



Decolorization of Reactive Dye Solutions by Electrocoagulation using Iron Electrodes

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ABSTRACT

The textile industry is facing major problems in the disposal of wastewater generated from textile dye and finishing processes. Textile dye wastewater has a strong colour, high COD, high total solids and is also biorefractory in nature. There is a need for most suitable and effective pretreatment technique. The present work focuses on the feasibility of electrocoagulation for the reactive dye solutions. The experiments were conducted for the optimized electrolysis duration at different applied currents and pH. The Study revealed that at a neutral pH there was a colour removal efficiency of 90% with minimum sludge production and anode consumption.

INTRODUCTION

Textile industry is one of the most polluting industries in terms of the volume and complexity of its effluent discharge. The dyeing and finishing operations in textile industries contribute a major share to wastewater generation (Mohan et al. 2001).

Dyes are organic colorants used in textile, pharmaceutical, cosmetic, food and other industries for imparting different shades of colours. Dye manufacturers and users, particularly the textile industries, release wastewaters in massive quantities containing dye to the extent of 0.001-0.7% (w/v), often with dissolved inorganic salts, dispersing agents, surfactants, and organics washed out from the materials. Reports also suggest that dye house effluents contain 0.1-2% (w/v) dye resulting in 2-9% of total global annual dye production, which is equivalent to nearly 50,000 tons. This situation will be further aggravated in the ensuing years as the demand for cotton and other fabric increases exponentially. The pH values of these discharges vary between 2 and 12, depending upon the dye and its application (Sanjay et al. 2005).

The pollution induced by dyestuff in the textile industry has been a serious environmental problem for years; dyes in the wastewater undergo chemical as well as biological changes, consume dissolved oxygen from the stream, and destroy aquatic life because of their toxicity. It is therefore necessary to treat the textile effluents prior to their discharge into the receiving water (Can et al. 2003).

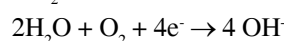
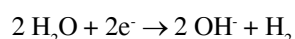
Due to large variations in the effluent composition, most of these traditional methods are inadequate. Although the biological degradation is the most economic process, it is ineffective to degrade molecules of refractive nature. Though ozonation is quite effective for decolorization of textile wastewater, the biodegradability is difficult. The electrochemical methods appear to be effective for the treatment of different effluents compared to conventional methods. Above all, the electrochemical reactors are compact, simple and the rate of pollutant removal is very rapid (Muthukumar et al. 2007).

Most of electrochemical discoloration studies are focused on reactive dyes. They represent about 20-30% of the total market because of their solidity and brilliant colour. Their structure consists of a reactive group (which reacts with fibre) and a chromophore group (which gives the colour). The most used chromophore group is the azo (R-N=N-R') followed by anthraquinone group. Azo group constitute, more than half of worldwide production, approximately 65%. Moreover, this kind of dyes produces toxic aromatic products in their degradation. The high consumption of reactive dyes mainly in the cotton industry, increases this environmental and aesthetic problem, due to their low degree of exhaustion and their presence both in dyeing and soaping effluents (Mireia Sala et al. 2012).

A promising electrochemical process is by coagulation. Aluminium and iron sheets have been used as consumable

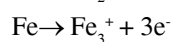
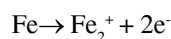
anodes to generate coagulants that adsorb and remove organic dyes. An aluminium coagulant removes colorant by simple adsorption without involving chemical reactions while an iron-based coagulant provides ferrous ions to further degrade the dyes. Iron process seems more effective for removal of reactive dyes while the aluminium process is superior for removal of dispersed dyes.

The main pathway for removing colorant from aqueous solutions is coagulation. At large cathodic potentials, local hydroxyl ions (OH^-) can be generated due to water and oxygen reduction:

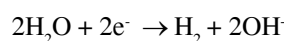


With mild steel sheets as anode and cathode, ferrous and ferric ions are produced on the anodes.

Anode:



Cathode:



During the process, an increase in pH is expected. As a result of the high pH, precipitates of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are formed and remain in the solution. The gelatinous suspension removes colorants by complexation and electrostatic attraction followed by coagulation (Chen et al. 2005).

In the present work, the removal of reactive dye Remazol Red RB 133 from aqueous was studied by electrocoagulation. The reactive dye is considered as a potential health hazard. An attempt was made to understand the mechanism of decoloration and degradation of azo dye during the electrochemical process.

The commercially available reactive dye remazol red RB 133 was obtained from a textile mill with a molecular structure as shown in Fig. 1. The characteristics of Remazol Red RB 133 are summarized in Table 1. Double distilled water was used to prepare the desired concentration of dye solutions and all the reagents.

MATERIALS AND METHODS

Standard solution of simulated dye wastewater containing reactive red was prepared by dissolving 1g of dye in 1 L of distilled water. NaCl was used as an internal electrolyte. The conductivity and pH of the solution was measured before and after each experiment. The pH was adjusted using either 0.1 N NaOH or 0.1 N H_2SO_4 .

The experimental setup (Fig. 2) consisted of a glass beaker of 500 mL capacity, in which two electrodes having an

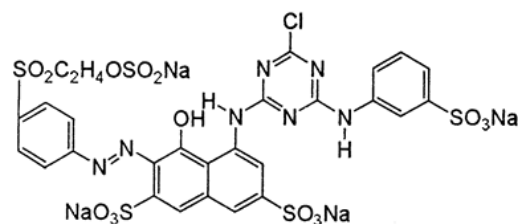


Fig. 1: Molecular structure of the reactive dye remazol Red Rb 133.

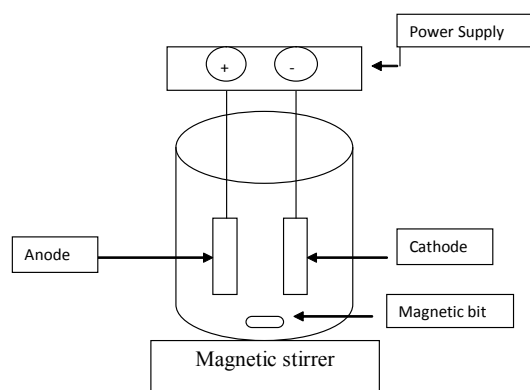


Fig. 2: Experimental setup.

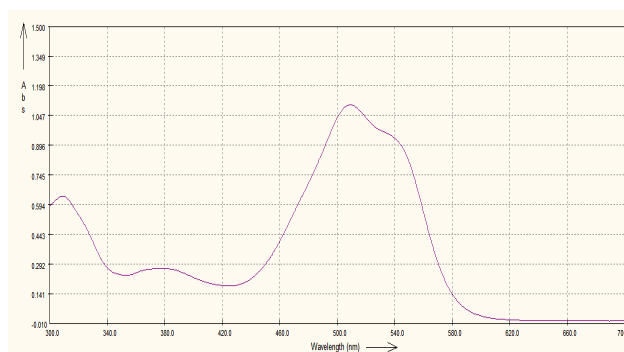


Fig. 3: Spectrum scans for dye sample.

inter-electrode gap of 2 cm were placed vertically and parallel to each other. Commercially available mild steel (MS) of dimension 5 cm \times 5 cm was used as the anode and cathode. The effective area of electrode was 25 cm² (0.0025 m²). The experiments were carried out with the dye sample at room temperature and with constant agitation. The electrodes were connected to a DC power supply (Textronix 35D, 0-15V, 0-10A). During the experiment, samples were collected at regular intervals and analysed for various parameters. After the experiment, the power was switched off and the electrodes were disconnected. The electrolytes (solution) resulting from electrochemical treatment was analysed for COD, colour and pH according to the standard methods suggested by APHA (1998).

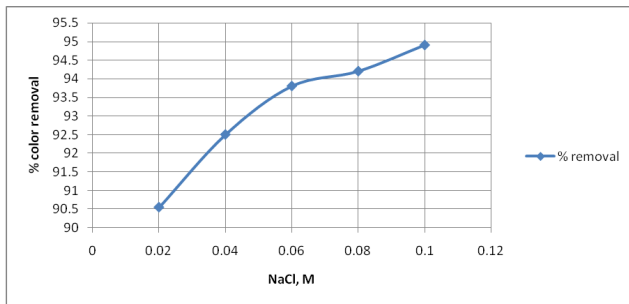


Fig. 4: Percent colour removal at different moles of sodium chloride.

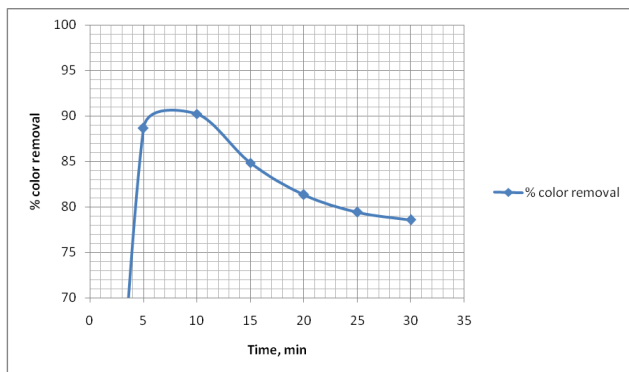


Fig. 5: Variation of colour removal as a function of electrolysis duration.

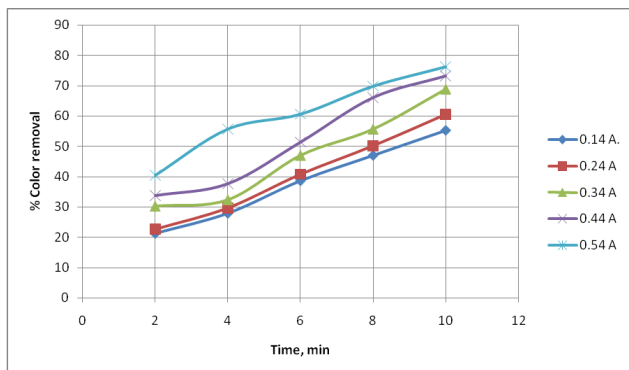


Fig. 6: Percent variation of colour at different current, iron anode.

The pH measurement was made on Elico Ion Analyser (LI 126). The chemical oxidation demand was estimated by the open reflux method. Determination of the colour of the wastewater was carried out by measuring the absorbance at a wavelength of 510nm (λ_{max}). The percentage of colour removal was calculated as follows;

$$\text{Colour removal (\%)} = \frac{(\text{abs}_{max} - \text{abs}_t)}{\text{abs}_{max}} \times 100$$

Where, abs_{max} = Absorbance of the raw sample at 510nm, abs_t = Absorbance of the samples collected at regular time intervals t at a fixed wavelength of 510 nm.

Table 1: Characterization of the remzaol Red RB 133.

Sl. No.	Parameter	Value
1	Colour index	Reactive RED RB 133
2	Chromophore	Azo
3	Reactive anchor systems	MCT and VS
4	Molar mass nonhydrolyzed dye	984.2
5	Percentage of pure dye	63%
9	pH value (at 10 g/L water)	7
10	COD value (mg/g)	540
11	BOD value (mg/g)	<10

The removal rate for COD has been calculated in terms of COD removed/hr/A/m². The energy consumption for the removal of 1 kg of COD was calculated and expressed in kilo Watt hour (kWh). The cell voltage during the electrolysis was taken for calculating the energy consumption. Dye concentration was determined using a working curve by plotting the absorbance versus known concentrations at λ_{max} . The anodic efficiency of electrochemical treatment has been calculated in terms of kg COD removed per hour per ampere per square meter area of the electrode (kg COD/h/A/m²).

RESULTS AND DISCUSSION

Fig. 3 shows the spectrum graph of absorbance values at different wavelength. At 510 nm a peak absorbance of 1.082 was observed. For further decolorization, efficiency of electrodes was measured at that particular wavelength.

The effects of electrolyte concentration: The addition of NaCl would lead to the decrease in power consumption because of the increase in conductivity. Therefore, the effect of electrolyte concentration on electrochemical oxidation of reactive dye was investigated. Fig. 4 shows the results of variation of NaCl with respect to removal of colour. It indicates that the colour removal efficiency increased from 90.55 % to 94.90 %, when the electrolyte concentration was increased from 0.02 M to 0.1 M. Similar effects were reported by Lin et al. (1996), Kobya et al. (2003) and Mollah et al. (2004). Conductivity of the solution also increased linearly from 2.40 to 10.57 mS/cm with electrolyte concentration.

The effect of an increase in conductivity of the dye solution on the colour removal efficiency exhibited similar behaviour as in the case of increasing electrolyte concentration. Subsequent experiments were carried out with 0.02 M NaCl solution in order to minimize the addition of excess Cl⁻ ions in solution as well as to lower the current density.

Determination of optimum electrolysis duration: Initially, studies were conducted to find out the optimum electrolysis duration at which maximum colour removal takes place. During the experiment, the maximum current was fixed and

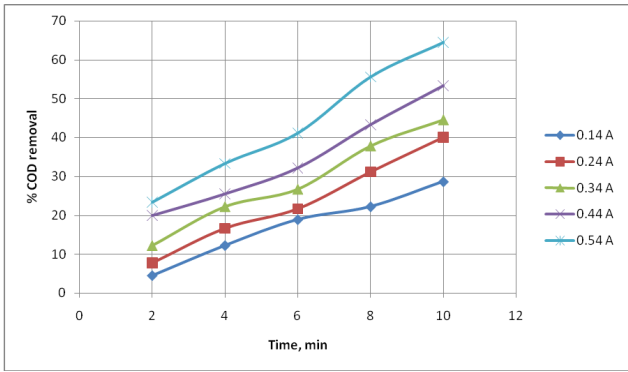


Fig. 7: Percent COD variation at different current, iron anode.

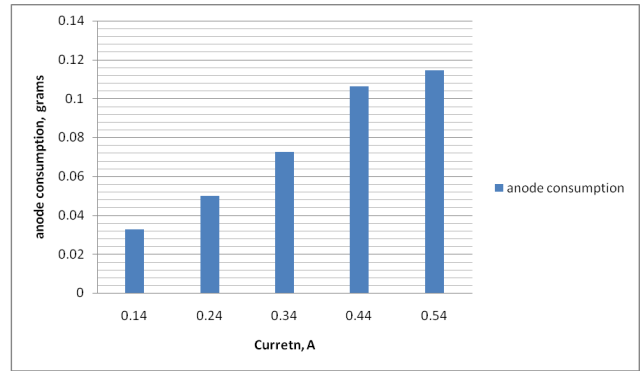


Fig. 10: Anode consumption in grams at different current, iron anode.

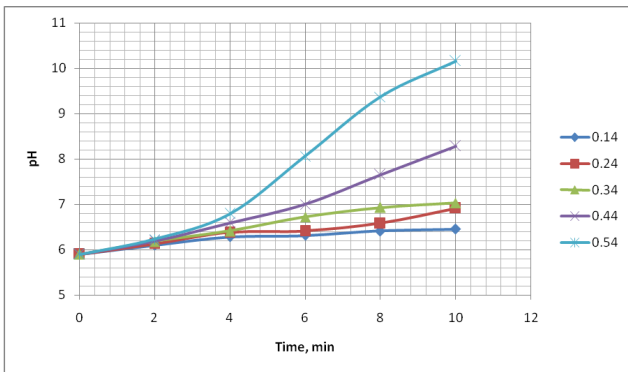


Fig. 8: pH variations at varying applied currents.

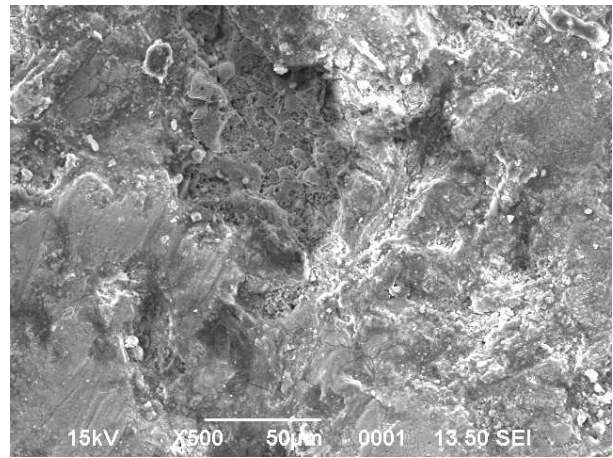


Fig. 11: SEM image of iron anode before treatment.

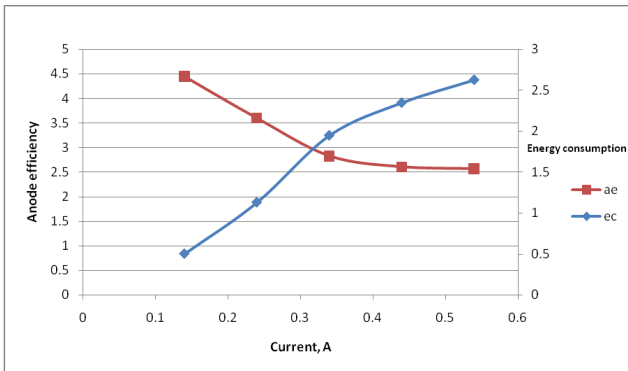


Fig 9: Energy consumption (kWh/kg of COD) and anode efficiency (kg of COD/h/A/m²) at different applied currents.

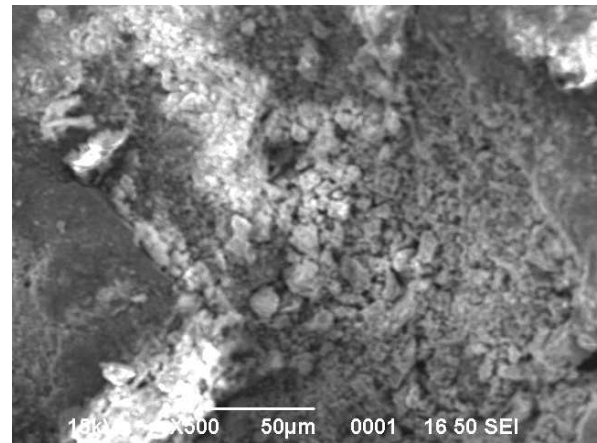


Fig. 12: SEM image of iron anode after treatment.

the experiments were carried out till the decolorization of dye. The samples were collected at regular time intervals of 5 minutes and the results are shown in Fig. 5. It can be observed that the colour removal increased between 6 min and 10 min, and later on decrease in removal efficiency was observed. In 10 min of electrolysis duration, colour removal of 90.24% was achieved, which is considered as optimum electrolysis duration. The decrease in colour removal at a later

stage might be due to the exhaustion of hypochlorite and free chlorine generation *in situ* in the reactor.

Effect of applied current: To study the effect of varying current on colour and COD, experiments were carried out at

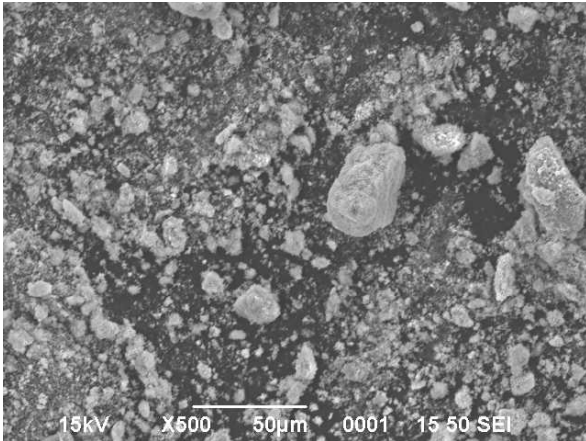


Fig. 13: SEM images of sludge generated during electrochemical coagulation.

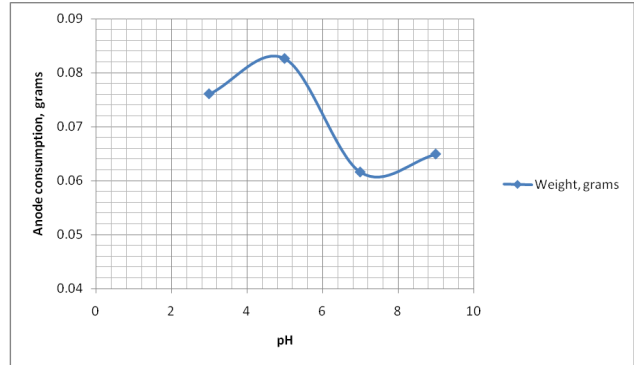


Fig. 16: Anode consumption with varying pH.

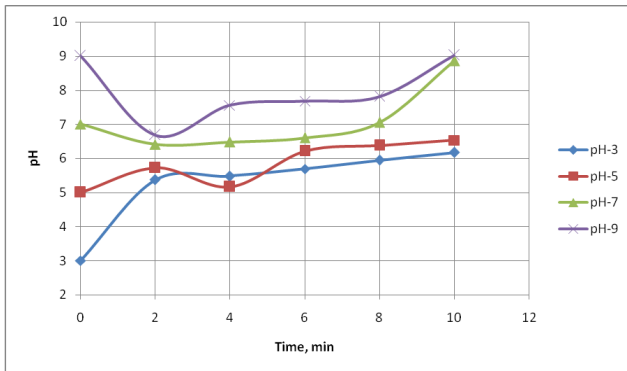


Fig. 14: Variation of initial pH at different time interval at 0.44 A.

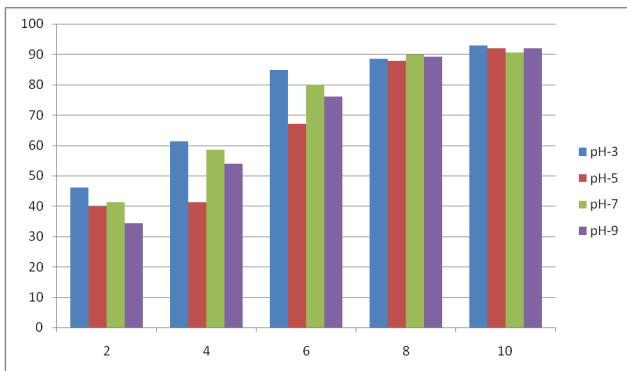


Fig. 15: Variation of colour removal at different pH.

0.14, 0.24, 0.34, 0.44 and 0.54 A. Based on the previous experiments, 10 min of electrolysis duration was maintained. Figs. 4 and 5 show the variation of colour and COD respectively.

As shown in Fig. 6, the absorbance decreases with increasing electrolysis time, which is in good agreement with literature. As the current intensity increases, the pollutant

degradation rate increases initially. However, once the current intensity reaches a certain value, referred as limiting current intensity, the degradation rate does not increase any more and is determined by the mass transfer rate (Miled et al. 2010). The decolorization efficiency increases gradually at varying applied current. At a current of 0.44A, 73.12 % colour removal and 53.44% of COD removal was achieved. Fig. 7 shows that at different applied current there is a decrease in COD also. The trend of pH variation is shown in Fig. 8. Table 2 shows energy consumption, anode efficiency and sludge settled for the various applied current. Also, Fig. 9 and 10 show the variation of energy consumption and anode efficiency with respect to varying current and anode consumption respectively.

From Figs. 9 and 10, it can be observed that, as current increases, energy consumption increases and removal efficiency decreases, sludge generated (Table 2) and anode consumption increases. Figs. 11 and 12 show the SEM images of the surface of iron anode before and after treatment by electrocoagulation, which exhibits the corroded surface of iron anode. Fig. 13 shows the SEM images for sludge settled. At an applied current of 0.44 A, colour removal efficiency and COD removal was 73.12 % and 53.34 % with a settled sludge volume of 7.5 mL.

Effect of pH: Studies were conducted on the effect of pH on colour and COD removal efficiency. The pH of the solution was adjusted using H₂SO₄ and NaOH. The effect of pH was investigated between 3 and 9 under optimized conditions at 0.44 A. During the process, an increase in pH was expected as shown in Fig. 14. As a result of the high pH, precipitates of Fe(OH)₂ and Fe(OH)₃ were formed and remained in the solution. The gelatinous suspension removes colorants by complexation and electrostatic attraction followed by coagulation (Chen et al. 2005). But variation of pH had no influence on the colour removal capacity as shown in Fig. 15, because at the end of the reaction, removal efficiency remained almost same. But at neutral pH the anode consump-

Table 2: Energy consumption and anodic efficiency of iron anode.

Applied current, A	Voltage V	Anode consumption, Grams	Energy consumption kWh/kg of COD	Anodic efficiency (COD removal rate)	Kg of dye removed/kg of anode	Sludge generated, mL
0.14	2.8	0.0328	0.5	4.45	1.676	-*
0.24	5.1	0.0498	1.13	3.60	1.184	1.5
0.34	6.9	0.0724	1.95	2.83	0.939	5.0
0.44	7.7	0.1063	2.35	2.61	0.682	7.5
0.54	8.5	0.1144	2.63	2.57	0.660	16.0

*Precipitate not formed.

tion was less and colour removal efficiency also greater than 90% (Fig. 16).

CONCLUSIONS

Electrocoagulation is an effective treatment process for colour removal from textile effluents. The optimized conditions for the reactive dye were 0.44 A at a neutral pH with reaction time of 10 min.

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