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Degradation of dyes by UV/O₃/H₂O₂ and electrooxidation techniques

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Abstract

The soil and aquatic environment around the tannery and textile industrial clusters were severely affected over the years. Various technological options are being evaluated to address the treatment of these effluents. The efficacy of cleaner technologies such as advanced oxidation and electro oxidation for the mineralization of four different dyes namely CI Acid black 66, CI Acid brown 16, CI Acid brown 75 and CI Acid brown 85 was studied. The mineralization of dyes is almost complete by advanced oxidation involving UV/O₃/H₂O₂, whereas it is only around 60% by electro oxidation. Conversely, the electrooxidation consumes 10-20 kWh/m³ whereas the photo oxidation requires 2500 kWh/m³. Hence electrooxidation followed by photo oxidation could be economical to treat the effluent solutions containing wide range of organics.

Keywords: electrooxidation, UV/O₃/H₂O₂, azodye, purification, environment, wastewater

INTRODUCTION

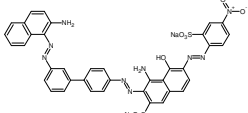
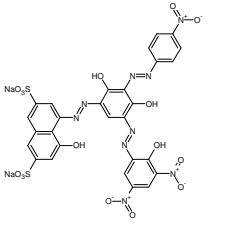
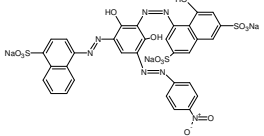
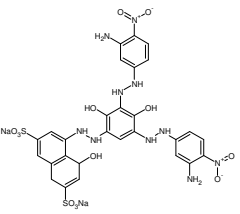
During dyeing and finishing of leather, huge quantity of wastewater containing high concentrations of un-reacted dyes are generated. Continuous exposure to certain dye intermediates was proved to be harmful. For example, the dysfunction of liver (Shimizu *et al.*, 2002) among the workers handling 5-nitro-ortho-toluidine and hepatic malfunction (Singh *et al.*, 2003) in the workers exposed to benzanthrone illustrates the hazardous nature of organic compounds used in dyeing industry. Since the wastewater emanating from dyeing industry contains high concentration of sodium chloride, the growth of microbes and in turn the process efficiency is affected. Further, the microbial metabolites formed during the process are highly stable and resist degradation. Above all, the biological treatment is very slow process. For example, 48 hours of residence time is required to remove 76% color of the coloderm black using white- rot fungi (Chander *et al.*, 2004). In physical processes like coagulation and adsorption, waste is transferred from one phase to another and thus the scope for complete elimination is very limited. Thus there is an urgent need to identify suitable technology for the treatment of textile and tannery wastewaters.

Recently, electrochemical techniques are gaining importance for the treatment of wastewater containing dyes (Muthukumar *et al.*, 2007; Bhaskar Raju *et al.*, 2008; Karuppaiah *et al.*, 2009), tannins (Muruganathan *et al.*, 2005) and hexavalent chromium (Lakshmipathiraj *et al.*, 2008). Combination of electrochemical and ultrasonication was recommended (Rivera *et al.*, 2009) for the decolorization of di-azo dyes where as ozonation was found to be effective to treat the wastewaters containing bio-resistant chloro-nitro-benzenes (Bingzhi *et al.*, 2009). Advanced oxidation process was suggested for the effective mineralization of bisphenol-A (Javier Rivas *et al.*, 2009), m-prolol, naproxen, amoxicillin and phenacetin (Javier Rivas *et al.*, 2009). Due to increasing demand on natural water resources and unabated pollution posed by industrial discharges in to the environment, it has become necessary to implement zero discharge concepts in India. Various technological options are being examined to cope with the environmental regulations. The combination of electrooxidation, advanced oxidation and reverse osmosis are being tried to address the environmental issues of tannery effluents. In the present study, the efficacy of electro

oxidation and advanced oxidation processes in the degradation of certain dye molecules which are extensively used in leather industry is reported.

MATERIALS AND METHODS

The dyes used in the present study were obtained from colortex India limited, Surat [India]. The common name, CI number and the structure of various dyes are given below. The other chemicals used in this study were procured from MERCK.

Name of the dye and CI Number	Chemical Structure
CI Acid black 66 CI Number: 30275 Molecular weight: 861.78	
CI Acid brown 75 CI Number: 34905 Molecular weight: 843.58	
CI Acid brown 16 CI Number: 17610 Molecular weight: 889.69	
CI Acid brown 85 CI Number: 34900 Molecular weight: 790.8	

Electrochemical cell

Electro oxidation experiments were carried out in a batch type reactor whose working volume is 3L. Graphite rods each measuring 2.54 cm diameter and 15 cm length were used as electrodes. Four such rods connected to the common aluminum strip form an anode assembly and equal number of rods with similar assembly was used as cathode. The electrodes were arranged in unipolar mode and minimum distance of 0.5 cm was maintained between the electrodes to minimize the ohmic losses. The effective surface area of anode was estimated to be 249.8 cm². The schematic diagram of electrochemical reactor was shown in Figure 1.

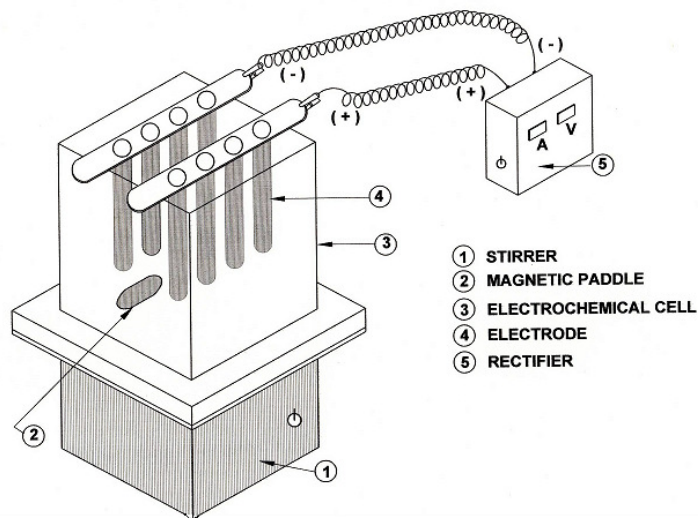


Figure.1 | Schematic diagram of electrochemical reactor.

2.0 L of dye solution with a concentration of 300 ppm prepared in 0.5M NaCl solution was taken for each experiment. The initial pH of the solution was adjusted to 7.0. The electrodes were connected to the respective anode and cathode leads of the rectifier and energized for a required duration at a constant current. The magnetic stirrer was used to keep the solution in agitation during the experiment. The degradation of each dye was studied over a period of 10 hours at a current density of 4.0 mA/cm^2 . The bath temperature was maintained at 30°C . During the experiment, samples were collected at different time intervals and analyzed for TOC.

UV Photo Reactor: The radiation source (HML-LP 88) was a high pressure mercury vapor lamp which emits a monochromatic light at 365 nm. The solution was simultaneously exposed to UV rays and ozone.

Ozone Generator: The corona discharge ozone generator (Model: L10G) supplied by Faraday Instruments, Coimbatore, India was used. Ozone was passed through the silica glass reactor filled with dye solution at a constant flow rate of 1.5 LPM. Known quantity of dye sample was dissolved in double distilled water and its pH was adjusted to 7.0. The solution was transferred in to the photo reactor and the oxidation was carried out in the presence of UV, ozone and H_2O_2 . The peroxide was injected in to the dye solution before ozone was passed at a constant flow rate.

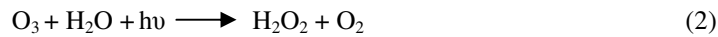
RESULTS AND DISCUSSION

Synthetic wastewaters of all the dyes with an initial concentration of 300 mg.L^{-1} were prepared and their degradation by UV/ O_3 and UV/ O_3 / H_2O_2 processes was followed. The kinetics of degradation is presented in Figures 2–5. It is known that many organic molecules absorb UV energy and degrade to smaller molecules due to direct photolysis or excited and oxidize easily in the presence of chemical oxidants. Also, the decomposition of O_3 and H_2O_2 is accelerated in the presence of UV radiation. The mineralization of CI Acid black 66, CI Acid brown 16, CI Acid brown 75 and CI Acid brown 85 by ozonation or by photolysis alone was found to be very marginal (5–10%). Conversely, the mineralization is very effective when UV and O_3 are applied simultaneously. In the presence of UV/ O_3 , the mineralization of CI Acid black 66 and CI Acid brown 16 is almost complete where as CI Acid brown 75 and CI Acid brown 85 were mineralized

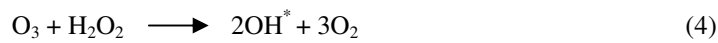
to the extent of 70% and 55% respectively. The mineralization of all the dyes was drastically improved in the presence of UV/O₃/H₂O₂. Since the ozone is highly electrophilic, dyes are expected to react instantaneously with ozone. The color of the solution was disappeared within 10 minutes indicating the change in chromophoric groups of the dye molecules. It is well known that molecular ozone is highly unstable and it can be converted to oxygen molecule and nascent oxygen in the presence of UV radiation.



Also, peroxide and oxygen molecule is produced by photolysis of ozone dissolved in water



The hydroxyl radicals are also generated by self decomposition of H₂O₂ in the presence of UV light and reaction between H₂O₂ and O₃ and also by reaction of oxygen atom with water molecule according to the following reactions.



Earlier researchers reported the generation of variety of intermediates such as O₃^{-*}, O₂^{-*}, HO₂^{-*} that can act as secondary oxidants (Hoigne and Bader, 1976; Staehelin and Hoigne, 1985). The degradation path way of organics by hydroxyl radical is less selective because of very high oxidation potential (2.8V).



The electrophilic reactions occur mainly in aqueous solutions where the concentration of aromatic compounds is very high. The aromatic compounds substituted with electronic donor groups such as OH and NH₂ impart high electronic density on the carbon atoms situated in ortho and para positions. Consequently ozone attacks at these positions. The nucleophilic reactions mainly takes place where there is shortage of electrons, particularly on aromatic ring with electron withdrawing groups such as -COOH and NO₂.

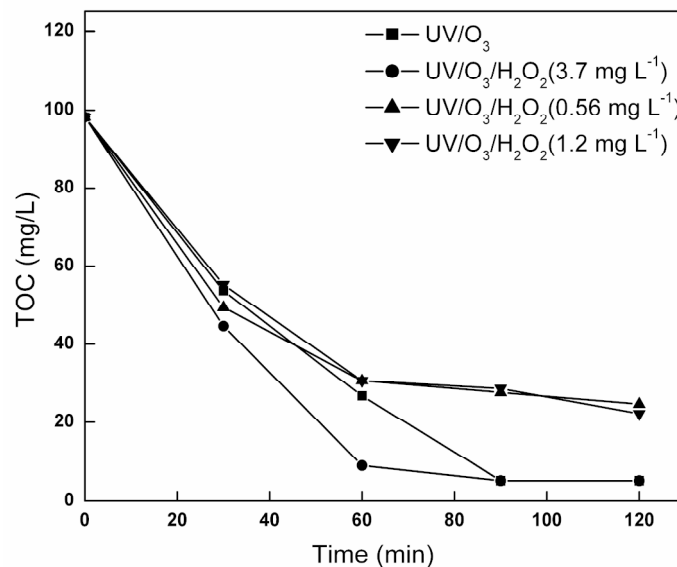


Figure.2 | Mineralization of Cl Acid brown 16 by advanced oxidation. Initial Concentration of dye: 300 ppm, Initial pH: 7.0, Flow rate of O₃:1.5 LPM, Sample Volume: 0.3L.

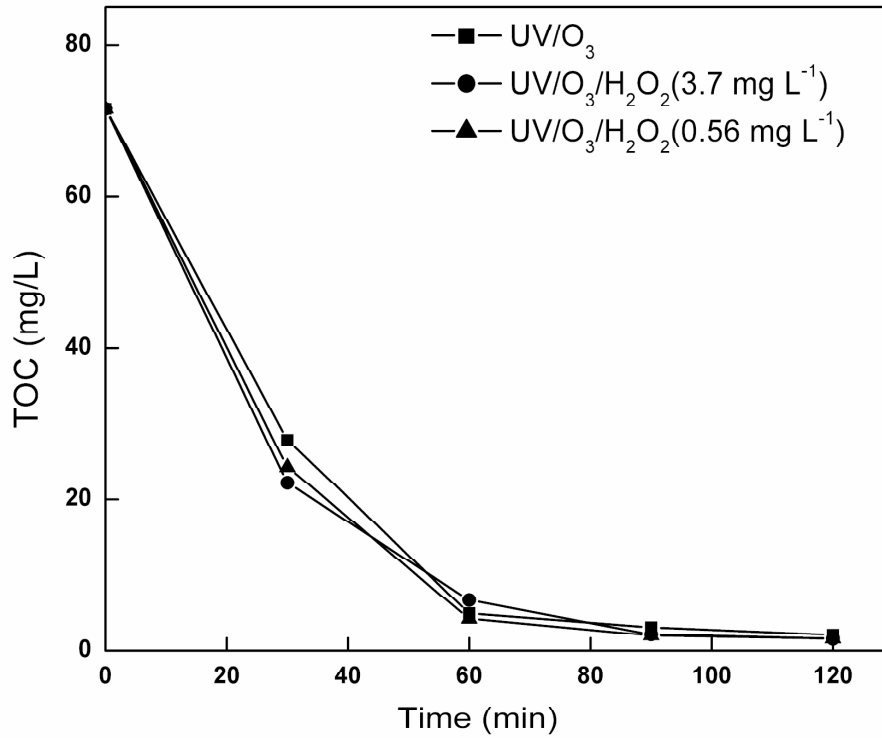


Figure.3 | Mineralization of CI Acid Black 66 by advanced oxidation. Initial Concentration of dye: 300 ppm, Initial pH: 7.0, Flow rate of O₃:1.5 LPM, Sample Volume: 0.3L.

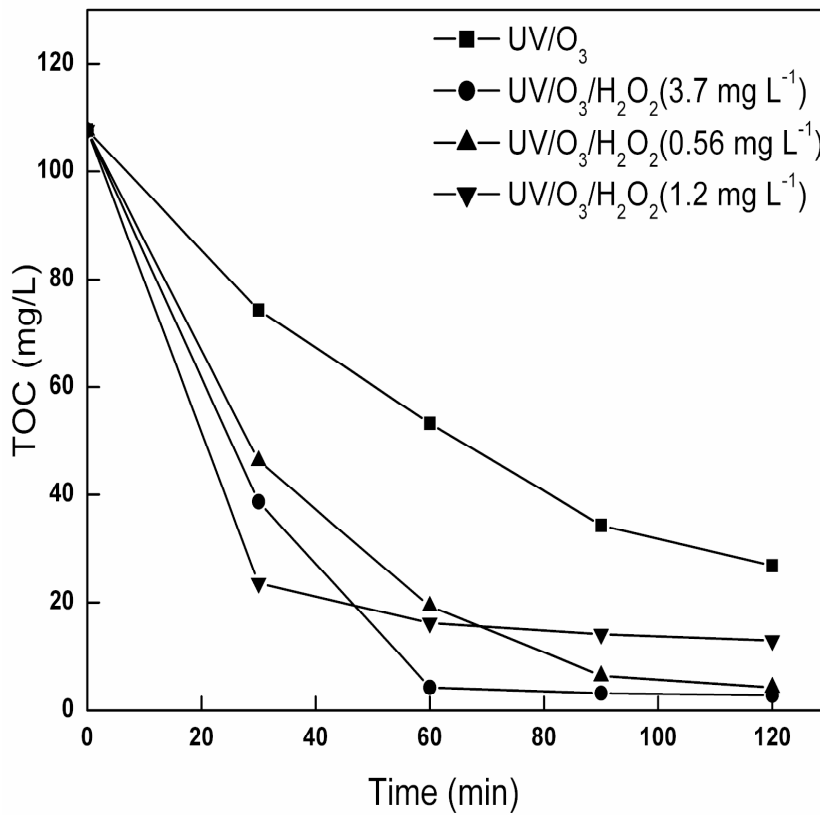


Figure.4 | Mineralization of CI Acid Brown 75 by advanced oxidation. Initial Concentration of dye: 300 ppm, Initial pH: 7.0, Flow rate of O₃:1.5 LPM, Sample Volume: 0.3L.

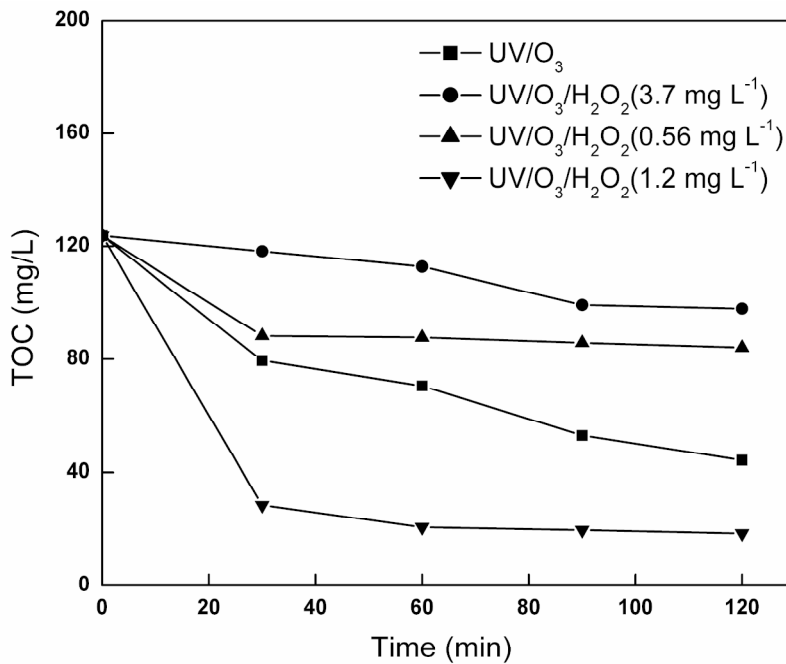
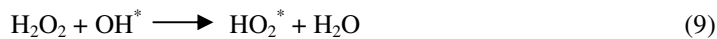


Figure.5 | Mineralization of CI Acid Brown 85 by advanced oxidation. Initial Concentration of dye: 300 ppm, Initial pH: 7.0, Flow rate of O₃:1.5 LPM, Sample Volume: 0.3L.

It could be seen that the rate of mineralization is high at initial stage and gradually decreased at the later stage. The mineralization efficiency was increased by the addition of H₂O₂. However the dosage of H₂O₂ was found to vary with the nature of molecule. For example 3.7 ppm of H₂O₂ was required to achieve near complete mineralization of CI Acid brown 16 and CI Acid brown 75 where as 1.2 ppm of H₂O₂ was found to be enough in the case of CI Acid brown 85. It was observed that the mineralization is adversely affected in the presence of excess H₂O₂. The excess hydrogen peroxide is expected to scavenge OH^{*} and consequently impede the decomposition.



The oxidation of carbon to CO₂ is relatively easy when compared to de-aromatization of the organic molecules. It was observed that the pH of the aqueous solution becomes acidic during the oxidation process. The decrease in TOC and pH to acidic region confirms the mineralization of dye molecules to CO₂ and H₂O via low molecular weight carboxylic acids.

Removal of Acid brown and Acid black dyes by electro oxidation using graphite as electrode material was studied at a constant current density of 4.0 mA/cm² and the results were presented in Figure 6. The current efficiency was measured using the following formula (Comminellis and Pulgarin, 1991).

$$\text{CE} = \text{VF} (\text{TOC}_0 - \text{TOC}_t) / 8It \quad (10)$$

Where TOC₀ is initial total organic carbon, TOC_t is total organic carbon at time t, I is applied current, F is Faraday's constant and V is the volume of the effluent. It is apparent that CI Acid brown 16 was removed to the extent of 80% where as the removal of other dyes by electrooxidation is hardly 60% or less. The current efficiency in the initial stages of oxidation was observed to be 30 % in the case of CI Acid brown 16 and CI Acid brown 75. It was gradually decreased to below 5% after 10 hours of electrooxidation. The low mineralization of CI Acid black 66 and CI Acid brown 85 may be attributed to the formation of refractory intermediates. The concentration of oxidizing agents generated during the electrolysis may not be sufficient to degrade these highly stable intermediates.

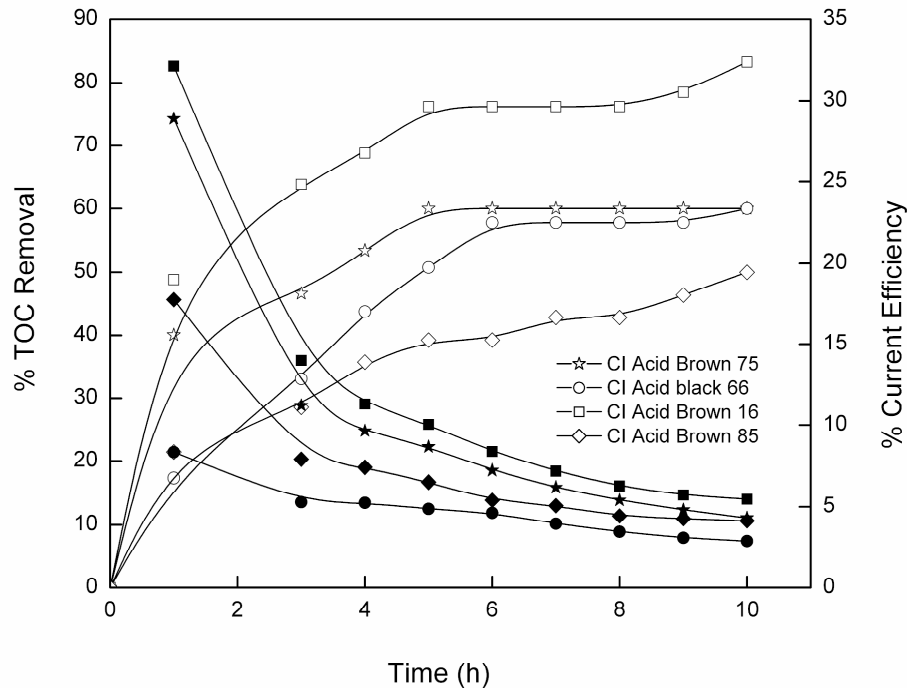
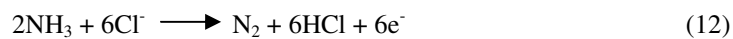
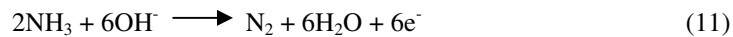
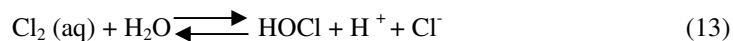


Figure.6 | Mineralization of dyes by electro oxidation and current efficiency. Current density: 4.0 mA/cm², Initial Concentration of dye: 300 ppm, Initial pH: 7.0, Sample Volume: 2.0L (Closed symbols for current efficiency and Open symbols for TOC removal).

During oxidation, N-atom is converted to NH₄⁺/NH₃, nitrate and nitrite ions or eventually into N₂ gas. Calza *et al.*, (2005) observed that the formation of NH₄⁺ predominate over NO₃⁻ if the molecule contains extractable hydrogen. On the other hand, it is converted to nitrate ion when there is no extractable hydrogen. As long as the carbon holds extractable hydrogen, the degradation is expected to proceed mainly through OH attack on carbon atom resulting in the release of NH₄⁺ ion. The radical attack on the nitrogen atom and subsequent detachment of nitrate ions are favored if there is no extractable hydrogen. The oxidation of ammonia to molecular nitrogen is favorable in alkaline medium (Mogyorody, 2006) and by electro-chlorination path.



In the typical scenario of electrolytic oxidation, various oxidants such as nascent oxygen, ozone, hydrogen peroxide, free chlorine and free radicals such as ClO*, Cl*, and OH* are generated. The oxidation of pollutants may also occur by oxidation of chloride involving active chlorine (HOCl and OCl).



In general, the oxidation of organics depends mostly on active chlorine generated during electrolysis. Serikawa *et al.* (2000) observed strong catalytic effect in the conversion of organic pollutants to innocuous CO₂ and H₂O in the presence of chloride ion. But, the formation of chlorinated organic compounds is high in the case of electrooxidation. Since it is not possible to achieve complete mineralization by electrooxidation, the resultant wastewater will be more hazardous due to chlorinated intermediate compounds. Conversely, the advanced oxidation involving ozone is very attractive and environment friendly. Ozone has a proven ability to convert bio-refractory organic materials to biodegradable materials.

The kinetics of degradation was found to fit into first order rate equation. Hence power consumption for advanced oxidation (batch operation) was estimated using the following equation (James *et al.*, 2001).

$$E_{EO} = [P * t * 1000] / V * \log (C_i - C_f) \quad (14)$$

Where E_{EO} is electric energy per order required to degrade a contaminant by one order of magnitude in a unit volume (1.0 m^3) of a contaminated water expressed in $\text{kWh}/\text{m}^3/\text{order}$, P is rated power in kW, V is the volume of water treated in L, t is time in hours, C_i and C_f are initial and final concentration of contaminant expressed in mol.L^{-1} . The calculated E_{EO} values were found to vary from 1532–2668 $\text{kWh}/\text{m}^3/\text{Order}$. In the above calculations, oxidation time was taken as 1.0 hour as there is no appreciable change in the degradation beyond 1.0 hour. In the case of electrooxidation, the estimated power consumption was found to vary from 10–20 kWh / m^3 depending on the complexity of the dye molecule. Since the mineralization beyond five hours of electrooxidation is very marginal, the duration of electrooxidation was taken as 5 hours while calculating the power consumption. It may be noted that the power consumption for electrooxidation is less compared to that of UV/O_3 process. Thus the electrooxidation is very attractive in terms of power consumption.

CONCLUSIONS

The efficacy of photo oxidation and electrooxidation techniques for the mineralization of four different dyes namely CI Acid black 66, CI Acid brown 16, CI Acid brown 75 and CI Acid brown 85 was studied. The mineralization of dyes is almost complete by photo oxidation where as it is hardly 60% by electrooxidation. Conversely, the electrooxidation process consumes less power compared to UV/O_3 process. The advanced oxidation is very effective in converting bio-refractory organic materials to biodegradable and environment friendly compounds. Hence electro oxidation followed by $\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$ process could be economical to treat the effluent solutions containing wide range of organics.

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REFERENCES

- Bhaskar Raju, G., Thalamadai Karuppiyah, M., Latha, S. S., Parvathy, S. & Prabhakar, S. 2008 Treatment of wastewater from synthetic textile industry by electrocoagulation-electrooxidation. *Chem. Eng. J.* **144**, 51–58.
- Bingzhi Li., Xiangyang Xu & Liang Zhu 2009 Ozonation of chloronitrobenzenes in aqueous solution: kinetics and mechanism. *J. Chem. Technol. Biotechnol.* **84**, 167–175.
- Calza, P., Pelizzetti, E. & Minero, C. 2005 The fate of organic nitrogen in photocatalysis: an over view. *J. Appl. Electrochem.* **35**, 665–673.
- Chander, M., Arora, D. S. & Bath, H. K. 2004 Biodecoloration of some industrial dyes by white rot fungi. *J. Ind. Microbiol. Biotechnol.* **31**, 94–97.
- Comninellis, C. H. & Pulgarin, C. 1991 Anodic oxidation of Phenol for waste water treatment. *J. Appl. Electrochem.* **21**, 703–708.
- Hoigne, J. & Bader, H. 1976 The role of hydroxyl radical reactions in ozonation process in aqueous solutions. *Water Res.* **10**, 377–386.

- James, R. Bolton., Keith, G. Bircher., William Tumas & Chadwick, A. Tolman. 2001 Figures of merit for the technical development and application of advanced oxidation technologies for both electric and solar driven systems. *Pure Appl. Chem.* **73** (4), 627–637.
- Javier Rivas, F., Angel Encinas., Benito Acedo. & Fernando, J. Beltran. 2009 Mineralization of bisphenol A by advanced oxidation processes. *J. Chem. Technol. Biotechnol.* **84**, 589–594.
- Javier Rivas, F., Francisco J. Real., Juan L Acero & Gloria Roldan. 2009 Removal of selected pharmaceuticals in waters by photochemical processes. *J. Chem. Technol. Biotechnol.* **84**, 1186–1195.
- Lakshminathiraj, P., Bhaskar Raju, G., Raviatul Basariya, M., Parvathy, S. & Prabhakar, S. 2008 Removal of Cr (VI) by electrochemical reduction. *Sep. Purif. Technol.* **60**, 96–102.
- Mogyorody, F. 2006 Reaction pathways in the electrochemical degradation of thiocarbamate herbicides in NaCl solutions. *J. Appl. Electrochem.* **36**, 635–642.
- Murugananthan, M., Bhaskar Raju, G. & Prabhakar, S. 2005 Removal of tannins and polyhydroxy phenols by electrochemical techniques. *J. Chem. Technol. Biotechnol.* **80**, 1188–1197.
- Muthukumar, M., Thalamadai Karuppiyah, M. & Bhaskar Raju, G. 2007 Electrochemical removal of CI Acid orange10 from aqueous solutions. *Sep. Purif. Technol.* **55**, 198–205.
- Rivera, M., Pazos, M. & Sanroman, M. A. 2009 Improvement of dye electrochemical treatment by combination with ultrasound technique. *J. Chem. Technol. Biotechnol.* **84**, 1118–1124.
- Serikawa, R. M., Isaka, M., Su, Q., Usui, T., Nishimura, T., Sato, H. & Hamada, S. 2000 Wet electrolytic oxidation of organic pollutants in wastewater treatment. *J. Appl. Electrochem.* **30**, 875–883.
- Shimizu, H., Kumada, T., Nakano, S., Kiriyaama, S., Sone, Y. & Honda, T. 2002 Liver dysfunction among workers handling 5-nitro-o-toluidine. *Gut.* **50**, 266–270.
- Singh, R. P., Khanna, R., Kaw, J. L., Kanna, S. K. & Das, M. 2003 Comparative effect of benzantrone and 3-bromobenzanthrone on hepatic xenobiotic metabolism and antioxidative defense system in guinea pigs. *Arch. Toxicol.* **77**, 94–99.
- Staehelin, J. & Hoigne, J. 1985 Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environ. Sci. Technol.* **19**, 1206–1213.
- Thalamadai Karuppiyah, M. & Bhaskar Raju, G. 2009 Anodic degradation of CI Reactive blue 221 using graphite and IrO₂/TaO₂/RuO₂ coated titanium electrodes. *Ind. Eng.Chem.Res.* **48**, 2149–2156.