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Removal of Indigo Carmine Dye from Synthetic Wastewater by Electrochemical Oxidation in a New Cell with Horizontally Oriented Electrodes

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The electrochemical oxidation of a synthetic wastewater containing indigo carmine dye was investigated using a new cell with horizontally oriented electrodes. The study dealt with colour removal and chemical oxygen demand (COD) reduction using an array of Pb/PbO_2 cylinders as anode and stainless steel screen as cathode in a batch recycle electrochemical unit. Operating variables such as current density, initial dye concentration, NaCl concentration, pH, and solution flow rate were investigated. The results indicate that complete decolourization and 88.2% COD reduction can be achieved under the optimum operating conditions. Kinetic study at different flow rates has shown that decolourization takes place through a first order diffusion controlled reaction. Energy consumption was calculated at different operating parameters. The use of horizontally oriented array of lead cylinders as anode has the potential of acting also as a built-in heat transfer facility to control the cell temperature especially in case of large scale cells where heat generation could adversely affect the process via increasing lead solubility and decreasing the current efficiency of Cl_2 generation.

Keywords: Pb/PbO_2 anode; Anodic oxidation; Decolourization; Dyes; COD

1. INTRODUCTION

Over the last few decades, society has become increasingly sensitive towards the protection of the environment against potential adverse effects of the chemical industry on the environment. The effluent water from carpet manufacturing, dyeing, textile, pulp and paper industries contains various types of dyes which should be removed before discharging the effluent to the environment to avoid health hazards and destruction of the ecosystem [1]. Dyes are highly visible material. Thus even minor release into the environment may cause the appearance of colour, for example in open waters, which attracts the critical attention of public and local authorities.

There is thus the requirement on industry to minimize environmental release of colour, even in cases where a small but visible release might be considered as toxicologically rather innocuous.

The industrial dye compounds are often suspected to be carcinogens [2]. In addition, colour interferes with the transmission of sunlight into the stream and therefore reduces photosynthetic action. Since dyes usually present high stability under sunlight and resistance to microbial attack and temperature, the large majority of these compounds are not degradable in conventional wastewater treatment plants. The search for a powerful tool to decolourize and degrade dyeing wastewaters to decrease their environmental impact has then attracted increasing interest over the past two decades [3].

Many researchers have studied different techniques for removal of coloured dye from wastewater, e.g., micellar enhanced ultrafiltration [4], several oxidation processes [5-9], ozonations [10-12], nanofiltration [13-16], adsorption onto agricultural solid waste [17], different bentonites [18], various types of activated carbon [19,20], and surfactant impregnated montmorillonite [21], coagulation [22-24], biological treatments [25-27] etc. Ultrafiltration (UF) and nanofiltration (NF) can be used for complete removal of all classes of dye, but care is needed to avoid membrane fouling which decreases the flux. Due to low biodegradability of dyes, the conventional biological wastewater treatment process is not very efficient in treating dye containing wastewater [28].

In recent years, the electrochemical technique has gained wide acceptance as a powerful alternative for wastewater remediation. It currently offers promising approaches for the prevention of pollution problems from industrial effluents. The application of electrochemistry to environmental pollution abatement has been the topic of several books and reviews [29-39]. The main advantage of this technology is its environmental compatibility, due to the fact that its main reagent, the electron, is a clean reagent [30]. Other advantages are related to its versatility, high energy efficiency, amenability of automation and safety because it operates at mild conditions [30, 34, 37]. The strategies of electrochemistry include both the treatment of effluents and waste and the development of new processes or products with less harmful effects, often denoted as process-integrated environmental protection.

Electrochemical oxidation or electro-oxidation (EO) is the most popular electrochemical procedure for removing organic pollutants from wastewaters [30, 32, 34, 37]. This technique has been recently used for decolourizing and degrading dyes from aqueous solutions. Electrochemical oxidation of pollutants can be take place through two different oxidation mechanisms: (1) direct anodic oxidation, where the pollutants are destroyed at the anode surface; (2) indirect oxidation where a mediator is electrochemically generated to carry out the oxidation. In presence of chloride, oxidation of organic compounds is mediated by active chloro species. The main reactions at the electrodes are [40]:

$$\text{Anode: } 2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (1)$$

$$\text{Cathode: } 2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (2)$$

In the solution bulk Cl_2 hydrolysis takes place as follows

$$Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^- \qquad (3)$$

$$HOCl \longleftrightarrow H^+ + OCl^- \qquad (4)$$

At the anode O_2 evolution competes with Cl_2 evolution according to the reaction:

$$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e \qquad (5)$$

The generated hypochlorite ions act as main oxidizing species in the degradation of dye present in the effluent. The overall desired reaction may be written as [41]:

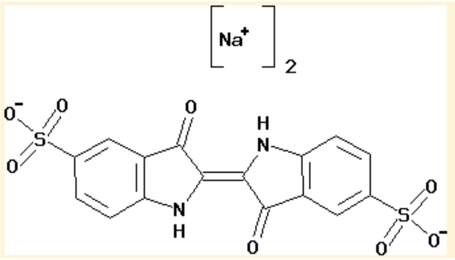
$$\text{Dye} + OCl^- \longrightarrow \text{intermediates} \longrightarrow CO_2 + Cl^- + H_2O \qquad (6)$$

In the present work a new batch recycle electrochemical oxidation cell was used to remove indigo carmine dye from wastewater. An array of horizontally oriented cylinders made of lead/ lead dioxide was used as anode, the cathode was made of two horizontal stainless steel screens, an upper screen and a lower screen to ensure uniform current distribution at the anode. Lead dioxide anodes have a long history of use as electrode materials for the oxidation of organics because of their good conductivity and large oxygen overpotential, this properly favours incineration of organics [3] with high current efficiency. The present cell design offers the following advantages:- (i) the internal surface of the lead cylinders can be used potentially in practice as a heat exchanger where a cooling fluid is passed to absorb excess heat generated during electrolyses in order to minimize Pb^{++} dissolution and to prevent the decrease in oxygen overpotential which leads to decreasing the current efficiency of Cl_2 generation. (ii) H_2 bubbles evolved at the lower screen cathode contributes to improving the rate of mass transfer and the mixing conditions at the horizontal lead cylinder anode [42] with a consequent increase in the rate of dye oxidation.(iii) the use of a screen cathode below the tube array anode improves the mixing conditions at the anode by virtue of the turbulence generated downstream of the screen cathode[43]. The influence of the main operating parameters, such as current density, flow rate, dye concentration, NaCl concentration, initial pH on colour removal and COD reduction has been investigated. Literature survey shows that no previous studies have been reported on the removal of dyes using the present new cell.

2. EXPERIMENTAL TECHNIQUE

Indigo carmine dye was used for the preparation of synthetic dye solution. The dye was obtained from Alpha chemika, Mumbai, India. The chemical structure and some characteristics of dye are given in Table 1. Sodium chloride, dye, sulfuric acid and sodium hydroxide used were of analytical grade. Distilled water was used to prepare the desired concentration of dyestuff solution.

Table 1. Properties of Indigo Carmine dye

Chemical structure	
Molecular formula	$C_{16}H_8N_2Na_2O_8S_2$
Molar mass	466.36 g/mol
C.I.Number	C.I. 73015
Absorption maximum (water)	608 - 612 nm
CAS number	860-22-0
Bulk density	700 - 900 kg/m^3

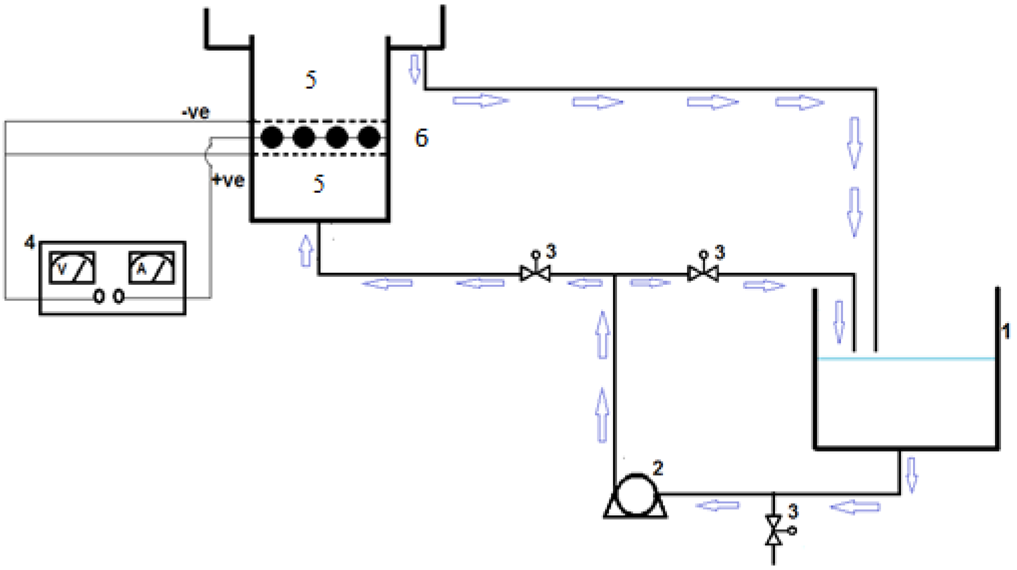


Figure 1. Electrochemical oxidation unit (1. Storage tank; 2. Centrifugal pump; 3. Valve; 4. D.C power supply; 5. Stainless steel screen cathode; 6. An array of lead cylinders (anode))

The Pb/PbO_2 electrodes were prepared by anodic oxidation of lead at a current density of 10 mA/cm^2, in a 10% sulphuric acid solution and 25°C, during 90 min according to the following reactions [44] :

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e \qquad (7)$$

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e \qquad (8)$$

The experimental setup is shown in figure 1. It consisted of a rectangular cell, flow circuit and electrical circuit. The cell was plexiglass container of 11 cm × 11 cm square base and 15 cm height. The anode was made of an array of separated horizontal cylinders and positioned at the center of the cell. The cylinder length was 12 cm and 1.5 cm diameter. The distance between each cylinder was 1 cm. The cathode consisted of two stainless steel screens (mesh no10) one is placed above and the other below the anode at a distance 0.5 cm. Stainless steel was used as a cathode in view of its stability in the solution. Besides, the screen cathode acts a turbulence promoter and improves the mixing efficiency of the cell. The flow circuit consisted of 8 L glass storage tank and 0.125 hp plastic centrifugal pump to circulate the solution between the storage tank and the cell. The solution flow rate was measured volumetrically by means of a graduated cylinder and a stopwatch. A by-pass is used to control the flow rate. All valves were made of plastic. The electrodes were connected to a dc power supply (20V, 10A) with a voltage regulator and a multi-range ammeter connected in series.

Before the beginning of each run, 5 liters of dyestuff solution was placed into the electrochemical unit after mixing with the appropriate amount of a sodium chloride. The pH of the solution was measured by pH meter and adjusted by adding sodium hydroxide or hydrochloric acid solutions. Solution flow rate was controlled by a manual valve. The current density was adjusted to the desired value by using the power supply regulator. Samples were collected every ten minutes during each run, using a 10 ml pipette. Each run lasted for 60 minutes giving 6 samples. All the experiments were performed at room temperature.

The dye concentration was determined using UV-vis spectrophotometer (Labomed, USA) with the calibration method at maximum wavelength of 610 nm. The colour removal efficiency in the treatment experiments was calculated as follows:

$$\%\ \text{Colour Removal} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (9)$$

Where C_o and C_t are the initial dye concentration and concentration of dye at time t in solution (mg/l), respectively.

The chemical oxygen demand (COD) was measured by a volumetric analytical method [45].

3. RESULTS AND DISCUSSIONS

Different current densities (4.42, 8.85, 13.27 and 17.69 mA/cm^2) were used to study the electrochemical degradation of indigo carmine dye in synthetic solution. In agreement with previous studies the amount of hypochlorite produced increased with increasing applied current density [46] with a consequent increase on the rate of dye removal as shown in Fig.2.

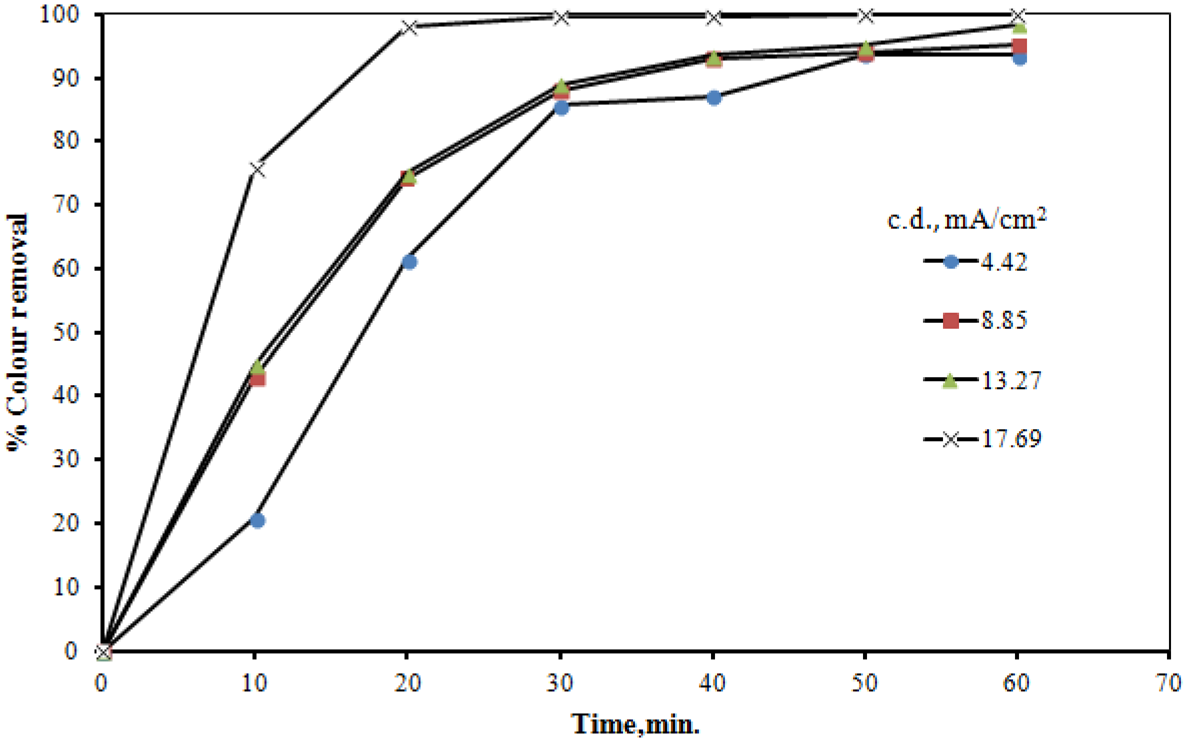


Figure 2. Effect of current density on % Colour removal
(C_0=50 mg/l, NaCl =1g/l,pH=7,flow rate =285 ml/min,Temperature =23±2 ˚C)

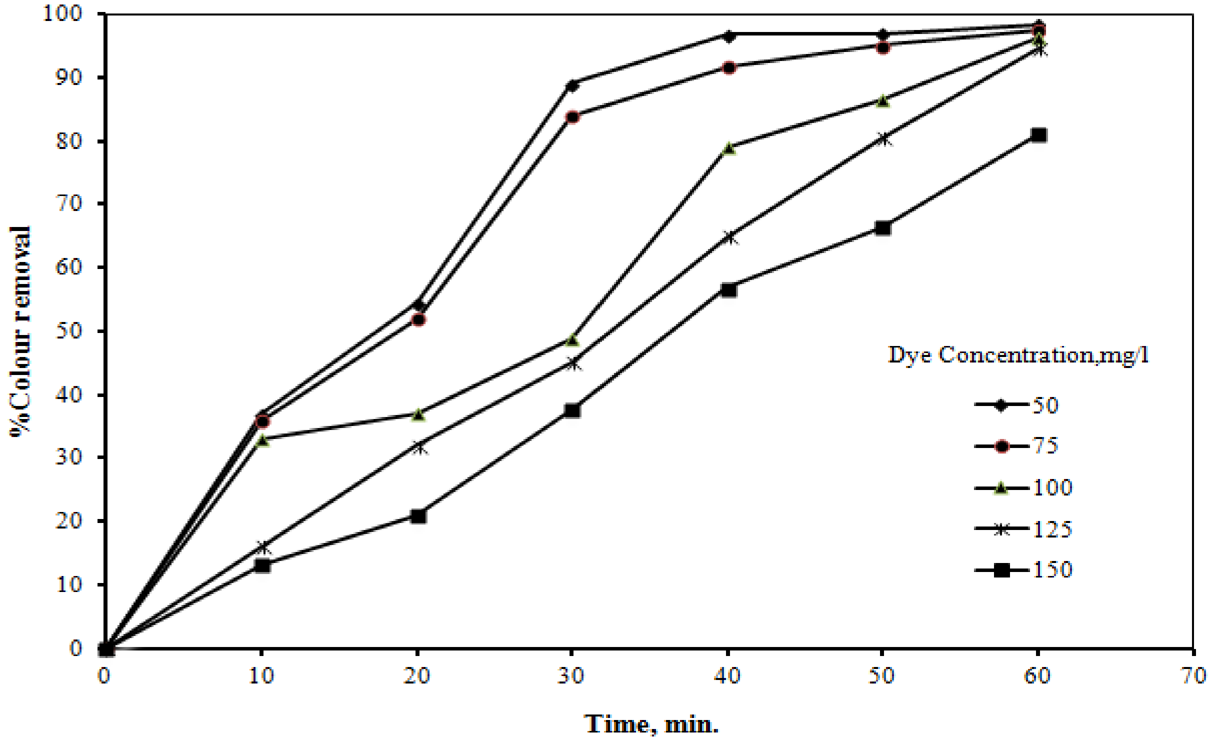


Figure 3. Effect of Initial dye concentration on % Colour removal
(NaCl=1g/L,pH=7,c.d = 13.27mA/cm^2,Temperature=23±2 ˚C,Flow rate =285ml/min)

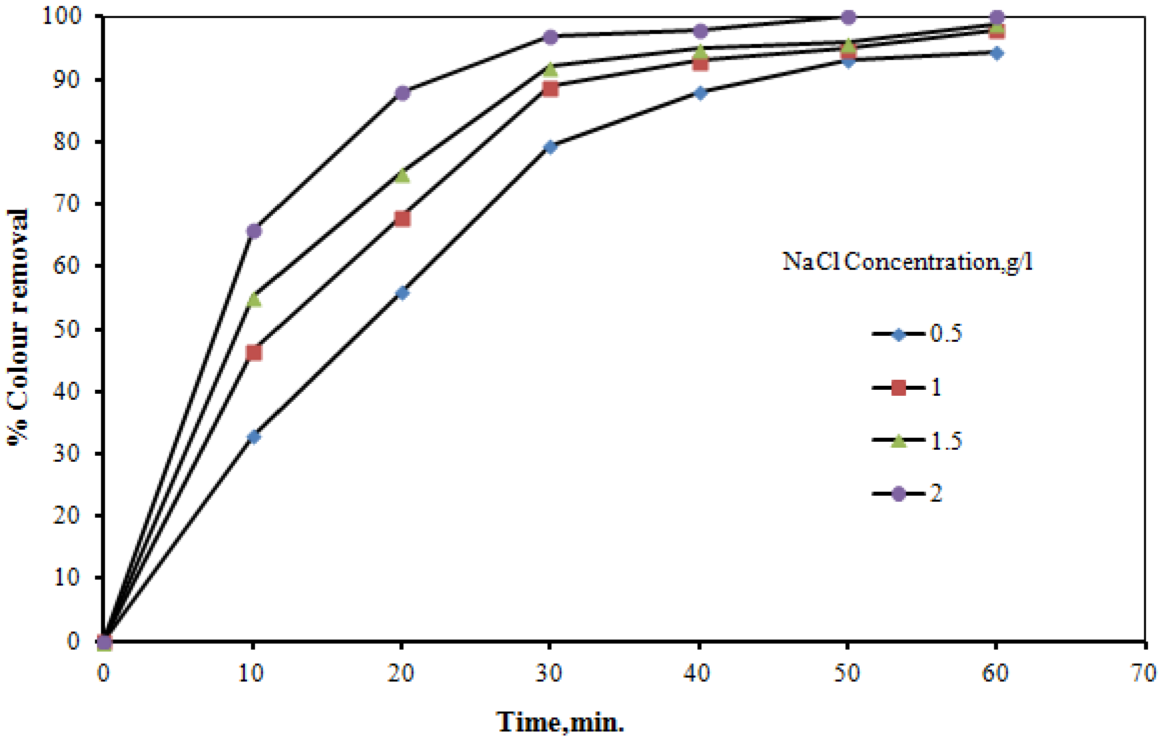


Figure 4. Effect of NaCl concentration on % Colour removal
(C_0=50mg/L pH=7,c.d = 13.27mA/cm^2,Temperature =23±2 ˚C,Flow rate =285ml/min)

The influence of the initial dye concentration on decolourization process was studied at broad range of dye concentration (50–150 mg/L). Fig. 3 shows that the rate of dye decolourization decreased with increasing dye concentration. This may be explained by the fact that the ratio Cl_2/OCl^- to the initial dye concentration decrease at a given current density [41]. Also, by increasing dye concentration, dye molecules tends to associate to larger molecules of low diffusivity, this lowers the rate of dye diffusion to the anode surface with a consequent decrease in dye removal rate [47].

Fig.4. depicts the effect of NaCl concentration on the rate of dye removal. It is obvious that increasing chloride concentration increases the rate of removal of the dye. This may be ascribed to the fact that as the concentration of NaCl electrolyte increases the current efficiency of Cl_2 discharge increases at the expense of O_2 evolution as a result of the decrease of the discharge potential of Cl_2 with increasing Cl^- concentration according to Nernst equation [48]. The variation of initial pH on the colour removal of indigo carmine dye during electrochemical oxidation is shown in Fig.5. It is clear that, in acidic medium the rate of colour removal increase and this is may be due to (i) the increasing of chlorine/hypochlorite and in low pH chlorine is present in the solution in the form of hypochlorous acid, which possesses higher oxidation potential than that of hypochlorite [49]. No experiments have been done in basic solution to avoid the release of toxic lead ions.(ii) acidity increase the discharge potential of O_2 according to Nernst equation and hence increases the current efficiency of Cl_2 discharge and the rate of dye oxidation.

Fig. 6 shows the effect of solution flow rate on the rate of dye oxidation, the data show that the rate of dye removal increases with increasing solution flow rate, this indicates that the dye oxidation on Pb/PbO_2 is a mass-transfer controlled process.

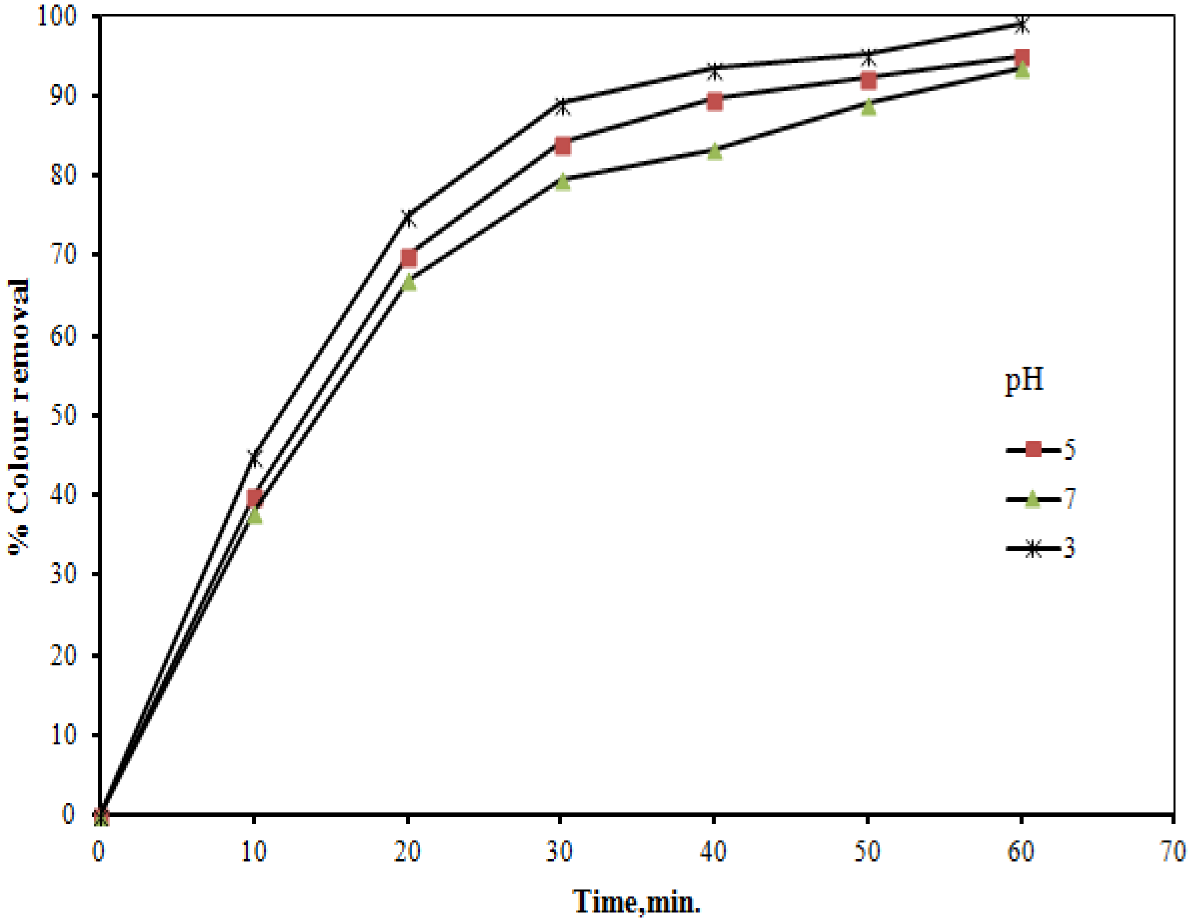


Figure 5. Effect of pH on % Colour removal
(C_0=50mg/L, NaCl=1g/l,c.d = 13.27mA/cm^2,Temperature=23±2 ˚C,Flow rate =285ml/min.)

Similar results were also obtained by Yavuz et al. [50]. It should be added that mass transferred at the horizontal anode under the present conditions by two means, namely: (i) upward solution flow past the cylinders leads to boundary layer separation and the turbulent wake formation behind the horizontal cylinder, the generated turbulence increases the rate of mass transfer and the rate of the diffusion controlled dye oxidation via thinning the diffusion layer surrounding the cylinders [51]. (ii) the upward rising cathodic H_2 bubbles collide with the anode surface and disturb the diffusion layer surrounding the anode with a consequent increase in the rate of mass transfer [42] and the rate of dye oxidation. (iii) the use of screen cathode below the anode generate turbulence which enhances the rate of mass transfer at the downstream cylindrical array anode [43].

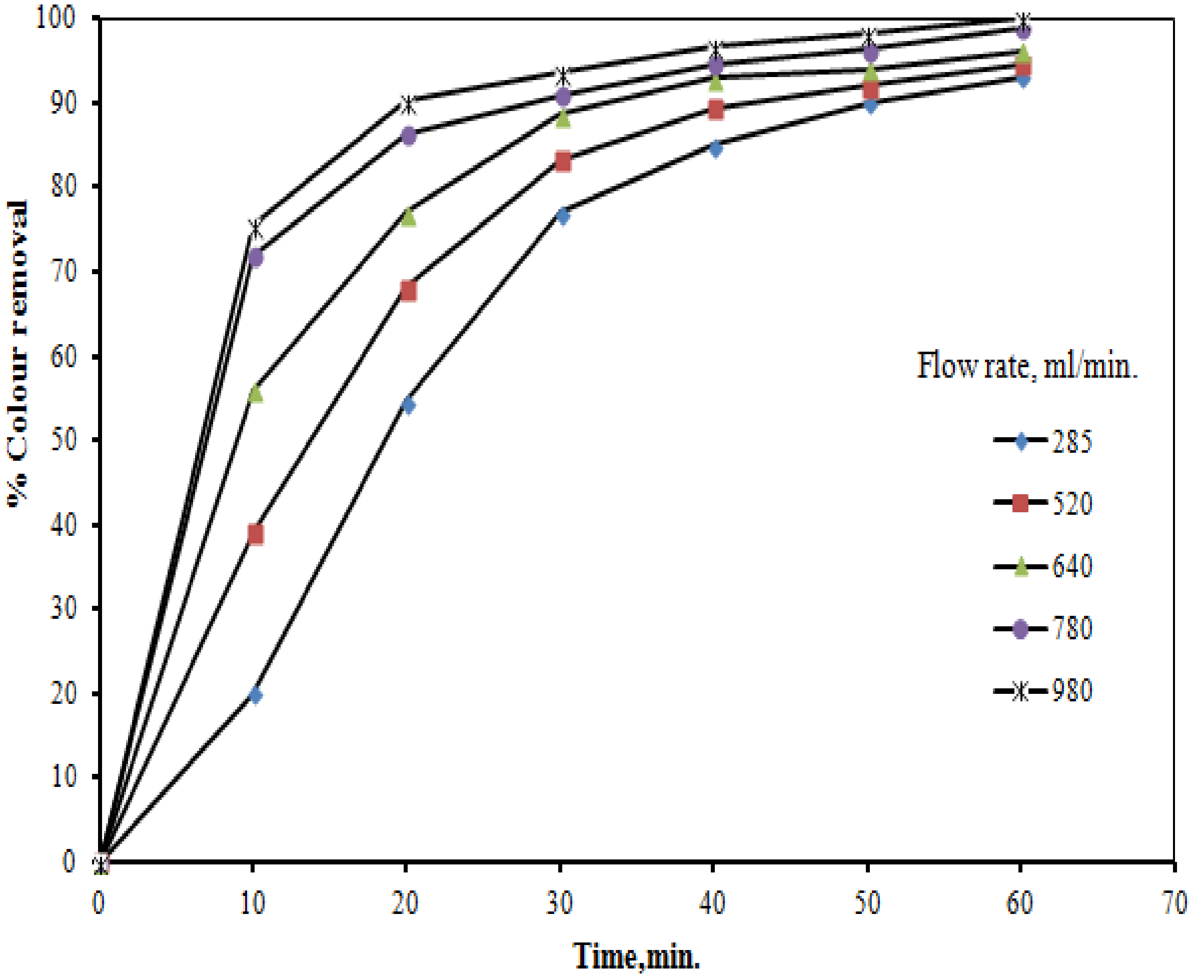


Figure 6. Effect of solution flow rate on % Colour removal
(C_0=50 mg/l,NaCl=1g/l, pH=7,c.d= 13.27mA/cm^2,Temperature=23±2 ˚C)

It is noteworthy that in contradistinction to the early stage of dye oxidation, the rate of dye oxidation during the last stages of the process becomes less sensitive to solution flow rate probably because the effect of anodically evolved Cl_2 bubbles on the rate of mass transfer becomes more pronounced.

Chlorine bubble evolution at the anode surface generates strong eddies [52-54] which contribute along with forced convection and the effect of cathodically generated H_2 bubbles to enhancing the rate of mass transfer and dye oxidation at the anode.

In this work, COD results were taken as one of the parameters to judge the feasibility of the electrochemical oxidation process for the treatment of coloured dye effluent. Usual open reflux method was applied for the COD determination and the treated solution showed a significant reduction in COD value with the increase in current density, solution flow rate and sodium chloride concentration. The percentage COD reduction decreases with the increase in initial dye concentration and initial pH of dye solution. Table 2 shows the percentage COD reduction at different operating conditions.

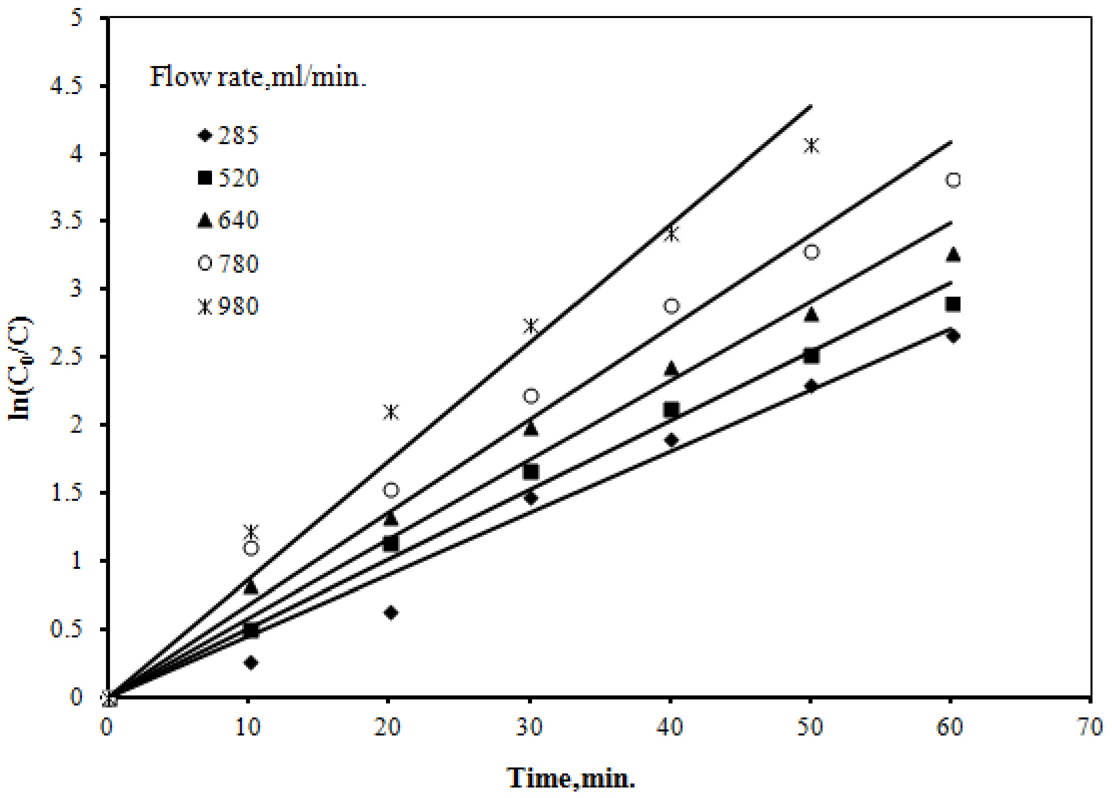


Figure 7. $\ln(C_0/C_t)$ Vs time at different flow rate

Table 2. COD measurements at different operating conditions

COD reduction, %	c.d, mA/cm^2				NaCl concentration, g/l				Flow rate, ml/min.					pH			Dye concentration,mg/l				
	4.42	8.85	13.27	17.69	0.5	1	1.5	2	285	520	640	780	980	3	5	7	50	75	100	125	150
	49.6	62.5	79.3	85.9	70.2	79.3	81.1	83.3	79.3	80.4	82.8	84.1	88.2	85.7	82.1	79.3	79.3	78	77	75.2	65.5

In an attempt to correlate the present data with a kinetic equation a first-order reaction was assumed, fig. 7 shows that the present data fit the equation:

$$\ln\left[\frac{C_0}{C_t}\right] = K\ t \tag{10}$$

Which is the integrated form of the equation:

$$-Q\frac{dc}{dt} = K^{-}A\,dt \tag{11}$$

Where $K = \frac{K^{-} A}{Q}$

A is the electrode area (cm^2).
C_o, C_t are the initial and residual concentration of dye solution (mg/l).
K is the rate constant (min^{-1}).
K^{-} is the mass transfer coefficient (cm/min).
Q is the volume of the solution (cm^3)

The value of rate constant is shown in table 3, the increase in K with volumetric flow rate confirms the diffusion controlled nature of the dye removal reaction.

Table 3. Values of rate constant at different flow rate

Flow rate,ml/min.	285	520	640	780	980
Rate constant, min^{-1}	0.995	1.12	1.28	1.5	1.92

Finally, an estimation of the energy consumption (kWh/kg dye removed) during electrochemical oxidation of a solution containing indigo carmine dye was calculated according to the following equation [55]:

$$\text{Energy consumption (kWh/kg dye removed)} = \frac{V\, I\, t \times 10^3}{60(C_o - C_t) \times treated\ \ volume(l)} \quad (12)$$

where V is the cell voltage (V), I is the current (A), t is the electrolysis time (min.), C_o and C_t are the initial dye concentration and concentration at time t (in mg/l). The results showed that the energy consumption increases with increasing current density and decreases with increasing NaCl concentration and solution flow rate. Table 4 presents the values of energy consumption at various operating parameters.

Table 4. Energy consumption during the electrochemical treatment of dye solution at various conditions

Energy consumption, kWh/kg dye removed	c.d, mA/cm^2				NaCl concentration, g/l				Flow rate, ml/min.				
	4.42	8.85	13.27	17.69	0.5	1	1.5	2	285	520	640	780	980
	9.72	11.1	13.7	16.2	16.8	13.7	11.2	9.89	13.7	12.8	12.4	11.9	11.6

4. CONCLUSIONS

Electrochemical oxidation of indigo carmine dye was carried out in a new cell with a horizontally oriented electrodes; the anode which is an array of horizontal Pb cylinders is located between two horizontal screen cathodes. This geometry allows the use of the inner side of the anode cylinders as a heat exchanger to remove excess heat from the cell especially in large scale cells where the considerable heat generation could adversely affect the process via increasing lead anode dissolution and decreasing oxygen overpotential on Pb. This design also benefits from the cathodically evolved H_2 bubbles in enhancing the rate of heat and mass transfer at the cylinder anode. Furthermore the use of screen cathode upstream the array anode generate turbulence which contribute to enhancing the mixing conditions at the anode. The influence of current density, initial dye concentration, NaCl concentration, pH, and solution flow rate on the % colour removal and COD reduction was investigated. The results showed that the colour removal and COD reduction increase with the increase in current density, NaCl concentration, and solution flow rate while they decrease with the increase in pH and initial dye concentration. The results showed that the present data fit a pseudo first order kinetic model for the process.

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