

Degradation of reactive dyes using supporting electrolytes by electrochemical oxidation method

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ABSTRACT

Treatment of real reactive dye effluent (RRDE) containing Reactive Yellow-17 and Reactive Blue 4 has been studied by electro oxidation (EO) using Ti/RuO₂ as anode and stainless steel (SS) as cathode. The experimental study focused on the effect of applied current density (2, 5 and 7 A/dm²) on decolorization and removal of COD. Results have indicated that the treatment efficiency was enhanced appreciably by increasing the applied current density with respect to time. Different concentration of NaCl and Na₂SO₄ were used as supporting electrolytes. It was observed that increase in the concentration of NaCl increases the degradation of dyes than Na₂SO₄. It was noted that instantaneous current efficiency was good throughout the experiment. The maximum efficiencies of COD reduction and color removal were found to be 82% and 99% respectively when NaCl used as supporting electrolyte. FTIR and UV spectral studies were also carried out. Energy consumption for this process was determined and found to be good in NaCl.

Keywords: *e*Effluent; removal efficiency; NaCl; Electrochemical oxidation, Ti/RuO₂ anode.

I. INTRODUCTION

Textile industries generate effluent at an average of 100–170 l kg⁻¹ of cloth processed, which is characterized by strong color, high COD with wide variation in pH [1, 2]. The treatment of wastewater generated by the textile preparation, dyeing and finishing industry remains a significant environmental pollution problem due to its huge quantity, variable nature and biologically-difficult-to-degrade chemical composition. Physicochemical processes such as membrane filtration, coagulation-flocculation, ozonation at high pH, Fenton's reagent and sequential anaerobic + aerobic treatment, have been employed for the treatment of reactive dye bath effluent, however with limited success and/or at unaffordable costs [3]

The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. In addition to the operating parameters, the rate of pollutant degradation depends of the anode material. When electrochemical reactors operate at high cell potential, the anodic process occurs in the potential region of water discharge, hydroxyl radicals are generated [4]. On the other hand, if chloride is present in the electrolyte, an indirect oxidation via active chlorine can be operative [5, 6]. Naumczyk et al. [7] have demonstrated several anode materials, such as graphite and noble metal anodes successfully for the mediated oxidation of organic pollutants.

Due to dwindling supply and increasing demand of water in the textile industries, a better alternative is to attempt to further improve the water quality of treated wastewater for reuse standard. Meanwhile, high treatment costs of these methods have stimulated, in recent years, the search for more cost effective treatment methods and reuse standards. In the present study, an attempt has been made to study the effect of NaCl and Na₂SO₄ on the degradation of real reactive dye effluent by electrooxidation process.

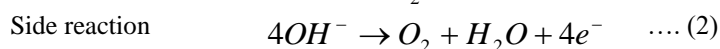
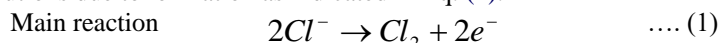
Theory

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 is depending on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, p^H and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are

added to the wastewater for better conductivity and generation of hypochlorite ions [8]. The reactions of anodic oxidation of chloride ions to form chlorine are given as below:

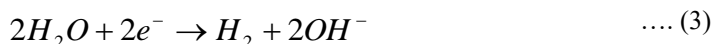
A. Anode reactions

Since dye molecules of the effluent are electrochemically inactive, the reaction occurs at the anodes is chloride ion oxidation Eq.(1) with the liberation of Cl_2 , which is a robust oxidizing agent. As regards to the reactions in the bulk, gaseous Cl_2 dissolves in the aqueous solutions due to ionization as indicated in Eq. (2).



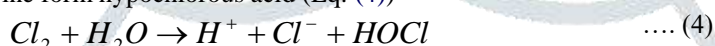
Cathode reaction

The counter reaction Eq.(3) at the cathode would be the reaction of the only water when no other reducible species are present.



Reaction in bulk solution

The liberated chlorine form hypochlorous acid (Eq. (4))

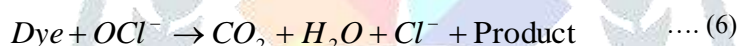


and further dissociated to give hypochlorite ion (Eq. (5)).



The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation. The direct EO rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density.

In the same way indirect EO mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment [9–11]. The role of hypochlorite in electrochemical treatment of dye effluent via chlorine generation (Eq.(6)) is



EXPERIMENTAL METHODS

MATERIALS AND METHODS

In this chapter the instruments, chemicals, equipments used and methodology of the experiment is explained in detail

All the reagents used were of Analytical grade. RRDE containing Reactive Yellow-17 and Reactive Blue 4 was collected from a textile industry located in Tirupur, Tamilnadu, India. Molecular structure of the dyes is given in Table 1.

Table 1 Molecular structure of RRDE.

S. No.	Name of dye	Molecular structure
1	Reactive Yellow-17	
2	Reactive Blue-4	

Electrochemical cell for EO

The electrolysis cell (Fig.1) used in EO process consists of a glass beaker of 600 ml capacity closed with a PVC lid having provision to fit a cathode and an anode. Commercially available Ti/RuO₂ and stainless steel were used as anode and cathode respectively. It was connected to 10A and 15V DC regulated power supply. A magnetic stirrer with Teflon coated magnetic pellet was used for stirring the solution.

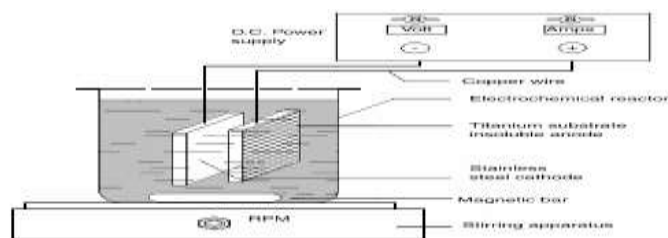


Fig.1 Experimental set up for electro oxidation process

Experimental procedure

Five hundred millilitres of RRDE containing (Reactive Yellow-17 and Reactive Blue 4) were taken in a glass beaker containing anode and cathode. In EO process the effluent was treated at different current densities from 2, 5 & 7 A/dm². Different concentration of NaCl and Na₂SO₄ from 6, 9 & 12 g were added individually to the effluent to study their effects as supporting electrolyte on the degradation of the dye.

Samples were collected at regular intervals of time for estimation of COD [12] and colour. Instantaneous current efficiency was calculated. Spectral studies were carried out using FTIR (NEXUS-672) and UV-visible spectrophotometer (Vation Cary 5000).

DETERMINATION OF COD

DEFINITION

Chemical oxygen demand is the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant.

The test was based on treating the waste with a known amount of dichromate, digesting at an elevated temperature to oxidize the organic matter and titrating the unconsumed dichromate. The oxygen equivalent of dichromate destroyed is reported as the COD

APPARATUS

Reflux apparatus, consisting of a 500 ml flat-bottomed flask with ground glass joint and a condenser.

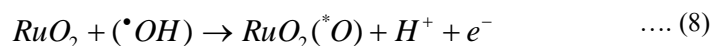
RESULTS AND DISCUSSION

It is known that the organic compounds are completely oxidized to carbon dioxide. The electrode materials with high electro catalytic the complex organic compounds to its simple fragments than can be easily oxidized to carbon dioxide and water so as to split activity the organic compounds are degraded to CO₂ and H₂O.

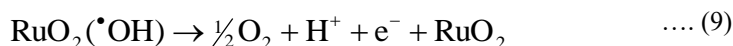
In case of EO, (•OH) generated electrochemically by splitting of H₂O, gets discharged at the anode resulting in radical (•OH) as shown in Eq.(7)



Later, the (•OH) radical, gets adsorbed on to the RuO₂ forming a complex of the type (RuO₂(•OH)) which in turn gets converted to (RuO₂(•O)) of higher oxidation state as shown in Eq. (8).



Thus both physisorbed (RuO₂(•OH)) active oxygen and chemisorbed (RuO₂(•O)) active oxygen release di-atomic-oxygen. It can be considered that at the anode surface two states of “active oxygen” can be presented in Eqs. (9) and (10):



It may be speculated in this case that physisorbed active oxygen predominantly oxidized the organics and chemisorbed oxygen $\text{RuO}_2(\cdot\text{O})$ decides the fate of the intermediate product.

Effect of supporting electrolytes

It is well known that supporting electrolyte has an important effect on the electrochemical process. In this work RRDE wastewater samples was treated using NaCl or Na_2SO_4 as supporting electrolyte to clarify the influence of the nature of the electrolyte on the degradation process. The effect of NaCl dosage on the percentage of COD reduction and colour removal for RRDE are presented in Fig. 2, 3 and Fig. 4 respectively. It is obvious that NaCl causes quicker and more complete decolorisation than Na_2SO_4 for the dye. Decolorisation shows that the dyes are fully degraded, giving smaller and colorless organic or inorganic products. It is well known that the electrolysis of NaCl results in some very strong oxidants, such as free chlorine (Cl_2) and hypochlorite anions (ClO^-) [13, 14, 15,16]. On the contrary, Na_2SO_4 electrolysis drives mainly to the formation of SO_2 , which is just a moderate reductant. The whole decoloration proceeds mainly via direct redox reactions on the electrodes, enhanced by indirect redox reactions by the produced oxidants or reductants. The stronger the oxidants or reductants are the better enhancement to achieve. Concerning the current values during the decoloration process, NaCl showed a smaller increase in performance and at the same time Na_2SO_4 also degrade the effluent to some extent. This means that treatment under Na_2SO_4 , produces more ionic products, increasing the ionic strength of the wastewater. Significant quantities of HOSO_3^- anions degrade the dye molecules. These anions together with other ionic degradation products cause the increase of the current. In the case of NaCl, the increase is smaller probably because many of the ionic products are rapidly further degraded in non-ionic final products (N_2 , CO_2 , SO_2/SO_3). These results indicate that a significant amount of dye can be removed. It was also observed that removal efficiencies of both COD and colour increases with increase of NaCl concentration. COD reductions of 78% and 96% of colour removal were obtained at 12g of Na_2SO_4 at 7 A/dm². But it has been improved in NaCl that 82% of COD reduction and 99% of colour removal were obtained at same concentration and current density. It shows that the performance of NaCl is better than Na_2SO_4 . In general, dye baths are normally containing NaCl is the main salt used for the optimal fixation of the dyes on the textile substrate. Hence smaller quantity of NaCl is required to carry out the electrochemical treatment.

Effect of current density

Current density was one of the most important parameters that affected the colour and COD removal. The current density was changed within technically reasonable limits of 2–7 Adm⁻². Figures 2, 3 and 4 showed the effect of current density on reduction of COD in different concentration of NaCl. Similarly figures 5, 6 and 7 showed the effect of current density on reduction of COD in different concentration of Na_2SO_4 . It was found from these figures that increase in current density could result in faster removal of COD. In low concentrations of NaCl and Na_2SO_4 (6 and 9g), the percentage removal of COD was less. At current densities of 2 and 5Adm⁻², the COD removal was also low in all the cases. Only at higher current densities and higher in concentration of supporting electrolytes, it was able to enhance the removal of COD. Results also showed higher COD reduction occurred at higher charge input and electrolysis time. The maximum COD removal of 82% was obtained at the current density of 7Adm⁻² in 12g NaCl and 78% at 7Adm⁻² in Na_2SO_4 respectively. Further increase in the current density leads to insignificant increase in the COD removal. The electrolysis time was reduced at higher densities with respect to removal of COD. Therefore, an optimum point must be carefully determined giving a faster removal rate. It was suggested that the removal of COD resulted from the carbonization of the dye. These enhancement effects were attributed to both the increasing current, which could cause a higher production of oxidizing $\cdot\text{OH}$ radicals from water oxidation (17), and the higher concentration of organic pollutant in the dye, which might enhance the probability of collision with hydroxyl radicals (18). This trend could be mainly associated with the parasitic reactions, such as electrolysis of water, which might compete with the electro oxidation of the contaminant (19). The COD removal was higher in NaCl than Na_2SO_4 was due to the generation of large amount of OCl^- .

Instantaneous current efficiency (ICE)

Taking into account of the instantaneous current efficiency (ICE) of the electrolysis, it could be calculated using the following relation Eq. (11) [2]:

$$\text{ICE} = \frac{\text{COD}_t - \text{COD}_{t+\Delta t}}{8I\Delta t} FV \quad \dots (11)$$

where COD_t and $\text{COD}_{t+\Delta t}$ are the chemical oxygen demands at times t and $t + \Delta t$ (in g $\text{O}_2 \text{ L}^{-1}$), respectively, and I is the current (A), F the Faraday constant (96,487Cmol⁻¹) and V is the volume of electrolyte (L). Fig.8 showed the variation of ICE as a function of time at 7A/dm². It was observed from the figure that ICE was better in NaCl than Na_2SO_4 .

Color removal (%)

The oxidized products and the reduction in dye concentration were measured by using a UV–Visible Spectrophotometer, the colour removal was calculated by the following Eq. (12):

$$Color\ removal\ (\%) = \frac{Abs_i - Abs_f}{Abs_i} \times 100 \quad \dots (12)$$

where *Abs* is the average of absorbance values as it is maximum absorbency visible wavelength. *Abs_i* the value before electrolysis, *Abs_f* the value after electrolysis. Figures 9 and 10 showed percentage of colour removal with respect to time. Current density was fixed at 7A/dm². Increase in concentration of supporting electrolytes, the increased the percentage of colour removal. Maximum removal of colour was obtained in 12g of NaCl and Na₂SO₄, 99.4% and 96.1% respectively.

The energy consumption (EC) for the removal of 1 kg of COD (measured in kWh kg⁻¹ COD) was obtained by the use of the following Eq.(13) [40]:

$$EC = \frac{tUIV}{\Delta COD} \times 10^3 \quad \dots (13)$$

where *t* is the electrolysis time (h), *U* the average electrolysis cell voltage (V), *I* the applied electrolysis current (A), *V* the simulated-wastewater volume (L), and Δ COD the difference in COD (mg L⁻¹). Figures 11 and 12 showed the energy consumption with respect to time in NaCl and Na₂SO₄ respectively. It was found that energy consumption was increased with increasing applied current density. When current density increases from 2 to 7A/dm², the electrolysis time was reduced drastically from 4 to 2 hours to degrade the dye in NaCl. The 82% COD and 99% colour removal were achieved within 2 hours at 7A/dm². From the results, it is understood that, the process involving in NaCl, degrade the dyes better than Na₂SO₄ at all current densities with less energy consumption.

FTIR analysis of the sample

The sample was given for FTIR spectrum analysis before and after treatment. Fig. 13 shows the FTIR spectra of untreated and treated by electro-oxidation. Major peaks were obtained for untreated sample at 3363.34, 3282.40, 1637.20 and 663.38 cm⁻¹. The absorbance of peak at 3363.34 cm⁻¹ was due to the stretching of N-H. The appearance of peak at 1636.47 cm⁻¹ indicates the presence of C=C conjugated diene groups. The broader peaks may be due to hydrogen bonding and also vibration of hydrogen in bound with OH groups of carboxylic acid. It shows that the sample contain high content of water molecule and considerable amount of alkanes (C-H). After decolourization showed absence of peak at 1600 cm⁻¹ indicates breakdown of amide N-H functions. Intensity of peak at 663.38 cm⁻¹ has been reduced due to the loss of aromatic or benzene ring.

The absorbance of peaks at 2107.99 cm⁻¹ was due to the vibration of C=O and intense absorbance of the bands at 1620-1640 and 1510-1540 cm⁻¹ was also observed, indicating enrichment in amide and aromatic. This is due to the functional group of aromatic carbons. The absorbance of peaks at 709.23 cm⁻¹ (out-of plane bending modes of aromatic C-H bonds) was found to be due to the vibration of aromatic compounds and benzene ring. Fig 4 (b) shows the FTIR spectra of treated sample by Electro-Oxidation. After the EO method, decolourization showed absence of peak at 1636.47 cm⁻¹ indicates breakdown of aromatic rings.

UV-Vis spectra analysis

The samples were given for UV-Vis spectra analysis before and after EO treatment and are shown in figure 14. The intensity of peaks was reduced by EO (Fig. (b)) and followed by BT method (Fig. (c)). The dye UV spectrum before treatment exhibited absorption bands at 545 nm. The characteristic band at 485 to 570 nm could be assigned to the n-π* transition of -N=N- group [38]. The weak band below 350 nm could be attributed to the π-π* transition related to the aromatic ring attached to the -N=N- group in the dye molecule. It is apparent that the intensity of characteristic band (545 nm) of dye solution was found to diminish gradually during the experiment and disappeared totally after EO and BT. The disappearance of the bands indicates the effective destruction of the azo. The intensity of the absorption spectra was reduced further by BT (Fig.5(b)) after EO(Fig.5(c)). It could be concluded that the dye molecule undergoes degradation in the presence of microorganisms. This clearly indicates that the intensity of the absorption spectra was reduced drastically after the combined effect of both the treatments.

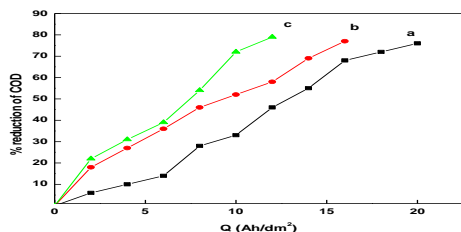


Fig.2 Percentage of COD as a function of the specific electrical charge passed in RRDE with 6g NaCl (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

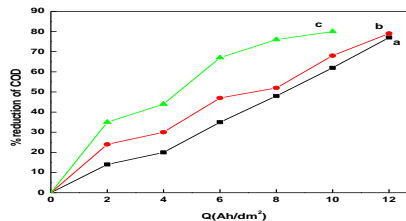


Fig.3 Percentage of COD as a function of the specific electrical charge passed in RRDE with 9g NaCl (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

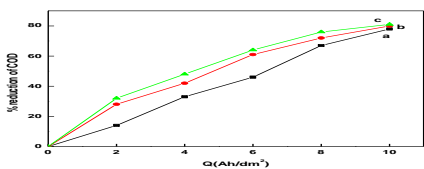


Fig.4 Percentage of COD as a function of the specific electrical charge passed in RRDE with 12g NaCl (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

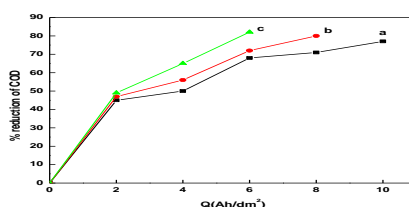


Fig.5 Percentage of COD as a function of the specific electrical charge passed in RRDE with 6g Na₂SO₄ (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

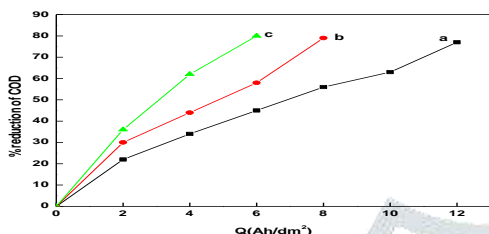


Fig.6 Percentage of COD as a function of the specific electrical charge passed in RRDE with 9g Na₂SO₄ (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

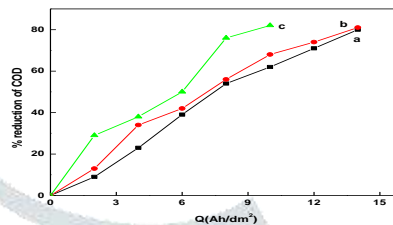


Fig.7 Percentage of COD as a function of the specific electrical charge passed in RRDE with 12g Na₂SO₄ (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

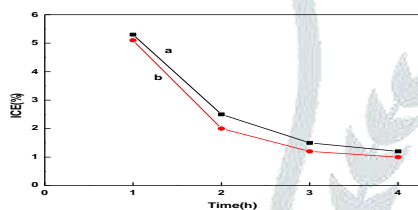


Fig.8 Variation of ICE as a function of time at 7A/dm² (a) 12g NaCl (b) 12g Na₂SO₄

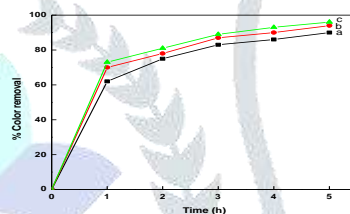


Fig.9 Percentage removal of colour as a function of time at 7 A/dm² (a) 6g Na₂SO₄ (b) 9g Na₂SO₄ (c) 12g Na₂SO₄

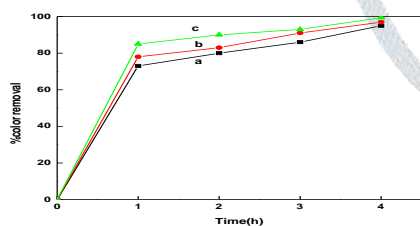


Fig.10 Percentage removal of colour as a function of time at 7 A/dm² (a) 6g NaCl (b) 9g NaCl (c) 12g NaCl

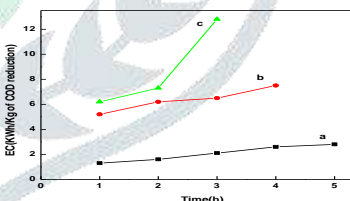


Fig.11 Energy consumption as a function of time in 12g NaCl at different current densities (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

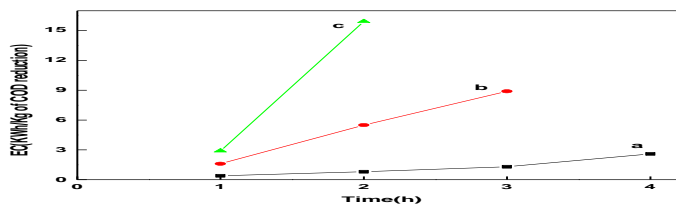


Fig.12 Energy consumption as a function of time in 12g NaSO₄ at different current densities (a) 2 A/dm² (b) 5 A/dm² (c) 7 A/dm²

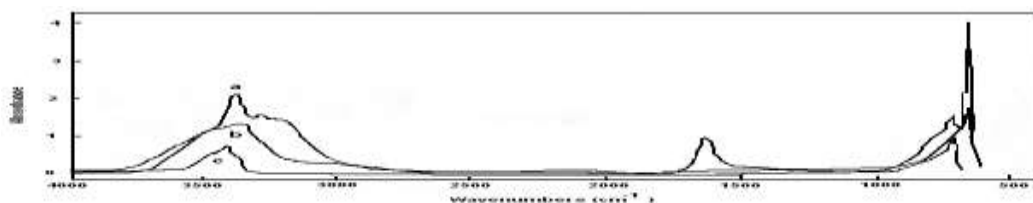


Fig.13 FTIR spectra of treated and untreated RRDE during electrooxidation
 (a) untreated effluent (b) Treated with 12g Na₂SO₄ at 12 A/dm²
 (c) Treated with 12g NaCl at 12 A/dm²

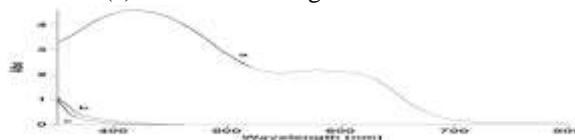


Fig.14 UV-visible spectra of treated and untreated RRDE during electrooxidation.
 (a) Untreated effluent
 (b) Treated with 12g Na₂SO₄ at 12 A/dm²
 (c) Treated with 12g NaCl at 12 A/dm²

CONCLUSION

In the present study, EO using Ti/RuO₂ and stainless steel (SS) electrodes was experimentally investigated to remove color completely and COD at least 82% from RRDE. The following conclusions could be drawn from the experimental study; NaCl acts as a best supporting electrolyte than Na₂SO₄ for the degradation of reactive dye under study.

In terms of color removal efficiency, by the application of EO almost 99% decolorization could be achieved. The best performance was achieved at a current density of 7 A/dm² corresponding to an electrical energy consumption of 7 kWh/m³. It took 180 min to make the RRDE as colorless at 7 A/dm²; where as in other current densities, the time was more than 200 min.

Increase in the current density increases the power consumption. Hence, the optimization of energy consumption of the treatment methods studied, the maximum COD removal 82% (7 A/dm²) with minimum energy consumption (19.29 kWh/kg of COD) could be achieved at EO.

This method is indented to treat the textile wastewater to a level that meets the discharge standards required by the government. The quality of treated wastewater was observed to be consistently excellent.

REFERENCE

1. S. Rajagopalan, *Pollution Management in Industries*, vol. 7, Environmental Publication, Karad, India, 1989, pp. 31–33.
2. Panchiao, *Internal Technical Report for Eastern Textile Company*, Taiwan, 1994, p. 15.
3. Y.M. Slokar, A.M. leMarechal, *Methods of decoloration of textile wastewaters*, *Dyes Pigments* 37 (1998) 335–356.
4. O. Simond, V. Schaller, Ch. Comminellis, *Theoretical model for the anodic oxidation of organics on metal electrodes*, *Electrochim. Acta* 42 (34) (1997) 2009–2012.
5. R. Kotz, S. Stucki, B. Carcer, *Electrochemical wastewater treatment using high over voltage anodes. Part I. Physical and electrochemical properties of SnO₂ anodes*, *J. Appl. Electrochem.* 21 (1991) 14–20.
6. L. Szpyrkowicz, N.K. Santhosh, R.N. Neti, S. Satyanarayan, *Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater*, *Water Res.* 39 (2005) 1601–1613.
7. J. Naumczyk, L. Szpyrkowicz, M. De Faveri, F. Zilio Grandi, *Electrochemical treatment of tannery wastewater containing high strength pollutants*, *Trans. I Chem. E* 74 (1996) 58–59.
8. K. Rajeshwar, J.G. Ibanez, *Environmental Electrochemistry*, Academic Press, Inc., 1997.
9. Buso, L. Balbo, M. Giomo, G. Farmia, G. Sandona, *Electrochemical removal of tannins from aqueous solutions*, *Ind. Eng. Chem. Res.* 39 (2000) 494–499.
10. N. Mohan, *Studies on electrochemical oxidation of acid dye effluent*, Ph.D. Thesis, Anna University, Chennai, India, 2000.
11. D. Rajkumar, K. Palanivelu, N. Mohan, *Electrochemical degradation of resorcinol using mixed metal oxide coated titanium for waste water treatment-A kinetic study*, *Indian J. Chem. Technol.* 10 (2003) 396–401.
12. American Public Health Association (APHA), *Standard Methods for Examinations of Water and Wastewater*, 18th ed., American Water Works Association and Water Environment Federation, 1992.

13. A.G. Vlyssides, M. Loisdou, P.K. Karlis, A.A. Zorbas, D. Papaioannou, *Electrochemical treatment of a textile dye wastewater using Pt/Ti electrode*, J.Hazard. Mater. B70 (1999) 41–52.
14. D. Pletcher, F.C. Walsh, *Industrial Electrochemistry*, 2nd ed., Chapman and Hall, New York, 1990, pp. 353–357.
15. S.I. Agadzhanian, R.G. Romanova, G.V. Korshin, P.A. Kirpichnikov, *Physicochemical properties of sodium chloride solutions after electrochemical treatment in a flow electrolyzer*, Russ. J. Appl. Chem. 69 (3) (1996) 380–384.
16. E.A. Ananeva, G.L. Vidovich, M.D. Krotova, G.A. Bogdanovskii, *The study of a photochemical and electrochemical treatment of aqueous solutions of azo dyes*, Russ. J. Electrochem. 32 (8) (1996) 936–938.
17. O.J. Murphy., Hitchens, G.D., Kaba, L., Verotsko, C., 1992. *Direct electrochemical oxidation of organics for wastewater treatment*. Water Res. 26, 443–451.
18. C. Galindo, Jacques, P., Kalt, A., 2001. *Photochemical and photocatalytic degradation of an indigoid dye: a case study of acid blue 74 (AB74)*. J. Photochem. Photobiol. A: Chem.
19. D.W Kirk, Shrifian, H., Foulkes, F.R., 1985. *Anodic oxidation of aniline for waste water treatment*. J. Appl. Electrochem. 15, 285–292.

