) 'Electrochemical Treatment of Wastewater Industrial Cartons', *Int. J. Electrochem. Sci., 8, 12672 – 12682.*

[6.] Gardiner, D. K., and Borne, B. J. (1978) 'Textile wastewaters: treatment and environmental effects', *Journal of the Society of Dyers and Colorists*, 94(8), pp. 339-348.

[7.] Guohua Chen., (2011) 'Electrochemical technologies in wastewater treatment', *Separation and Purification Technology 38 (2004), pp. 11–41.*

[8.] Holme, I. (1984) 'Ecological aspects of colour chemistry', In : J.Griffiths (Ed), Developments in the Chemistry and Technology of Organic Dyes. *Blackwell Scientific Publications, Oxford, UK, pp.111-128.*

[9.] Homing .R.H., (1977) 'Characterisation and treatment of textile dyeing wastewaters', *Textile Chemist and Colourist, vol.9 (4), pp. 26-27.*

[10.] Jelena Radjenovic., 'Challenges and Opportunities for Electrochemical Processes as Next- Generation Technologies for the Treatment of Contaminated Water', *Environ. Sci. Technology, 49, 11292−11302.*

[11.] Kavitha.E (2012),'Electrochemical Oxidation of Textile Industry Waste Water Using DSA in tubular reactor', *International Journal of Engineering Research and Applications (IJERA)* Volu-2, Issue 6, pp.444-451.

[12.] Kouba, J. F., and Zhuang, P. (1994) 'Color removal for textile dyeing wastewater', *Fluid/Particle Separation Journal, vol. 7(3), pp. 87-90.*

[13.] Mahloch .J.L., (1975) 'Treating dye and finishing wastes', *American Dyestuff Reporter, vol. 64(11), pp. 24,26,28,46.*

[14.] Marcopanizza and Giacomocerisola (2004), 'Electrochemical Oxidation as a Final Treatment of Synthetic Tannery Wastewater'., *,Department of Chemical and Process Engineering, University of Genoa, P. le J.F. Kennedy 1, 16129 Genoa, Italy*

[15.] Naturgerechate Technologien, Bau- und Wirschaftsberatung GmbH, Frankfurt(Germany), April (2002) 'Treatment of Tannery Wastewater'.

[16.] Pools, V. J. P-, and McKay, G. (1976) 'Flow characteristics and parameters relating tothe use of peat and wood as cheap adsorbent materials for waste water purification', *Scientific Proceedings, Royal Dublin Society, Series A, 6, pp. 409-440.*

[17.] Qiyuan Gu., (2015) 'Study on the Electrochemical Oxidation Treatment of Coking Wastewater by DSA Anode', *Asia-Pacific Energy Equipment Engineering Research Conference*.

[18.] Rashed.I., (2005) 'OVERVIEW ON CHEMICAL OXIDATION TECHNOLOGY IN WASTEWATER TREATMENT', *Ninth International Water Technology Conference, IWTC9 2005.*

[19.] Smith, B., Koonce, T., and Hudson, S. (1993) 'Decolorizing dye wastewater using Chitosan', *American Dyestuff Reporter, pp.18-26.*

[20.] Solomon, (2014) 'Hydroxo Bridged Dicopper and Complexes: Models for Putative intermediates in Oxidation Catalysis', *Journal of the American Chemical Society, 136, pp. 7269-7272.*

[21.] Usha N Murthy., (2011) 'Performance of Electrochemical Oxidation in Treating Textile Dye Wastewater by Stainless Steel Anode', *International Journal of Environmental Science and Development, Vol. 2, No. 6, December 2011*

[22.] Venkatareddy B., (2011) 'Performance Evaluation of Electrochemical Oxidation System to Treat Domestic Sewage', *International Journal of Engineering Research & Technology (IJERT) ISSN: 2278-0181., Vol. 3 Issue 6.*