



Electro-oxidation of tannery soak water using solar photovoltaic stand-alone systems

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Abstract

The recalcitrant organics matters present in the tannery soak water and generation of CO₂ by the conventional grid-power, becomes a major problem to meet pollution control board norms in Tamil Nadu. Treatment of tannery soak water has become significant with the declining water resources. An eco-friendly electrochemical oxidation on tannery soak water was investigated using solar PV stand-alone systems (SPV) to supply constant power to eliminate the conventional grid-power. Electro-oxidation cell with cylindrical graphite electrode was used for this process and the treatment was found to be effective and almost all organic part were completely removed. The influence of the significant parameters of electro-oxidation such as pH, treatment time, salt concentration and current density on the removal of organic load was studied using graphite electrodes. A high concentration of sodium chloride about 40 g/L in this system makes the process effectively and improved the overall performances. In this SPV system with constant power, it was found that current density of 24 mA/cm² and at pH 10 with treatment duration of 120 min were the best results in terms of reduction in COD (91.5%) and TKN (95.7%). Bio-degradable index was also improved from 0.31 to 0.46. One of the soaking water in leather manufacturing process is pickling, where the treated reused waste was used continuously twice. The characteristics of the waste water and the quality of the leathers indicate that the reuse of saline streams with treatment is feasible. This treated soak liquor can be reused effectively, since no organic salt were accumulated. Soak liquor from tannery can be adequately rendering the wastewater suitable for reuse. It was noticed remarkably that the extraordinary capability of the technique, which was used to remove the organic part, color, and odor and improve the biodegradability.

Keywords: Solar PV, tubular lead acid battery, electro-oxidation, soak water, graphite electrode.

Introduction

The leather industry in India process 3000 tons of hide and skins per annum and the total production capacity of India covers about 22% of the world market share. This invites special attention to environmental issues related to the wastewater generated in leather industries. Normally, 300-600% of water is used for soaking process alone to remove the sodium chloride used to preserve the skins/hides and large quantity of waste water is being discharged to the open solar pan for natural evaporation. Apart from this, wastewater from tanneries usually contains high concentrations of chlorides, aliphatic sulfonates, sulfates, aromatic and aliphatic ethoxylates, sulfonated polyphenols, acrylic acid condensates, fatty acids, dyes, proteins, soluble carbohydrates and sodium sulfide (Na₂S). These substances are either derived from hides and skins or obtained upon addition of reagents during the process. The first step in leather processing is to wash the skins/hides with water to remove the salt and other particles. After this washing, a large quantity of water is released as wastewater. This stream, called soak liquor, consists of 2-4% sodium chloride by weight and contains traces of calcium chloride along with bio-particles such as blood, flesh, skin, and other suspended particles.

The dissolved salts, especially chlorides, are a matter of concern when the effluent is discharged into nearby lands or stored in ponds. In the long run, it makes the fertile land barren, in addition to polluting the surrounding groundwater. Therefore, it becomes necessary to tackle the problem on a top priority basis to control the severe environmental degradation. The most common method of disposing of soak liquor is evaporation in shallow solar ponds by natural evaporation process. This operation is slow and season-dependent. Hence, different types of treatment are being used like electro-oxidation treatment, advanced oxidation process with or without catalysts etc.

Abbreviations: AC: Alternating current; SPV: Solar photovoltaic cell; APHA: American public health association; BI: Biodegradable index; COD_{t. t+Δt}: Chemical oxygen demand at time t, and t+Δt time, mg/L; F: Faradays constant, 96487 C/eq; V: Volume of electrolyte, L; I: Current, Ampere; P: Potential, V; t: Electrolysis time, h; S_A: Surface area of anode, m²; TKN: Total Kjeldahl nitrogen, mg/L; I_{PV}: Photovoltaic cell current, A; V: SPV system voltage, V; I: SPV system current, A.



Numerous adsorbents materials have been investigated on waste water for the removal of heavy metal such as lead, chromium, cadmium, Arsenic. About 15-40% (w/w) of common salt is used for preserving the animal skins and it is removed during the first and second soaking operation. The waste stream of soaking contains mainly high organic load, salinity and suspended solids (Ludvik, 2000). Pickling is also one of the unit processes of leather manufacturing where common salt of 8-10% (w/w) is being used as reported by Lefebvre et al. (2005). Various experiments have been carried out on the electro-oxidation method of organic compounds and on the number of anode (catalytic, graphite, iron etc.) materials. Such methods have been effectively applied for the treatment of wastewater and COD, TKN and other organic emission loads were reduced considerably especially in tannery waste water (Apostolos et al., 1997; Lidia Szpyrkowicz et al., 2005; Carlos et al., 2006; Chandan Das et al., 2007; Samiha Hammami et al., 2009; Ahmed Basha et al., 2009), from distillery by waste (Manisankar et al., 2003), from paper mill waste (Paritam et al., 2010), from domestic sewage (Vlyssides et al., 2002) and also for landfill leachate (Chiang et al., 1995).

Furthermore, the social concern about the environment has led to the research and development of new forms of green energy like PV, wind, tidal etc. One of the most broad and most studied is the solar photovoltaic (PV) power (Markvar, 1994; Sen 2004). The advantages of the use of the PV power are that it is non-polluting, abundant and a renewable resource. It is also noiseless, the fuel is free sunlight, long-life and the low maintenance cost of these systems. The output power of PV systems can be varied drastically in fraction of time.



At high levels of PV penetration, this intermittency can cause problems with effective operations and on load-side equipment due to fluctuations in grid voltage and power factor (Hanley et al., 2009). These PV systems can be used in remote are for the self-sufficiency of electrical energy in a reliable and autonomous source (Irfan, 1997). PV system needs optimum design to have a maximum-power point voltage which is slightly higher than upper charge limit cut-off voltage, programmed into the battery bank control module (Gibson and Kelly, 2010). Integrated PV and green energy storage systems provides a combination of financial, operational, and eco-friendly profit to the system owner and to the utility through peak shaving and reliability applications (Manz et al., 2008). Energy consumption and CO2 emission were investigated effectively and reported from office building appliances (Huijun et al., 2012) and from an electrochemical reactor using conventional grid and SPV (David Valero, 2008; lyappan et al., 2008).

Electrochemical oxidation: Theoretical approach

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving the coupling of and electron-transfer reaction with a dissociate chemisorptions step. In the electrochemical oxidation, organic pollutants are removed by electro-generated oxidizing agents like chlorine and hypochlorite (Pletcher and Walsh, 1990). In general, the following reaction takes place during electro-oxidation using graphite electrodes in the presence of sodium chloride.

At the anode:	
$2Cl^- \rightarrow Cl_2 + 2e^-$	(1)
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	(2)
At the cathode:	

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

In the undivided cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypochlorites. Both the hypochlorite and free chlorine are chemically reactive and oxidize the organic pollutants in the effluent to carbon dioxide and water (Manisankar *et al.*, 2003). HOCl is then formed.

$$CI_2 + H_2O \rightarrow H^+ + CI^- + HOCI$$

The HOCl further dissociates into OCl⁻ and H⁺ ions. HOCl \leftrightarrow H⁺ + OCl⁻ (5)

This hypochlorite ions act as a main oxidizing agent in the organic degradation.

The overall desired reaction of electrolysis is:

 $\begin{array}{l} \text{Organic matter + OCl}^- \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{Cl}^- + \\ \text{H}_2\text{O} \end{array} \tag{6}$

Total current efficiency

Total current efficiency (TCE) was calculated using the formula given below (Comminellis, 1995):

$$TCE = \frac{[CODt - CODt + \Delta t] FV}{81\Delta t}$$
(7)

(4)

Where, COD_t and $COD_{t+} \Delta_t$ are chemical oxygen demands at times t and t+ Δ t in gram of O_2 per dm³ at times t = 0 (initial) and t respectively. F is Faraday's constant (96,487 C mol⁻¹); V is the volume of electrolyte in liters and I is the current in Ampere and 8 is the oxygen equivalent mass (g/equiv.⁻¹).

Anode efficiency

Anode efficiency was calculated as per the formula given below (Carlos 2006):

efficiency =
$$\frac{(\text{COD removed in (kg)})}{(\text{Time (h) × Current (A) × Surface area of anodes (m2)}}$$
(8)

Energy consumption

Energy consumption was also calculated on the basis of COD Reduction (Carlos, 2006):

Energy consumption = $\frac{tVA/S_v / 1 \times 10^3}{\Delta COD/1 \times 10^6}$ kWh/kg COD (9) Where t is the time of electrolysis in hours, V is the average cell voltage A is Ampere. Sy is sample volume

average cell voltage, A is Ampere, $S_{\rm V}$ is sample volume in liters and COD is the difference in COD in mg/L time in t.

In the present investigation, a first attempt has been made to investigate and to improve the effectiveness of the existing biological waste water using a SPV stand alone system. Soak water from tanneries was separately treated by an electro-oxidation technique with graphite electrode using SPV system. Even though various electrochemical techniques have been investigated for the treatment of soak water as said in introduction, their performance in treating soak water and improving biodegradability during the treatment has not been studied on soak liquor using SPV. The parameters of electrochemical oxidation such as pH, period of oxidation, concentration of sodium chloride and current density were varied.

Materials and methods

Electro-oxidation cell: The electro-oxidation (EO) cell is described briefly by Pletcher and Walsh (1990) which is used for the experiment was a rectangular vessel of 12 L working volume made of acrylic sheet having the dimensions, height of 23 cm, breadth of 30.5 cm, width of 22.5 cm and thickness of 1 cm. Cylindrical graphite electrodes 12 numbers with a diameter of 2.54 cm and a length of 13 cm were used both as a cathode and as an anode. Total surface area of the electrodes was 427.84 cm². The electrodes were arranged parallel to each other with a constant electrode gap of 1 cm to minimize the ohmic resistance drops. Ohmic resistance drop is potential drop due to real soak solution resistance. The electric power supply was provided by laboratory D.C. power source equipped with current and voltage monitoring and of maximum output of 30 A and the difference in potential required to move ions through the solution. Schematic view of the EO cell is shown in Fig. 1.

Fig. 1. Schematic view of electro-oxidation cell.



Drain valve

Collection and pretreatment of soak water: The raw soak liquors were collected from a typical tannery in Dindigul, TN, India. The wastewater sample was pretreated to remove the heavy and suspended coarse particles by passing it through the sand filter. The wastewater sample was characterized for physicochemical parameters by following the standard methods for analysis of water and wastewater (Clesceri, 1998). The characteristics of the wastewater are listed in Table 1.

Table 1. Characteristics of the soaking water.

Parameters	Soak-1
рН	6.8
$COD (mg L^{-1})$	4466
BOD (mg L^{-1})	1016
Total Dissolved Solids(mg L ⁻¹)	42400
Suspended solids (mg L ⁻¹)	10800
Total solids (mg L^{-1})	50700
Sulfates (mg L ⁻¹)	1550
Chlorides (mg L^{-1})	41200
Color	Dark brown

Analysis of wastewater: Pollution parameters such as chemical oxygen demand (COD), Total Kjeldahl Nitrogen (TKN) and chlorides (Cl⁻) were analyzed by following the standard procedure as reported (Clesceri, 1998). Mercuric sulphate was added to overcome the likely interference of Cl in the COD estimation. The results were ensured using standards as well as duplicates. All chemicals such as sulfuric acid (36 N, specific gravity 1.80, 99% purity) used in this study were analytically pure obtained from SD Fine chemicals. The pH of the solution was measured using pH meter of Elico model LI 617. The accuracy is \pm 0.01. Double distilled water was obtained from a Fischer distilled water purification system.

Electro-oxidation experiment using a conventional power supply: For conventional EO experiments, a continuous power supply (Waveforms power, Chennai, supply voltage: 0-12V, current: 30 A DC) was used.



Concentration is a main parameter in this study that is closely associated with cell applied voltage (V_{cell}) during the oxidation and consequently to the energy consumption. The values of COD_R and TKN_R efficiency were about 92.6% and 96.4% for each experiment with a maximum treatment period of 120 min.

Fig. 2.Schematic view of electro-oxidation cell supplied by SPV.



12 V-100 Ah tubular lead-acid batteries with 4 d autonomy were integrated with DCC. Tubular battery was tested as per standard specification: Bureau of Indian Standard, BIS 13369:1992 for stationary lead acid battery with tubular positive plates using Bitrode Life Cycle Tester LCN Model-1-25-12.

Electro-oxidation supplied by SPV stand-alone systems: In this experiment, the DC power supply was provided by PV modules MUMRH-12, that were made from poly crystalline silicon with a peak power of 42.3 W and a surface area of 0.5 m². Specifications are mentioned in the Appendix A (Table 3). A solar charge controller 40 A, 12 V, Xantrax, USA were connected with unidirectional diode, 12 V, and 30 A to the EO system (lyappan et al., 2012). The solar radiation incident on the surface of the PV array was measured using a pyranometer, range 0-2000 W/m², CM11B, Kipp and Zonen, USA. A data acquisition system (16 bit, 16 Channel, Akash Instruments, Chennai) was connected to a PC computer and was used to measure all parameters, such as current, voltage, ambient temperature etc. The laboratory prototypes of the SPV system are as shown in Fig. 2. 12 V-100 Ah tubular lead-acid batteries were integrated with this SPV system. This tailor made battery was prepared by the following procedure given in Appendix B (Linden et al., 2002; Balakrishnan, 2011) to improve storage capacity and increased the life cycle. The purpose of the battery is to make-up the energy generation variation between the PV modules during partial shading or poor weather condition.

Chennai (Madras) is located in costal of Bay of Bengal at a latitude angle of 13.04 °N and at longitudinal angle of 80.17 °E. The annual average solar radiation, sun shining days and average temperatures are measured ranging from 4.7 kWh-8.2 kWh/m²/d, 300-320/Annum and 30-32°C respectively. The solar panels were kept over the roof of the single storied building, at a place where there was no shade throughout the day at an angle of 13° to the horizontal facing south direction.

Results and discussion

The experiments were conducted with 3 consecutive days and the weather was pretty good. Table 2 represents the real I-V data of SPV system. At a solar intensity of 777 W/m² with a pretty weather, maximum I_{PV} of 10 A and a corresponding V of 3.5 V was generated by the SPV system. The bio-degradability index (BI) has been estimated during electro-oxidation of tannery soak water and the variation of bio-degradability index with process time is shown in Table 2. It was observed that soak water has the ratio of BOD/COD value of 0.4 and above can be treated efficiently by biological methods (Harmsen, 1996). The BI of soak water improved using this SPV system from 0.38 to 0.58 and corresponding average COD removal of 92.6% with 120 min duration. Continuation of electro-oxidation beyond 120 min did not show any significant improvement in bio-degradability index. But the average BI of soak water improved using this direct PV system was very less recording 0.38 and corresponding average COD removal of 65.8% with 360 min duration (Iyappan et al., 2008). Ahmed Basha et al. (2009) reported that an average COD removal of 94.4%, average BI of 0.0.55 within 8 h of treatment, at a current density of 2.5 A dm⁻² when 500 mL of the effluent is treated. Organic matter with long-chain can be broken into small chain or low molecular-weight by oxidation. This early stage occurrence will not only reduce the COD considerably, but also increases the BOD resulting in an improved BI. After a specific period of time, even though the oxidation mechanism removes the organic matter continuously, the ratio of BOD and COD easily degradable to very slowly. In electro-oxidation treatment, the initial reaction on slowly biodegradable long chain molecules, results in an increase in BI of waste water. The characterization of the soak liquor showed that this effluent is biodegradable, though not easily and highly variable depending on the origin and the nature of the hides.

Table 2. Tests results of electro-oxidation of soaking water for three days carried out by SPV.

Day of experiment	G ^a (W/m²)	V ^a _{EO} (V)	l ^a (A)	T (°C)	t _{EO} (min)	COD _R efficiency (%)	TKN _R efficiency (%)	Biodegradable Index
1 st day	780.4	3.50	10.4	36.1	120	92.00	95.80	0.46
2 nd day	777.8	3.55	10.0	36.5	120	93.60	95.40	0.46
3 rd day	770.3	3.46	10.1	35.0	120	92.30	95.60	0.46

Experimental conditions: Soaking water concentration: 40 g/L, pH: 10 and i: 24mA/cm². ^aAverage values of G, V_{EO} and I.

Variations of these parameters through all the tests were lower than 2%. t_{EO} was the time taken to treat 12 L of soaking water samples.



Fig. 3a. Effect of salt concentration with electro-oxidation time on COD reduction, pH = 10 and $i = 24 \text{ mA/cm}^2$.



Fig. 3b. Effect of salt concentration with electro-oxidation time on TKN reduction pH =10 and i = 24 mA/cm^2 .











Effect of salt concentration

The process standardization of electro-oxidation of tannery soak wastewater was carried out by studying the effects of pH, current density, salt concentration and electrolysis time. The concentration of sodium chloride in soak water was varied from 10-40 g/L with an increasing order of 10 g/L, the pH and current density are constants as 10 and 24 mA/cm² respectively. COD and TKN reduction rate was found to be directly proportional to the salt concentration as shown in Fig 3a and b. Reduction of COD and TKN was increased with increase in salt concentration. However, the increase in the reduction of COD and TKN with respect to increasing the salt concentration was insignificant. Highest reduction in COD and TKN were observed as 91% and 95% at salt concentration of 40 g/L. The observed results are in congruence with the reported literature and this trend probably could be attributed to the increased level of generation of chlorine and hypochlorite when the salt concentration is increased (Chiang, 1995).

Effect of pH

Soak water pH varied from 5 to 10, current density and NaCl concentration were kept constant at 24 mA/cm² and 40 g/L respectively. The rate of COD reduction and TKN reduction with respect to time is shown in Fig. 4a and b. COD was reduced by 68.2% and 83.8% at pH 5 and 6 respectively. TKN was reduced by 61% and 73% at pH 5 and pH 6 respectively. It is proved that the rate of COD reduction was found to be insignificant at pH 5 and pH 6, but increase in pH resulted in the increase in the degree of reduction of COD. At pH 10, COD was reduced by 93% and TKN was reduced by 96%. It can be explained through Eqn. (5) and (6) and the OCI ions are unstable in acidic conditions. The OCI and H⁺ ions in acidic conditions undergo the reverse reaction of combining with each other to produce as Eqn.: HOCI $(HOC|\leftrightarrow[H^+ + OC|^-]$. In alkaline conditions the reverse reaction is not favored and OCI⁻ ions may oxidize the organic matters.



Part of the treated wastewater was reused for pickling for 2 times (Lefebvre et al., 2005). Soak water before and after treatment was characterized and reused. The removal of organic load was assessed by estimating TKN and COD. It was observed that the reused treated water did not affect the quality of leather and result in the accumulation of pollutants as the recycling progresses. The important parameters for indicating the tanned leathers quality are chromium content and shrinkage temperature. Further, one batch of treated water used for solar evaporation and 250 g of salt was recovered, which was used for the pickling process. From both methods, there was not much variation in the quality of the tanned leathers on the reuse of the treated pickling wastewater. Energy cost is the main and principal cost component in electro-oxidation system either from conventional or SPV with battery system. The electrical energy required for the treatment of 1 m^3 of soak liquor is 5.3 kWh/m³ considering the treatment time of 120 min using the SPV system. Therefore the cost of treatment of 1 m³ of soak liquor using SPV is US\$ 1.15 (assuming the cost per unit of energy is US\$ 0.12). The cost of energy and the total cost of treatment would diminish significantly as the treatment is carried out at commercial scale. It can be seen from the above that the cost of treatment is relatively lower. Cost of other similar treatment systems such as advanced oxidation process, membrane process, ultrafiltration and nanofiltration is very high (Canizares et al., 2009) and CO₂ was also eliminated in the local atmosphere with an amount of 5.37 kg/m³.

Conclusion

Characteristics of the tannery soak water were studied by electro-oxidation using SPV system. This system is more effective like conventional systems. This effective system reduced the COD and TKN more than 90%. This system could be used as an alternative source for the conventional grid-power. Considerable amount of CO2 could be eliminated in the local atmosphere. This system indicates that there is no accumulation of organic load effected due to reuse for pickling process. Current density of 24 mA/cm², salt concentration equal or more than 40 g/L and at neutral and alkaline pH conditions brought better result for the treatment of tannery soak water to remove the organic pollution with respect to contamination reduction and energy requirement. To conclude, soak water streams from tannery can be treated effectively and adequately rendering the wastewater suitable for reuse. The results obtained from the prototype are promising.

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References

- 1. Ahmed Basha, C., Soloman, P.A., Velan, M. and Balasubramanian, N. and Roohil Kareem, L. 2009. Participation of electrochemical steps in treating tannery waste water. *Ind. Engg. Chem. Res.* 48(22): 9786-9796.
- Apostolos, G., Vlyssides, S., Cleanthes, J. and Israilides, M. 1997. Detoxification of tannery waste liquors with an electrolysis system. *Environ. Poll.* 97(1-2): 147-152.
- Apostolos, G., Vlyssides, S., Cleanthes, J. and Israilides, M. 1997. Detoxification of tannery waste liquors with an electrolysis system. *Environ. Poll.* 97(1-2): 147-152.
- 4. Balakrishnan, P.A., Arunagiri, A. and Rao, P.G. 2002. Ozone generation by silent electric discharge and its application in tertiary treatment of tannery effluent. *J. Electrostat.* 56(1): 77-86.
- Balakrishnan, P.G. 2011. Lead storage batteries, science, technology and application. Scitech publications (India) Pvt. Ltd: ISBN 978 81 8371 3986.
- Cãnizares, P., PazrSáez, C. and Rodrigo, M.A. 2009. Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes. *J. Environ. Manage.* 90: 410-420.
- Carlos, A.M. and Sergio, F. 2006. Electrochemical oxidation of organic pollutants for the wastewater treatment: Direct and indirect processes. *Chem. Soc. Rev.* 35: 1324-1340.
- Chandan Das, M., Sunando Das Gupta, S. and Sirshendu, D. 2007. Treatment of soaking effluent from a tannery using membrane separation processes. *Desalination*. 216:160-173.
- Chiang, L.C., Chang, L.C. and Wen, T.C. 1995. Indirect oxidation effect in electrochemical oxidation treatment of land II leachate. *Water Res.* 29(2): 671-678.
- 10. Clesceri, L.S., Greenberg, A.E. and Eaton, A.D. 1998. Standard methods for the examination of water and wastewater, 20th ed., APHA: Washington, DC.
- 11. Comminellis, C. and Nerini, A. 1995. Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. *J. Appl. Electrochem.* pp. 25-23.
- 12. David Valero, S., Juan M. Ortiz, Eduardo Exposito, k., Montiel V. and Aldaz, A. 2008. Electro-coagulation of a synthetic textile effluent powered by photovoltaic energy without batteries: Direct connection behavior. *Solar Energy Mater. Solar Cells.* 92: 291-297.
- Gibson, T.L. and Kelly, N.A. 2010. Solar photovoltaic charging of lithium-ion batteries. *J. Power Sources.* 195: 3928–3932.
- Gupta, V.K., Ali, I. and Saini, V.K. 2007a. Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA 13 from aqueous solutions using carbon slurry developed from a waste material. *J Colloid Interface Sci.* 315: 87-93.
- Gupta, V.K., Dinesh Mohan, Saurabh Sharma and Kuk T. Park. 1999. Removal of chromium (VI) from electroplating industry wastewater using bagasse fly ash-a sugar industry waste material. *Environ.* 19: 129-139.
- Gupta, V.K., Jain, R. and Varshney, S. 2007b. Removal of reactor fix golden yellow 3 RFN from aqueous using wheat husk-An agricultural waste. *J. Hazard. Mater.* 142: 448-448.
- 17. Gupta, V.K., Rastogi, A. and Arunima Nayak. 2010. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *J Colloid Interface Sci.* 342: 135-141.
- Hanley, C., Peek, G., Boyes, J., Klise, G., Stein, J., Dan, T. and Tien, D. 2009. Technology development needs for integrated grid-connected PV systems and electric energy storage. In: Photovoltaic specialist's conference (PVSC).



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- 19. Harmsen, G., Voortman, B. and Vogelpohl, A. 1996. Proc. of the Int. conf. on oxidation technologies for water and wastewater treatment, Goslar, Germany.
- Huijun, J., Wu Zengwei, W., Ling Zhang, Y. and Jun Bi. 2012. Life cycle energy consumption and CO₂ emission of an office building in China. *Int. J. Life Cycle Assessment*. 17(2): 105-118.
- 21. Irfan, A.A. 1997. Photovoltaic application in remote areas, Asian Instt. of Technol., Bangkok, Thailand.
- Iyappan, K., Suguna, L., Gayathri, V.S., Sundara Pandian, S. and Saravanan, P. 2008. Tannery effluent treatment by electrochemical method using solar power, Poster presented in LERIG, CLRI, Adyar, Chennai, India.
- 23. Iyappan, K., Suguna, L., Kannan Chandrababu, N. and Vedaraman, N. 2012. *J. Acad. Indus. Res.* 1(3): 118-123.
- Lefebvre, O., Vasudevan, N., Torrijos, M., Thanasekaran, K. and Moletta, R. 2005. Halophilic biological treatment oftannery soak liquor in a sequencing batch reactor. *Water Res.* 39(8): 1471-1480.
- Lidia Szpyrkowicz, M., Santosh, N., Kaul Rao, N., Neti, R. and Shanta Satyanarayan. 2005. Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater. *Water Res.* 39(8): 1601-1613.
- 26. Linden, D. and Magnusen, D. 2002. In: Linden D, Reddy T.R (Eds.) handbook of batteries, 3rd ed., McGraw Hill.
- Ludvik, J. 2000. The scope for decreasing pollution loads in leather processing. Regional program for pollution control in tanning industry in South East Asia, UNIDO: pp.11-51.
- 28. Manisankar, P., Viswanathan, S. and Rani, C. 2003. Electrochemical treatment of distillery effluent using catalytic anodes. *Green Chem.* 5: 270-274.
- 29. Manz, D., Schelenz, O., Chandra, R., Bose, S., Rooij, M.D. and Bebic, J. 2008. Enhanced reliability of photovoltaic systems with energy storage and controls, NREL, USA.
- Paritam, K., Dutta, S., Rabaey, K., Yuan, Z., René Rozendal, A. and Keller, J. 2010. Electrochemical sulfide removal and recovery from paper mill anaerobic treatment effluent. *Water Res.* 44(8): 2563-2571.
- 31. Pletcher, D. and Walsh, F.C. 1990. *Indus. Electrochem.* Chapman and Hall, London.
- Preethi, V., Parama Kalyani K.S., Iyappan, K., Srinivasakannan, C., Balasubramaniam, N. and Vedaraman, N. 2009. Ozonation of tannery effluent for removal of COD and color. *J. Hazard. Mater.* 166: 150-154.
- Samiha Hammami, Ali Ouejhani, Nizar Bellakhal, Mohamed Dachraoui. 2009. Application of Doehlert matrix to determine the optimal conditions of electrochemical treatment of tannery effluents. J. Hazard. Mater. 163(1): 251-258.
- Sen, Z. 2004. Solar energy in progress and future research trends. Prog. Energy Combust. Sci. 30: 367-416.
- 35. Vlyssides, A.G., Karlis, P.K., Rori, N. and Orpas, A.A. 2002. Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes. *J. Hazard. Mater.* 95: 215-226.

Appendix A

Table 3. Specifications of the SPV panels used at STC 1000 W/m² at temperature 25°C, AM-1.5.

Make and type	Maharishi solar,			
	mono-crystalline silicon			
Rated capacity	37 W _P			
Short circuit current (Isc)	2.60 A			
Open circuit voltage (Voc)	21 V			
Maximum power current (I _{max})	2.26 V			
Maximum power voltage (V _{max})	16.4 V			

Appendix B

Three numbers of tubular lead-acid batteries of 12 V, 100 Ah capacities were fabricated by conventional methods according to Balakrishnan (2011) with leady oxide and negative plates were prepared by including electrically conducting carbon black (CB) 0.5% (w/w), Philips make, China, with particle size of 6.34 μ m, BET surface area of 79 m²/g. The composition and preparation method are given below:

The paste was prepared in a mixer from leady oxide (72% PbO). The XRD pattern of the starting material showed the presence of tetragonal PbO and Pb. Leady oxide (LO) and suitable additives were mixed with water and H_2SO_4 with1.40 specific gravity as given in the Table 4.

Table 4. Composition of the paste.					
	Paste formulations				
Materials	Positive plate	Negative plate with additive	Negative plate without additive		
Gray oxide	1085 g per plate	1000 g per plate	1000 g per plate		
BaSO ₄	-	0.38%	0.38%		
Lignin	-	0.23%	0.23%		
Carbon black	-	0.5%	0.0%		
Distilled water	-	115 mL per kg of oxide	115 mL per kg of oxide		
H_2SO_4 solution	-	100 mL per kg	100 mL per kg		
Dynel Fibre	-	0.05%	0.05%		
Life avala improvementa: 1646 avalage at a DOD of 900/ and 1249 avalage at					

Life cycle improvements: 1646 cycles at a DOD of 80% and 1248 cycles at a DOD of 100%.

Grids cast from Pb-3% Sb alloy were pasted and cured. The dimensions of the positive and negative plates were of 257 mm X 220 mm X 8.2 mm and 255 mm X 210 mm X 2.5 mm, respectively. The tubular plates had tubes of inner diameter of 8.2 mm with a spine diameter of 3.5 mm. Number of spines per grid was 15. The tubular plates after being filled with oxide were directly taken to the formation tanks. The negative electrodes studied in this paper consist of lead alloy grid pasted with leady oxide and with carbon black (CB) 0.5%. Cells were assembled with a configuration of 1 negative and 2 positive plate per cell. The battery was filled with 1.240 special grade sulphuric acid (H₂SO₄) at 27°C. After initial charging, the charge-discharge capacity cycle tests were carried out using Bitrode life cycle tester Model LCN-1-25-12 with 5 deep (C/10) cycles of discharge up-to the cut-off voltage of 1.8 V per cell as per the test specification of Bureau of Indian Standard, BIS 13369:1992 for stationary lead acid battery with tubular positive plates. These 5 cycles of charge/discharge were done to achieve capacity stabilization.