

Degradation of C.I. Reactive Dyes (Yellow 17 and Blue 4) by Electrooxidation

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Abstract

Dyes are extensively used in textile industries which are responsible for different environmental problems. Conventional processes for effluent treatment are inefficient for the remediation of wastewaters containing toxic and bio recalcitrant organic pollutants. A large number of advanced oxidation processes (AOP's) have been successfully applied to degrade pollutants present in wastewaters. This paper examines the use of electro oxidation (EO) process for the recalcitrant of the textile dye effluent. The dye effluent containing C-I Reactive Yellow 17 and Blue 4 was treated using Ti/ RuO₂ and stainless steel electrodes. The experimental study focused on the effect of supporting electrolytes such as NaCl and Na₂SO₄. The degradation process was enhanced appreciably by increasing the concentration of supporting electrolytes at optimum current density of 7 A/dm² (pH=11). Efficiencies of COD reduction, color removal were also determined. It was established that NaCl was superior to Na₂SO₄ in terms of COD reduction as well as decolorization. The degradation was characterized by HPLC, FTIR and UV-Vis spectral analysis.

Keywords: Dye; Recalcitrant; HPLC

Introduction

Over 100,000 commercially available dyes exist and more than 7×10^5 metric tonnes of dyes are produced worldwide annually [1]. The treatment of wastewater generated by the textile preparation, dyeing and finishing industry remains as a significant environmental pollution problem due to its huge quantity, variable nature and biologically difficult to degrade chemical composition. The main characteristics of effluent from the reactive dyeing process deserve particular attention due the relatively low dye fixation rate, high organic and inorganic content and high alkalinity [2]. Various physical and chemical processes are available for the treatment of textile wastewater, such as membrane filtration, coagulation- flocculation and sequential anaerobic and aerobic treatment, have been employed so far, however with limited success and or at unaffordable costs [3]. Now a days, advanced oxidation processes (AOP's) are available for the treatment of waste waters, like electro oxidation, wet oxidation, ozonation, photo catalytic degradation etc., [4,5]. Treatment using these processes is based on the production of hydroxyl radicals, highly reactive species, which promote oxidation of hazardous organic compounds.

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 on 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 [6]. On the other hand, if chloride is present in the electrolyte, an indirect oxidation via active chlorine can be operated [7-12], Naumczyk et al., [13] have demonstrated several anode materials, such as graphite and noble metal anodes successfully for the mediated oxidation of organic pollutants. In textile industries, synthetic dyes from residual dye baths are released to waste streams. It is estimated that up to 50% of the applied dye, depending on the type, can be lost in effluents during textile dyeing processes. Azo dyes, characterized by nitrogen to nitrogen double bonds ($-N=N-$), account for up to 70% of all textile dyes produced, and are the most common chromospheres in reactive dyes. Due to the characteristics of colored wastewaters containing reactive azo dyes, their treatment is rather difficult, especially by the non-electrochemical wastewater treatment methods based on adsorption

and biodegradation. In order to assess the economic feasibility of EO to decolorize and at least partially oxidize reactive dye bath effluent, an evaluation of conception of electrical energy per volume of treated wastewater (KWh/l) was also conducted. During the dyeing process with reactive dyes, the addition of high concentrations of an electrolyte is necessary to obtain a better fixation and exhaustion. Generally an amount of 50- 80 g of litter of a salt is added as electrolyte, being NaCl or Na₂SO₄ the most common. Anastasios Sakalis et al., have also studied the use of different supporting electrolytes for the treatment of azo dyes by electrochemical method [14]. The main objective of the current work is to study the effect of concentration of supporting electrolytes for degradation of the dyes and optimize the operating conditions for economic feasibility.

Theory

Basically two different processes occur at the anode: 1. direct electrolysis and 2. indirect electrolysis. In direct electrolysis, anode has high electro-catalytic activity and oxidation occurs at the electrode surface. In indirect electrolysis, oxidation occurs via surface mediator on the anodic surface, where the oxidation occurs continuously. In indirect EO, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions [15]. The reactions of anodic oxidation of chloride ions to form chlorine are given as below:

Anodic reactions

Indirect oxidation at anode surface

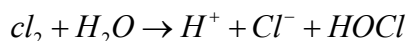
The generation of hypochlorous acid from chlorine (Eq. 1)

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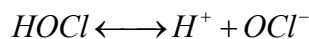
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The generation and dissociation of hypochlorite ion (Eq. 2)



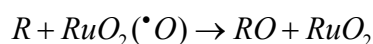
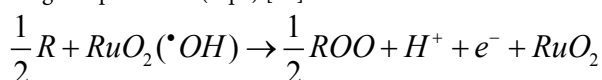
The hypochlorite ions act as main oxidizing agent for the degradation of dye effluents or other organic pollutants.

Direct oxidation at anode surface: A general scheme of electrochemical conversion of organic pollutants on RuO₂ coated Ti anode material is given below [16]: In first step, H₂O is discharged at anode to produce the hydroxyl radical, which get adsorbed on metal surface and form a complex (RuO₂(•OH)).

The dissociation of H₂O, adsorptions of hydroxyl radical into RuO₂ (Eq. 3)



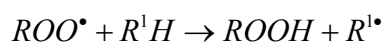
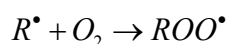
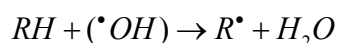
In the presence of organic pollutants, the active oxygen from hydroxyl radicals may involve in completely combustion of organics pollutants (Eq.4), and the active oxygen from higher oxygen radical can be involved in selective oxidation process and give respective products from organic pollutants (Eq.5) [17].



In the presence of NaCl as supporting electrolyte, the chloride ion can also interact with active hydroxyl radical and give a hypochlorite ion (Eq.6)

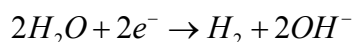


The hydroxyl radical is also involved in the oxidation process of organic pollutants [18-20]. This reaction is a chain reaction, and continued until the formation of carbon dioxide and water (Eq.7-9).

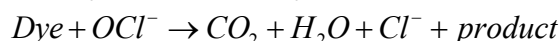


In the presence of Na₂SO₄ as supporting electrolyte, during the electrolysis, SO₂ is formed; it is a moderate reductant [14]. The degradation of organic pollutant or dye in the presence of Na₂SO₄ proceeds via direct redox reactions on the electrodes.

Cathodic reaction: Cathodic reaction is given in Eq.(10):



The role of hypochlorite in electrochemical treatment of dye effluent via chlorine generation (Eq.11) is given below:



Materials and Methods

Materials

Reactive dye effluent containing C.I. Yellow 17 and Blue 4 was collected from a textile industry located in Tirupur, Tamilnadu, India. The structure of the dyes is given in Table 1. Commercially available Ti/RuO₂ and stainless steel were used as anode and cathode respectively.

S.No	Name of dye	Molecular structure
1	C.I. Reactive Yellow17	
2	C.I. Reactive Blue 4	

Table 1: Molecular structure of reactive dyes used in this study.

Two supporting electrolytes NaCl and Na₂SO₄ were used in this study. All the chemicals and reagents (analytical grade) were purchased from Merck and used as such.

Apparatus

The schematic diagram of experimental setup is shown in Figure 1. A 600 ml capacity glass beaker was used as a reservoir. Effluent was stored in the reservoir and it was brought into effect by batch system. A DC power supply was used. The main component of the experimental setup is electrochemical reactor. It consists of stainless steel cathode of size (7 cm x 5 cm x 0.2 cm) and an anode which is RuO₂ coated Ti mesh were used. Anode is placed as close as to cathode and the same was fixed rigidly on a PVC lid with the help of araldite. A magnetic stirrer was used for stirring the solution. Necessary provisions were made in the lid for sampling during the process.

Methods: A known quantity of effluent 400 ml was taken in each experiment. Either NaCl or Na₂SO₄ was added to the effluent as supporting electrolyte of various concentrations 1.5, 2.25 and 3.0 g/l at different applied current density (2, 5 and 7 A/dm²). The pH of the effluent was adjusted to pH 11 by using 1 N NaOH and it was measured by using pH meter (Dot 491). Effluent was continuously stirred during the treatment using a magnetic stirrer. Experiments were carried out under batch conditions for maximum of 5 h. COD and color removal were determined periodically to know the extent of degradation of the effluent.

Extraction and HPLC analysis: Untreated and treated effluents were analyzed by the HPLC. Experiments were carried out on Shimadzu Instrument with UV detector at 254 nm. Each 5 ml of untreated and treated effluent was taken, centrifuged and filtered through a 0.45 μm membrane filter (Millipore make). The filtrate was then extracted by ethyl acetate. The extracted was dried over anhydrous Na₂SO₄ and evaporated to dryness in rotary evaporator. The obtained solid mass was dissolved in methanol and was analyzed by HPLC. A 20 μl sample was injected in to Octa Decyl Sinane (ODS -C18) column (4.6 mm ID x 250 mm length). Methanol of purity 100% was used as mobile phase with the flow rate of 1 ml/min for 10 minutes and UV detector was kept at 254 nm.

Extraction and FTIR analysis: Samples for FTIR analysis were prepared as mentioned in the HPLC analysis. Experiments were carried out on Thermo Nicolet Nexus 670 FT-IR spectrophotometer. The selected IR region was between 400 and 4000 cm⁻¹. To prepare pellets,

the samples were mixed with spectroscopically pure KBr.

UV-Vis analysis: UV-Vis experiments were carried out using Varian UV-Vis-NIR-500 spectrophotometer. Untreated and treated effluents were analyzed by the UV – Vis spectrophotometer. Spectrophotometer was used together with a cell with a 1 cm optical path length to measure the UV spectra.

Analysis of COD

Analytical method of the COD of all samples was determined by the dichromate closed reflux method using Thermo reactor TR620-Merck. COD is generally considered as the oxygen equivalent to the amount of organic matter oxidizable by potassium dichromate. The organic matter of the sample is oxidized with a known excess of potassium dichromate in a 50% sulfuric acid solution. The excess dichromate is titrated with a standard solution of ferrous ammonium sulfate solution [21].

Determination of color

The selection of suitable wavelength in the spectrum can be made during the course of preparing of the calibration curve for the unknown samples. The particular wavelength which provides a maximum absorbance value will be considered as the best choice of wavelength. Reactive dye solutions show maximum absorbance at a wavelength of 430 nm. The UV-Vis spectra of the effluent was measured by using the spectrophotometer Spectroquant NOVA 60 at $\lambda_{max} = 430$ nm.

Color removal was calculated by using the following formula (1) [22]:

$$\text{Color Removal (\%)} = \frac{Abs_i - Abs_f}{Abs_i} \times 100$$

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 5, 6 and 7 show the percentage of color removal with respect to time.

Determination of Instantaneous Current Efficiency (ICE)

Taking into account of the instantaneous current efficiency (ICE) of the electrolysis, it could be calculated using the following formula (2) [23]:

$$ICE = \frac{COD_t - COD_{t+\Delta t}}{8I\Delta t} FV$$

where, COD_t and $COD_{t+\Delta t}$ are the chemical oxygen demands at times t and $t + \Delta t$ ($g O_2 l^{-1}$), respectively, and I is the current (A), F the Faraday constant ($96,487 C mol^{-1}$) and V is the volume of electrolyte (l). Fig.8 shows the variation of ICE as a function of time at $7 A/dm^2$.

Determination of Energy Consumption (EC)

Energy consumption is for the removal of 1 kg of COD (kWh kg^{-1} COD) was obtained by using the following formula (3):

$$EC = \frac{tUI}{\Delta COD} \times 10^3$$

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 ΔCOD the difference in COD ($mg l^{-1}$).

Results and Discussion

Effect of anode

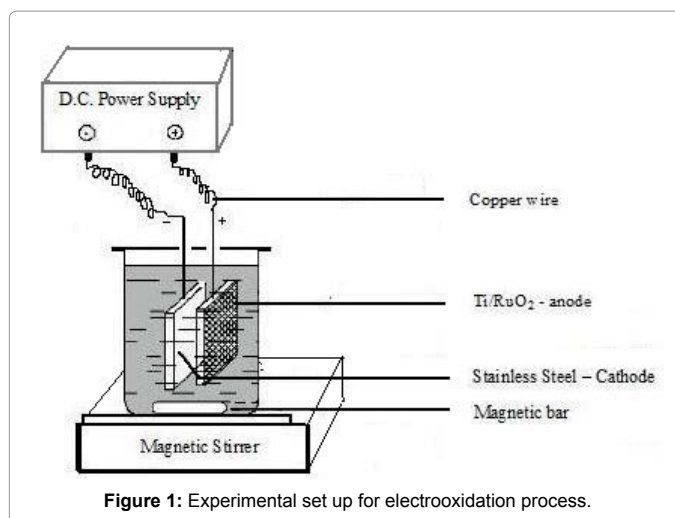


Figure 1: Experimental set up for electrooxidation process.

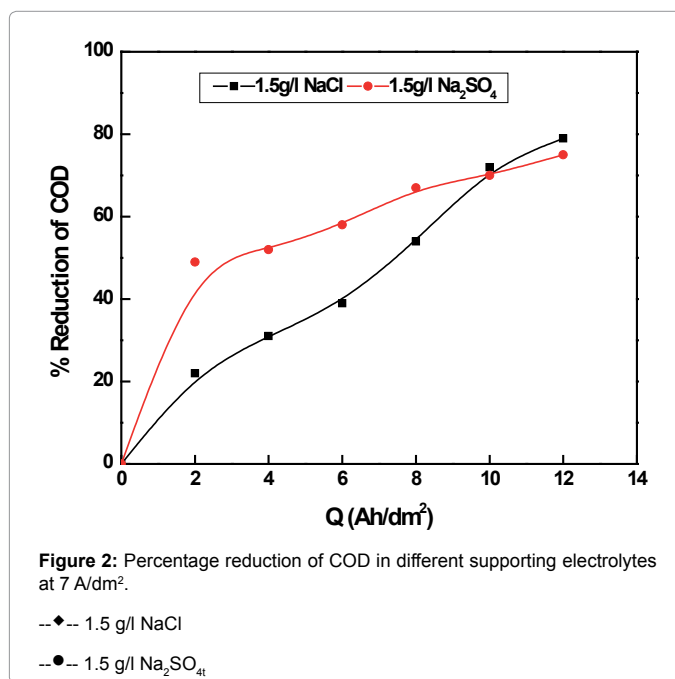


Figure 2: Percentage reduction of COD in different supporting electrolytes at 7 A/dm².

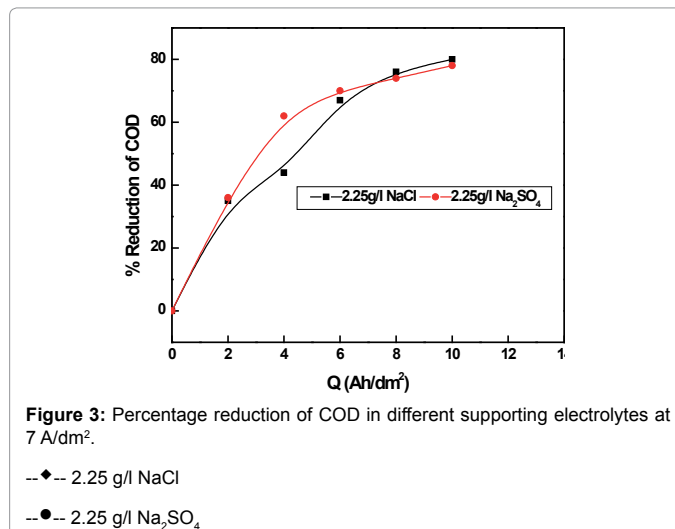


Figure 3: Percentage reduction of COD in different supporting electrolytes at 7 A/dm².

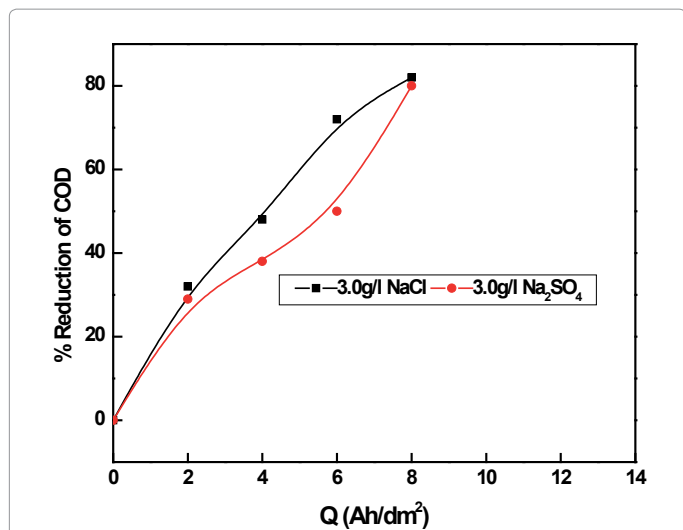


Figure 4: Percentage reduction of COD in different supporting electrolytes at 7 A/dm².

--◆-- 3.0 g/l NaCl
 --●-- 3.0 g/l Na₂SO₄

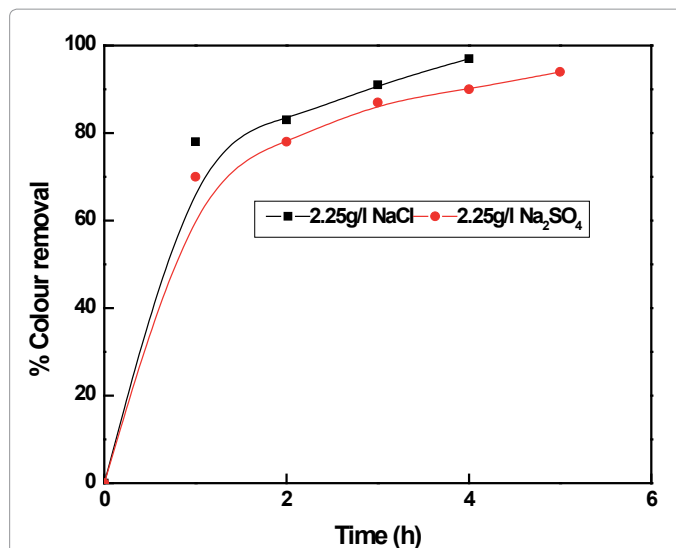


Figure 6: Percentage removal of color as a function of time at 7 A/dm².

--◆-- 2.25 g/l NaCl
 --●-- 2.25 g/l Na₂SO₄

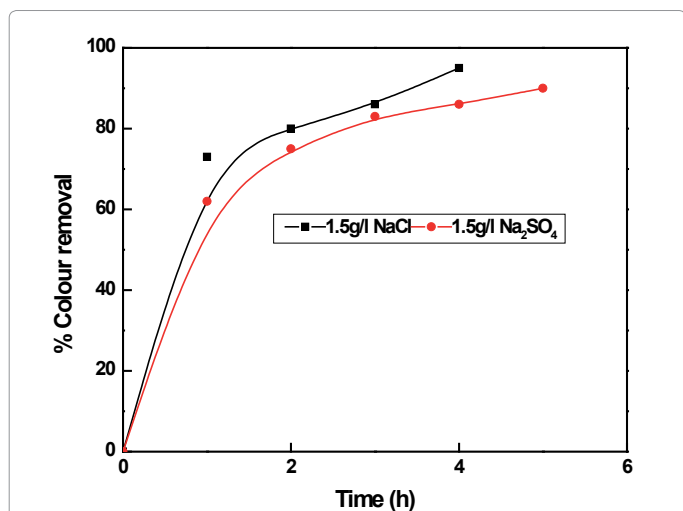


Figure 5: Percentage removal of color as a function of time at 7 A/dm².

--◆-- 1.5 g/l NaCl
 --●-- 1.5 g/l Na₂SO₄

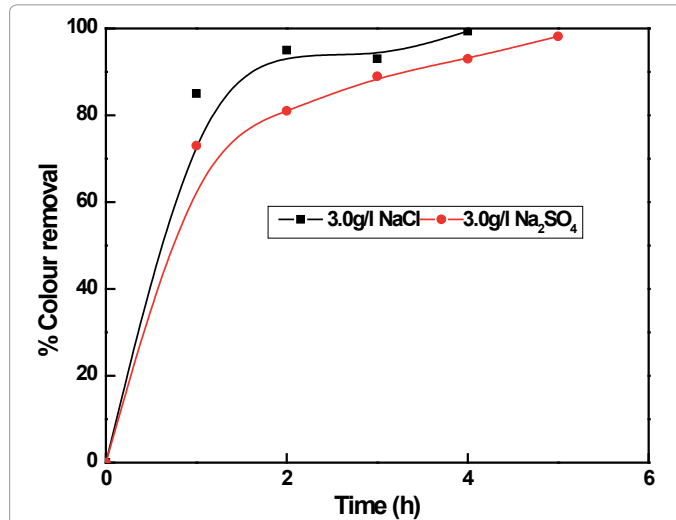


Figure 7: Percentage removal of color as a function of time at 7 A/dm².

--◆-- 3.0 g/l NaCl
 --●-- 3.0 g/l Na₂SO₄

It is well known that the organic compounds are completely oxidized to carbon dioxide and water at electrode surface. The electrode Ti / RuO₂ has high electro catalytic activity which leads to simple fragments of complex organic compounds.

Effect of current density and supporting electrolyte

Figures 2-4 show the percentage reduction of COD in different supporting electrolytes. It was observed from the figures that reduction of COD was directly proportional to the applied current density. An optimum point 7 A/dm² was determined finally which gives a faster removal rate of COD. The easily oxidizable pollutants present in the effluent contribute to the decrease in COD under this condition. It is evident that the extent of degradation of reactive dye increases with

time. In the presence of NaCl, the dye was indirectly oxidized by perchloride ion, which was produced by hydroxyl radical. Dye was directly oxidized by hydroxyl or other oxidant reagent electro generated from the electrolysis. The removal of color and reduction of COD was directly proportional to concentration of electrolyte. The formation of perchloride ion and SO₂ depends upon the concentration of NaCl and Na₂SO₄ respectively. It is well known that the electrolysis of NaCl results in some very strong oxidants, such as free chlorine (Cl₂) and hypochlorite anions (ClO⁻) [24-26]. The supporting electrolyte Na₂SO₄ degrades the dyes due to the formation of SO₂, which is a moderate reductant. The decoloration of dye proceeds mainly via direct redox reactions on the electrodes, enhanced by indirect redox reactions by oxidants or reductants. Also it produces more ionic products which

increase the ionic strength of the wastewater. Significant amount of HOSO_3^- was identified in the treated wastewater, as a result of the degradation of the dye molecules, this ionic molecule further degraded in non-ionic final products (SO_2/SO_3) [27]. It has been concluded from the results, that the efficiency of NaCl was found to be better than Na_2SO_4 regarding the degradation of C.I Reactive Yellow 17 and Blue 4.

Removal of color

Figures 5-7 show color removal efficiencies in different supporting electrolytes at 7 A/dm^2 . The maximum color removal efficiency was obtained as 99.4% and 96.2% in NaCl and Na_2SO_4 respectively. The same trend was also observed in the reduction of COD.

Figure 8 shows the instantaneous current efficiency (ICE) as a function of time at 7 A/dm^2 . From the figure, it was clearly observed that ICE was fairly good throughout the experiment in NaCl.

The energy consumption for the degradation of dyes was shown in Figures 9 and 10. Results indicate that energy consumption has been increased with increasing applied current density. 82% COD removal was obtained in 3.0 g/l NaCl at 7 A/dm^2 and energy consumption was 13 kWh/kg of COD. At the same time, 80% of COD removal was obtained in $3.0 \text{ g/l Na}_2\text{SO}_4$ at 7 A/dm^2 and energy consumption was 16 kWh/kg of COD. Therefore, an optimum condition was determined to reduce COD to a maximum level and removal of color almost completely from the effluent with less energy consumption. An optimal current density of 7 A/dm^2 was obtained from this study. From the results, it was understood that, the process involving NaCl, completely removes the color of the dye with less consumption of electrical energy.

FT-IR

Figure 10 (a) shows the FT-IR spectra of effluent. 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 aromatic C=C and also N=N groups. Figure 10 (b & c) show the FTIR spectra of treated samples with $30 \text{ g Na}_2\text{SO}_4$ and 30 g NaCl respectively. It showed an absence of peak at 1600 cm^{-1} indicates the breakdown of

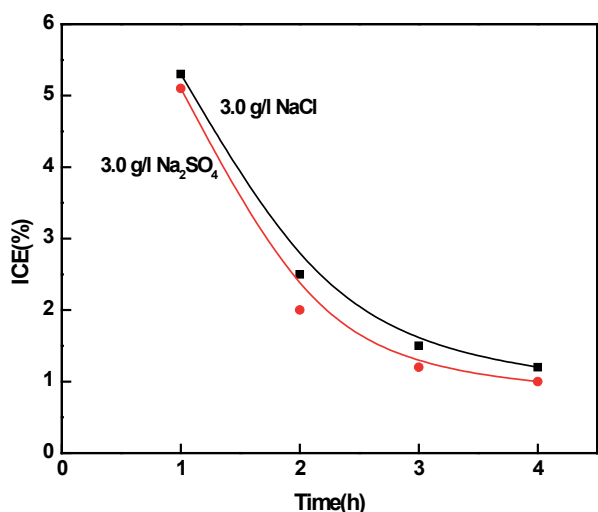


Figure 8: Variation of ICE as a function of time at 7 A/dm^2 .

--♦-- 3.0 g/l NaCl
--●-- 3.0 g/l Na_2SO_4

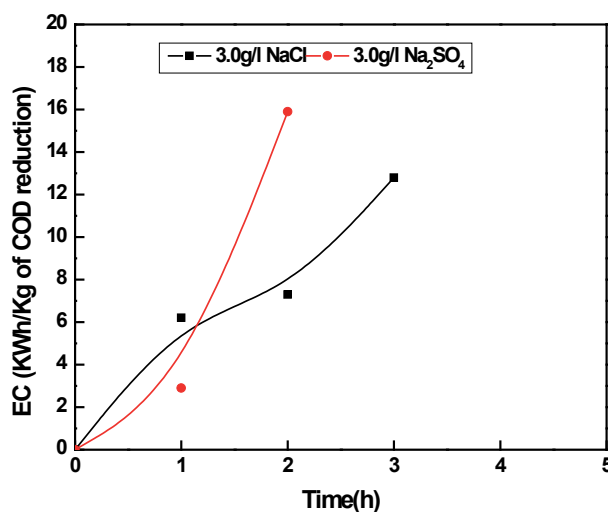


Figure 9: Energy consumption as a function of time in different supporting electrolytes at 7 A/dm^2 .

--♦-- 3.0 g/l NaCl
--●-- 3.0 g/l Na_2SO_4

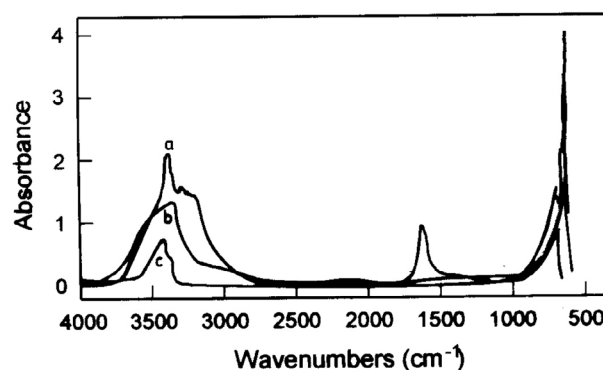


Figure 10: FTIR spectra of untreated and treated dye effluent during EO.

(a) Untreated effluent
(b) Treated with $3.0 \text{ g/l Na}_2\text{SO}_4$ at 7 A/dm^2
(c) Treated with 3.0 g/l NaCl at 7 A/dm^2

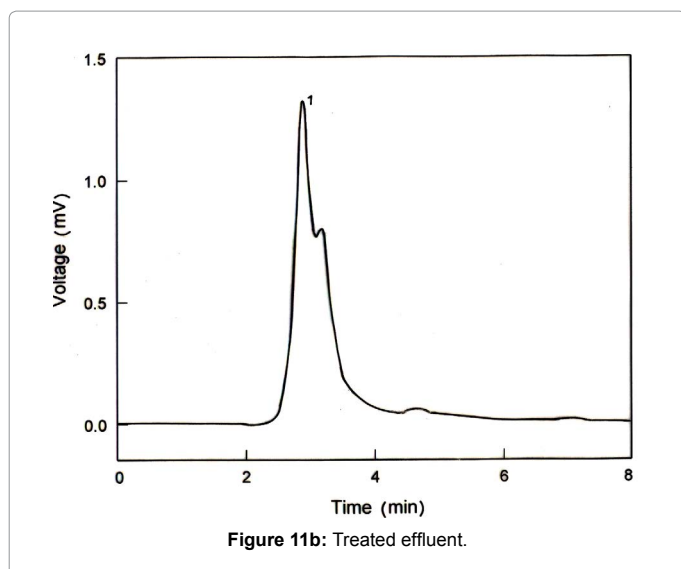
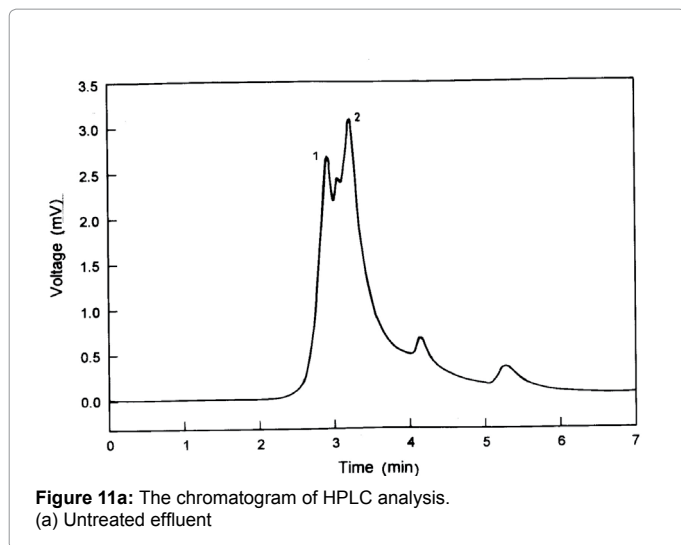
amine N-H functions and the absence of peak at 1636.47 cm^{-1} indicates breakdown of aromatic rings. Strong peaks at 686.38 cm^{-1} may be due to the presence of chlorine and hypo chlorite ion in the effluent.

HPLC

Figure 11(a) shows the chromatogram of untreated effluent, the major peak was obtained at 3.2 min (retention time). After treatment the intensity of peak was reduced drastically which was clearly shown in the Figure 11(b).

UV-Vis spectra

Figure 12 shows typical UV spectra for untreated and treated effluent. The spectrum of reactive dye in the visible region exhibits a

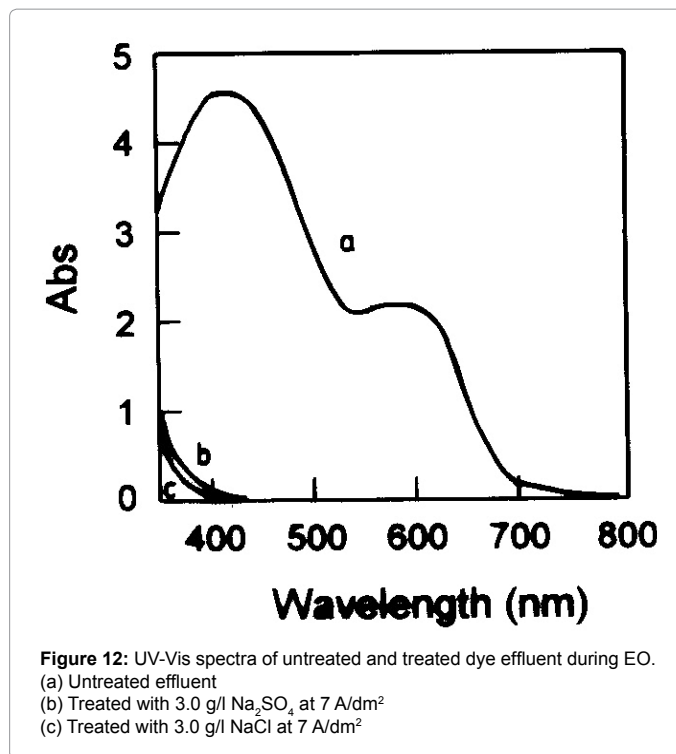


main band with a maximum at 430 nm. The decrease of adsorption peaks of reactive dye at $\lambda_{max} = 430$ nm which indicates a rapid degradation of reactive dye. The decrease in the intensity is due to the break of nitrogen double bond in the reactive dye, which is the most active site for oxidative attack. Complete discoloration of dye was observed after 3 h under the optimized conditions.

The characteristic band at 485 to 570 nm could be assigned to the $n-\pi^*$ transition of azo group. The weak band below 350 nm could be attributed to the $\pi-\pi^*$ transition related to the aromatic ring attached to the azo 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 treatment. The disappearance of the bands indicates the effective destruction of the azo.

Conclusion

EO process is a best technique for removal of color and COD for C.I. Reactive Yellow 17 and Blue 4. Degradation of the dye was better when NaCl was used as supporting electrolyte than Na_2SO_4 (Table 2) and it



Parameters	Before treatment
pH	
Conductivity (m S)	
BOD (mg/L)	
TOC (mg/L)	
COD (mg/L)	
TDS (g/10 ml)	

Table 2: Characteristics of dyehouse effluent.

is due to the formation of perchloride ion, which is used for indirect oxidation of dye. Maximum percentage removal of COD and color were 82 % and 99.4% at the optimum condition of 3.0 g/l NaCl and applied current density of 7 A/dm² (pH= 11). Results are concurred with HPLC, FT-IR and UV-Vis spectral analysis. It is evident that EO process is a better technique for degradation of reactive dye in wastewater from textile industries.

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