

Treatment of textile dye wastewater by using an electrochemical bipolar disc stack reactor

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Abstract: Textile dye house wastewater from a reactive dye processing unit was treated by using an electrochemical oxidation technique. The experiments were carried out in an electrochemical bipolar disc reactor using RuO₂ coated on titanium as anode and titanium as cathode. The sodium chloride present in the effluent was used as supporting electrolyte. Operating parameters such as current density, reservoir hold-up and electrolysis time were studied for maximum Chemical Oxygen Demand (COD) reduction and other relevant parameters such as current efficiency and power consumption per kg of COD removal were calculated. The higher flow rate and lower reservoir hold-up resulted in improved COD removal. The applied current density was also found to significantly influence the reduction of COD. A suitable mathematical model is also proposed to illustrate the relationship between the basic parameters. Pseudo mass transfer coefficients were also evaluated for different experimental conditions.

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Keywords: electrochemical oxidation; bipolar disc reactor; Chemical Oxygen Demand; reactive dye wastewater; textile wastewater

NOTATION

a	Specific electrode area (m ² m ⁻³)
A	Area of the electrode (dm ²)
C	Bulk concentration of dyestuff (mg dm ⁻³)
C'	Concentration of dyestuff in the reservoir at time t (mg dm ⁻³)
F	Faraday constant (26.8 A h)
I	Current (A)
K	Pseudo mass transfer coefficient (m s ⁻¹)
Q	Volumetric flow rate (dm ³ h ⁻¹)
r_o	Inner radius of the disc (m)
R	Outer radius of the disc (m)
S	Gap width (m)
V	Volume of the electrolyte (dm ³)
V_r	Volume of the reactor (m ³)
V_R	Reservoir volume (dm ³)
Δt	Increment in electrolysis time (s)
τ_r	Residence time of effluent in the reactor (s)
τ_R	Residence time of effluent in the reservoir (s)

INTRODUCTION

Textile dye and finishing processes are highly water-utilizing and are considered as one of the major polluting processes. In recent years, the textile industry has undergone modernization to a large

extent and incorporated the latest developments in textile technology. However, the textile industry is facing major problems in the disposal of wastewater generated from textile dye and finishing processes. Textile dye wastewater contains strong colour, high Chemical Oxygen Demand (COD), high total dissolved solids and is also bio-refractory in nature.¹ The mostly polluted and large amounts of wastewaters are generated from the dyehouses of the textile industry. Due to the enforcement of strict rules and regulations prescribed by government agencies, the treatment methods must treat the effluent efficiently to discharge into land at the prescribed threshold limit values.

Physical, chemical, biological and electrochemical methods are successfully used for the treatment of textile dye wastewater. The emerging technologies such as chemical reduction, Fenton oxidation, membrane filtration and photocatalytic oxidation are also efficiently implemented for the treatment of textile dye wastewater. Chemical reduction using zero valent iron, Fe⁰, in the form of powder is successfully applied for the treatment of wastewaters containing dyes. Bigg and Judd^{2–4} studied the remediation of dye-containing wastewaters by using zero valent iron as a reducing agent. Cao *et al*⁵ also reported the

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reductive degradation of azo dye by zero valent iron in aqueous solution. The Fenton oxidation technique using Fenton's reagent was effectively used for the treatment of textile dye wastewater.⁶ The Fenton oxidation technique was found to be cheaper and widely used in full-scale operation. The membrane filtration technique has also been used for the treatment of textile wastewater.⁷ But the selection of membrane is very important and regular cleaning is necessary to prevent membrane fouling. The major drawback of the filtration process is the disposal of concentrated streams obtained during the process. The Ozonation technique completely decolorizes and also considerably reduces the COD and Biological Oxygen Demand (BOD) of the effluent.^{8,9} Ozonation has normally been used as a final treatment process following chemical coagulation. Biodegradation of textile dye effluents by using aerobic and anaerobic techniques is effectively employed by the industry.^{10,11} Activated sludge systems and biosorption using dead biomass are also used to a considerable extent for the complete decolorization of the effluent.^{12,13} Photocatalytic degradation using UV/H₂O₂ has been successfully tested for the decolorization of dye wastewater.¹⁴ Several literature reports have stated that photocatalytic processes employing UV/TiO₂ seem more promising than UV/H₂O₂ for the degradation of dyes and other organic compounds.¹⁵⁻¹⁹ Physical methods such as coagulation, and adsorption, using various materials are also widely used for the treatment of dye wastes.^{9,20-22}

Recently there has been growing interest towards electrochemical techniques for the treatment of

wastewater containing organic pollutants. Two important features of the electrochemical process are converting non-biocompatible organics into biocompatible compounds and oxidation of organics into carbon dioxide and water. Electrochemical methods for the treatment of toxic effluents are widely reported in the literature.²³⁻²⁵ Electrochemical oxidation has been effectively used for the treatment of textile wastewater from a cellulosic azo dyeing and finishing process using Ti/Pt as anode and stainless steel as cathode.²⁶ The novel electrocoagulation technique has also been employed for the treatment of textile dye effluent using sacrificial anodes.²⁷

The degradation of organic and toxic materials present in the effluent in an electrochemical process is achieved by direct or indirect oxidation. In the direct oxidation technique, pollutants are destroyed directly at the anode. The process utilizing strong oxidizing agents such as hypochlorite and chlorine, generated during the electrolysis, for the oxidation of pollutants is called indirect oxidation.²⁶ In the present investigation, sodium chloride present in the effluent was used as a supporting electrolyte and it has generated strong oxidizing agents such as hypochlorite and chlorine during the process. Such oxidizing agents were used for the mineralization of organic pollutants.

Both direct and indirect oxidation methods are used for the treatment of textile dye wastewater. Though many papers have been published on the treatment of textile dye wastewater, the use of a bipolar disc stack reactor for the treatment of dye wastewater has not been given much importance. Bipolar disc stack reactors have received great interest recently due to their simple geometry (Figs 1 and 2). The

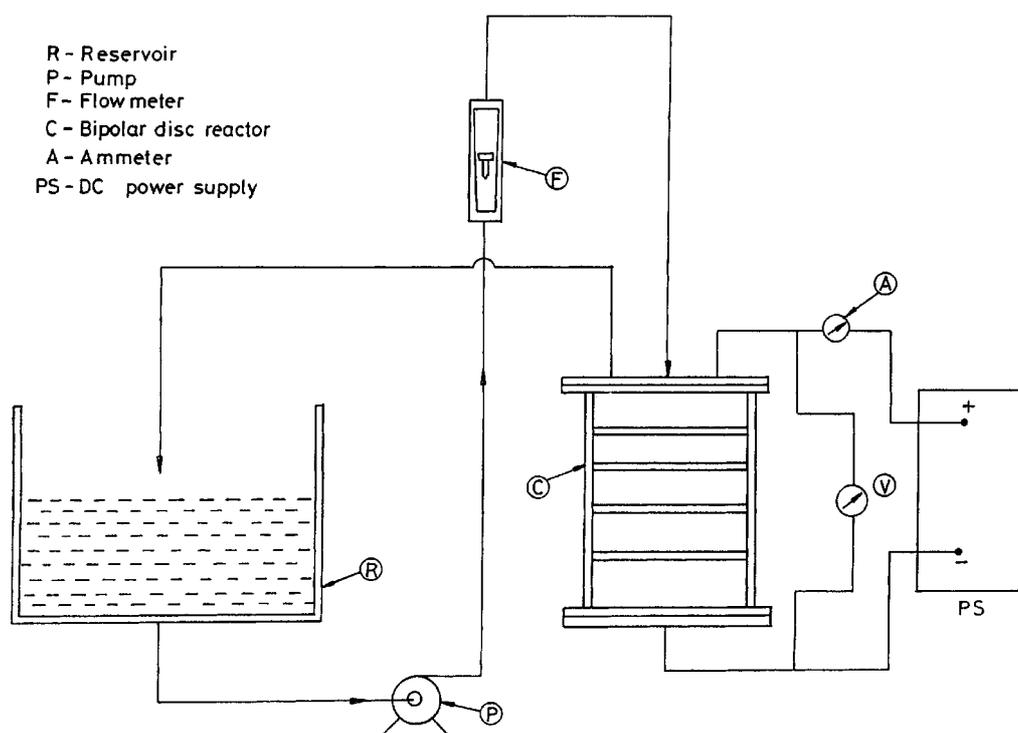


Figure 1. Schematic diagram of the experimental set-up.

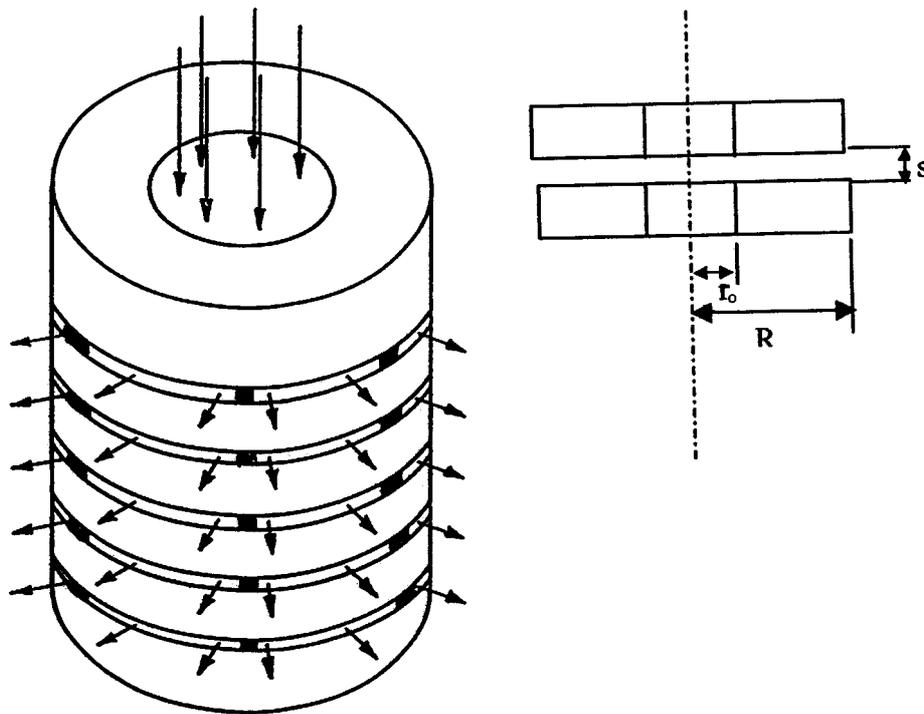


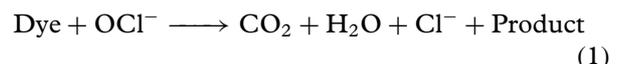
Figure 2. Perspective view of bipolar reactor.

radially divergent flow in gaps will highly enhance the rate of reduction for low-conducting fluids. Bipolar disc reactors are widely preferred for electrochemical reactions due to their compactness and the lower cost of the electrical equipment. The main disadvantage of this electrochemical reactor is the presence of parasitic electrical currents or bypass currents, in the electrolyte inlet and outlet of the electrode stack.²⁸ Hence the main objective of the present investigation is to investigate the applicability of electrochemical oxidation for the removal of colour and COD from textile dye wastewater using a bipolar disc stack reactor. The effluent for the present study was procured from a textile plant located in the southern region of India and the characteristics of the effluent are shown in Table 1.

Theory

An electrochemical reactor is a device that uses electrical energy to effect a chemical change. It has been carried out by the use of solution

conduction/electrode conduction at the interface between the electrodes and the solution. Normally an electrolyte must be added to enhance the electro-oxidation process.²⁹ In the present study, sodium chloride, present in the effluent at a concentration of about $32\,000\text{ mg dm}^{-3}$ was used as a supporting electrolyte and no excess electrolyte was added. Both hypochlorite and free chlorine generated *in situ* are strong oxidizing agents. Hence:



The reactor model can be derived by assuming that the bipolar disc stack reactor is under steady state conditions and also is an ideal Continuous Stirred Tank Reactor (CSTR). The performance equation for CSTR can be written as:³⁰

$$\tau_r = \frac{V_r}{Q} = \frac{C - C'}{(-r)} = \frac{C - C'}{KaC'} \quad (2)$$

where r is the rate of reaction and a is the specific electrode area. The a is given as

$$a = A/V_r$$

and C' is the concentration of dyestuff in the reservoir in terms of COD at time t .

Equation (2) can also be written as:

$$\frac{(\text{COD})'}{(\text{COD})} = \frac{1}{1 + (KA/Q)} \quad (3)$$

Table 1. Characteristics of the effluent

Serial No	Parameter	Value
1	Colour and type of effluent procured from textile industry	Procion Blue (reactive dye effluent)
2	Initial COD (ppm)	Around 3000
3	Chloride content (ppm)	32 000
4	Total dissolved solids (ppm)	12 000
5	pH	12
6	Suspended solids (ppm)	10 000

The material balance over the batch recirculation reactor can be written as:

$$V_R \frac{d(\text{COD})}{dt} = Q[\text{COD} - (\text{COD})'] \quad (4)$$

$$V_R \frac{d(\text{COD})}{dt} = Q \left(\frac{-[KA/Q](\text{COD})}{1 + (KA/Q)} \right) \quad (5)$$

Integration of eqn (5) leads to the following expression:

$$\ln \frac{(\text{COD})}{(\text{COD})_0} = \frac{-t}{\tau_R} \left(\frac{(KA/Q)}{1 + (KA/Q)} \right) \quad (6)$$

MATERIALS AND METHODS

The schematic diagram of the experimental set-up is shown in Fig 1 and the perspective view of the disc stack reactor is shown in Fig 2. The electrolytic cell is made up of Perspex and it consists of 11 electrodes. The electrodes used were ruthenium oxide coated on titanium as anode and titanium as cathode. The cell stack consisted of two frames and in between these two frames a hollow cylindrical Perspex rigid tube with internal diameter of 0.05 m and outer diameter of 0.06 m was placed. One titanium disc and another titanium disc having RuO₂ coating was placed at each end frame. These two discs acted as feeder electrodes and the remaining nine discs were arranged in between these two discs. The inner (*r*_o) and outer (*R*) radii of the disc are 5 mm and 24.5 mm respectively. Electrodes were isolated from each other by the spacer of 3-mm thick polypropylene bits. The top section of the reactor acted as cathode and bottom section acted as anode. The stack of circular electrodes had a 10 mm central hole through which the effluent flowed in and the overflow was collected from the top and again recirculated into the reactor. The total volume of the reactor and area of each disc were 0.04 dm³ and 0.18072 dm² respectively. The non-contacting magnetic pump was used for recirculation.

The efficiency of the electrochemical reactor was studied at various conditions such as different current densities, volumetric flow rates and reservoir hold-ups. The effluent was treated at three different current densities, viz 2.5, 5, or 7.5 A dm⁻² and the reservoir hold-up volume was 1.5, 2, or 2.5 dm³. The liquid flow rate into the reactor was varied (20, 40, 60, 80, or 100 dm³ h⁻¹). The flow rate of the effluent was measured by using a calibrated rotameter and the duration of electrolysis was 8 h. Samples were collected every 1 hour and were kept under acidic conditions. The samples were subjected to COD analysis and the analysis was made by strictly following the APHA method.³¹

The current efficiency (CE) of the electrolysis was evaluated based on the COD reduction and is defined as follows:^{32,33}

$$\begin{aligned} \text{CE}(\%) &= \frac{(\text{Decrease in COD})(\text{Volume of solution})}{(\text{Mass of oxygen equivalent to electricity})} \\ &= \frac{2F\Delta_{\text{COD}}V}{16It} \times 100 \end{aligned} \quad (7)$$

Therefore CE is given as

$$\text{CE}(\%) = \frac{(\text{COD})_t - (\text{COD})_{t+\Delta t}}{8It} FV \times 100 \quad (8)$$

Where (COD)_{*t*} and (COD)_{*t*+ Δt} are the chemical oxygen demands at times *t* and *t* + Δt (in grams of O₂ per dm³), respectively. The energy consumption for 1 kg removal of COD was calculated and reported in kWh.

RESULTS AND DISCUSSION

The amount of sodium chloride present in the textile dye effluent from the reactive dye processing unit was found to be 32 000 mg dm⁻³. Sodium chloride is mainly added to improve the efficiency of the dyeing process and the amount added is dependent on the nature of the dye. Vlyssides and Israllides²⁶ reported an investigation into the effects of not adding NaCl and HCl during the treatment of textile wastewater, showed minimal (2%) COD reduction. Hence, in the present investigation sodium chloride present in the effluent was used as a supporting electrolyte to enhance the COD reduction and the efficiency of the electrolyte was found to be significant. During the present investigation the operating parameters such as flow rate, current density and electrolysis time were varied to explore the effect of such parameters on COD removal. Results showed that higher COD reduction occurred at higher charge input and electrolysis time. The oxidation of organic compounds present in the effluent is mainly due to the generation of hypochlorite and free chlorine. The published literature^{29,34} reported that the production of such species was not affected by the initial pH conditions. Hence the initial pH of the effluent was not varied during the present investigation and all the experiments were carried out at the initial pH of the real effluent procured from a textile plant.

To enumerate the effect of current density on COD reduction, the current density was varied (2.5, 5, 7.5 A dm⁻²). The current density is defined as the ratio of current input to the electrolytic cell to the surface area of the electrode. The current supplied to the electrochemical reactor is usually expressed by current density and the applied current can be easily expressed as in terms of current density. Figure 3 shows the effect of current density on the removal of COD. The result showed that the current density influences the COD reduction and increased current density increases the reduction of COD. Figure 3 also shows that the flow rate of dye effluent into the reactor remarkably affected the reduction of COD. Higher flow rates showed significant reduction of COD and this may be due to the increased production of oxidants in the process. During the present investigation it was found that the power consumption for one kg of COD removal had increased remarkably with increase in current density. Figure 4 exhibits the effect of current density on power consumption per kg of COD reduction. The

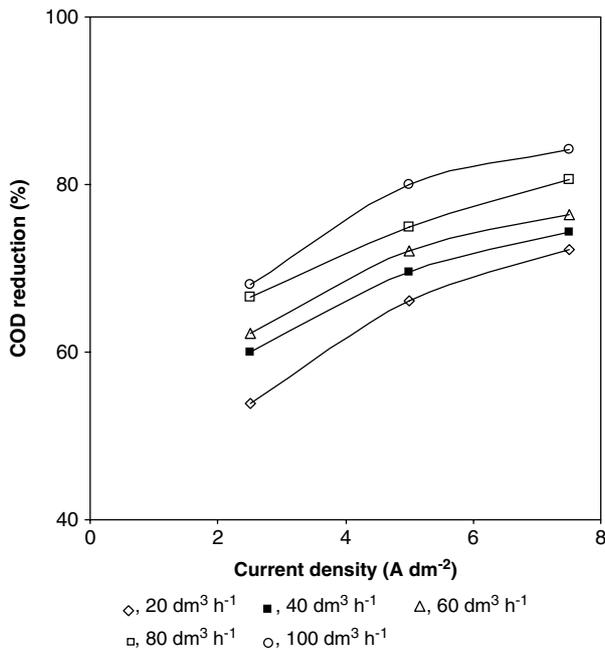


Figure 3. Effect of current density on COD reduction (reservoir volume = 1.5 dm³).

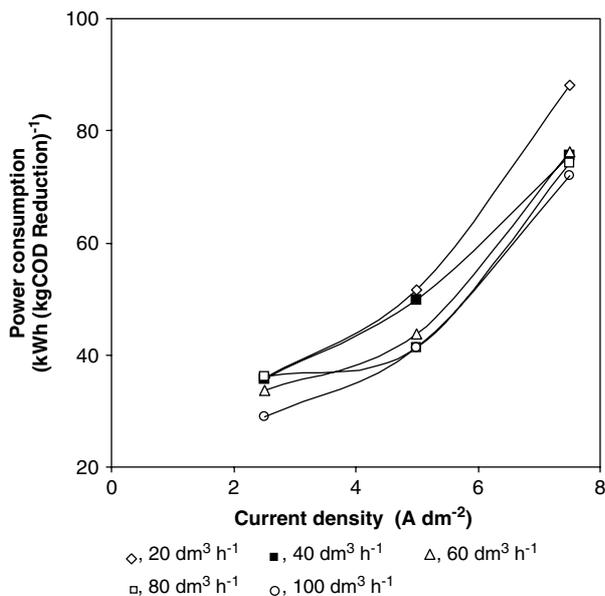


Figure 4. Effect of current density on power consumption (reservoir volume = 2 dm³).

results showed that the higher power consumption of 88.125 kWh per kg of COD removal was found to be obtained at a current density of 7.5 A dm⁻², reservoir volume of 2 dm³ and flow rate of 20 dm³ h⁻¹ and the COD reduction attained during these conditions was 72.2%.

The results also showed that the flow rate of effluent into the reactor also significantly influenced the power consumption. The flow rate of 20 dm³ h⁻¹ was found to produce higher power consumption per kg of COD removal and also it was found that the power consumption per kg of COD removal decreased as the

flow rate into the reactor increased. The higher power consumption leads to higher operating cost, and lower current density may increase the electrolysis time. Therefore the operation of the electrochemical reactor at optimized current density and flow rate is essential to reduce the operating cost of the process. From the experimental parameters studied, the optimum current density and flow rate were found to be 5 A dm⁻² and 80 dm³ h⁻¹. The reservoir hold-up does not have significant influence on power consumption. Figure 5 shows the effect of the flow rate of the effluent into the reactor on current efficiency during electrochemical oxidation of dye-containing effluents. It can be seen that the current efficiency increases with increase in flow rate and also increasing the current density greatly increased the current efficiency. During the investigation the higher current efficiency of 14.56% was found to be offered by the current density of 7.5 A dm⁻².

Figure 6 shows the effect of electrolysis time on COD reduction. The results showed that the reduction of COD increased with the increase in electrolysis time. Figure 6 also witnessed that the reduction of COD increased as the flow rate of the effluent increased. Figure 6 also shows the comparison between experimental and predicted COD reduction values. The reduction of COD is predicted by using eqn (6). In Fig 6, thick lines represent the predicted values and symbols denote the experimental values. The prediction of COD reduction from eqn (6) is found to be matched closely with the experimental values. The reservoir volume greatly influenced the efficiency of the recirculation reactor. Hence the amount of effluent charged into the reservoir of the reactor was varied (1.5, 2, 2.5 dm³) to enumerate their effect on the reduction of COD. The effect of reservoir volume on COD reduction is shown in Fig 7. The results illustrate that the higher reservoir volume

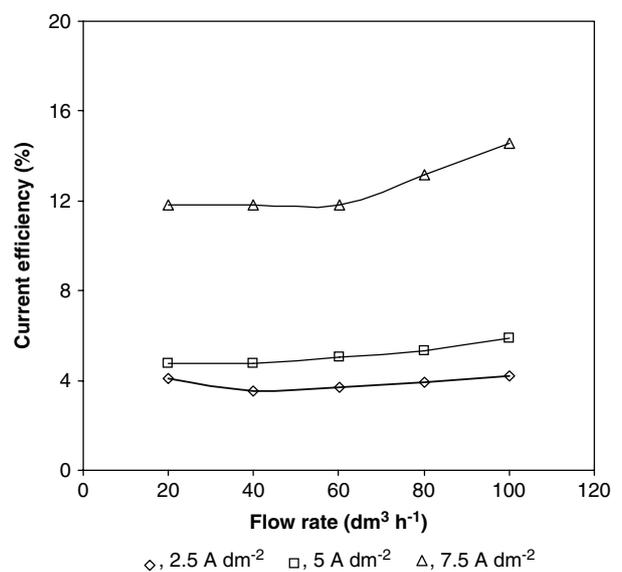


Figure 5. Effect of flow rate on current efficiency (reservoir volume = 1.5 dm³).

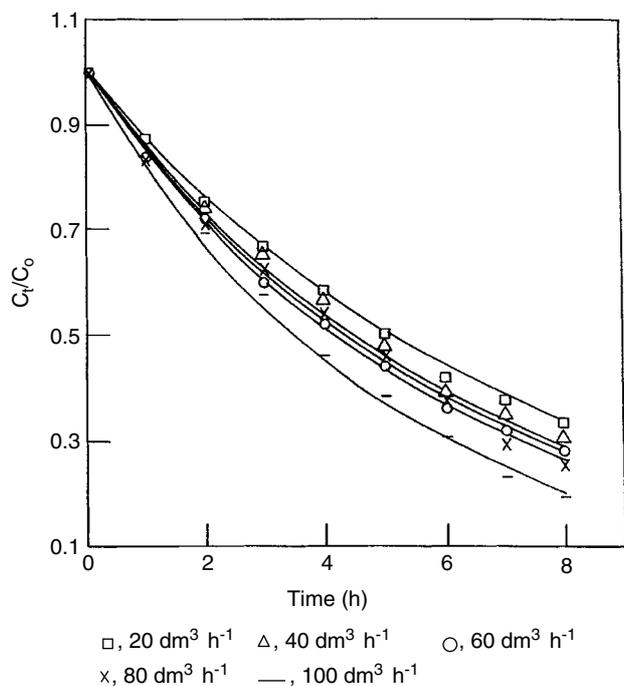


Figure 6. Effect of electrolysis time on COD reduction (reservoir volume = 1.5 dm³; current density = 5 A dm⁻²).

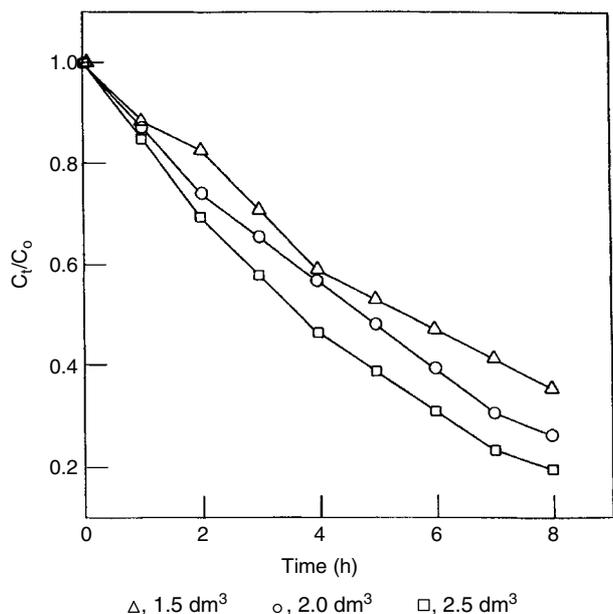


Figure 7. Effect of reservoir volume on COD reduction (flow rate = 20 dm³ h⁻¹; current density = 7.5 A dm⁻²).

decreased the reduction of COD. Hence the reactor must be operated at optimum reservoir volume.

According to eqn (6), the slope of the plot $\ln[(COD)_t/(COD)_0]$ versus time gives the value of the pseudo mass transfer coefficient and the results obtained are shown in Fig 8. The results showed that the higher mass transfer coefficient values occurred at higher current densities. The increase in flow rate of effluent into the reactor significantly increased the value of the mass transfer coefficient and the increase in the mass transfer coefficient resulted in faster COD reduction. The highest mass transfer coefficient

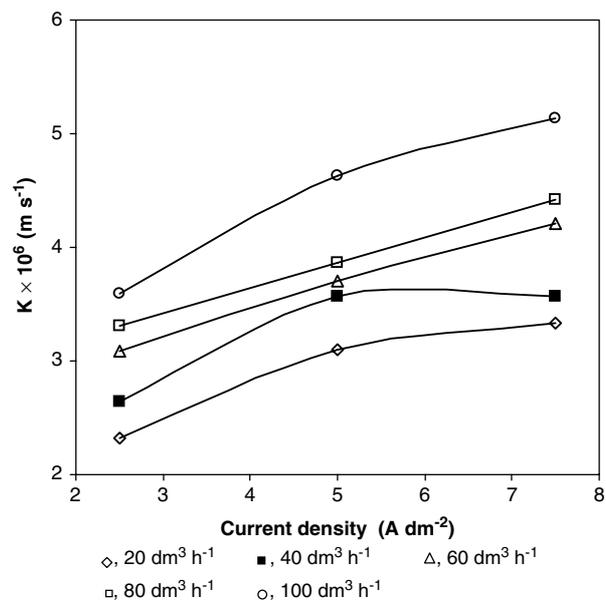


Figure 8. Effect of current density on mass transfer coefficient (reservoir volume = 1.5 dm³).

Table 2. Purity of colour

Serial No	Parameter	Value	
		Untreated	Treated
1	Colour	Blue	Very light greenish yellow
2	Purity	65%	10%

values were found to be obtained at a flow rate of 100 dm³ h⁻¹.

The purity of the colour was determined by using a spectrophotometric technique.³¹ Table 2 give the results obtained for both treated and untreated effluents. The purity of the colour was found to be reduced from 65% to 10%. The results of the spectrophotometric technique showed that the colour reduction by using electro-oxidation technique is significant.

CONCLUSION

From the results obtained it can be concluded that the electrochemical bipolar disc stack reactor can be effectively used for the treatment of textile dye wastewater. The electro-oxidation of textile dye wastewater by *in situ* generation of hypochlorite and free chlorine significantly reduced the COD and colour. The optimum operating conditions arrived at by considering maximum COD reduction and less power consumption were 80 dm³ h⁻¹ flow rate and a 5 A dm⁻² current density. The reactor model proposed postulates that the mass transfer of the process depends on the rate of generation of active species in the electrochemical reaction. The flow rate of effluent into the reactor significantly affected the reactor performance. The increase in flow rate and current density significantly increased the reduction

of COD. The ion exchange resin treatment may be adopted for the removal of total dissolved solids present in the effluent. An attempt also may be made to produce hypochlorite from textile dye wastes.

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