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Decolorization of Acid Brown and Reactive Blue Dyes by Anodic Oxidation in a Batch Recycle Electrochemical Reactor

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Decolorization and COD measurements of synthetic wastewater containing acid brown and reactive blue dyes were studied using a batch recycle annular electrochemical reactor. Graphite rod was used as anode while stainless steel screen was used as cathode. The effect of current density, sodium chloride concentration, initial dye concentration, pH and solution flow rate on color removal and COD reduction was evaluated. The results indicate that 100% color removal and 89 % in COD reduction can be achieved under suitable conditions. Energy consumption ranged from 1.2 to 10.4 kWh/kg COD removed depending on the operating conditions. These results recommend considering the present electrochemical oxidation technique to treat wastewater containing dyes.

Keywords: Anodic oxidation; wastewater; dyes; COD; Textile effluents; Annular electrochemical reactor

1. INTRODUCTION

Over the last few decades, society has become increasingly sensitive towards the protection of the environment. Due to this problem, mankind nowadays has concern about the potential adverse effects to the chemical industry on the environment, although the response in some parts of the world has been much faster and more intense than in others. The world annual production of dyes is estimated at more than 80000 tons used mainly in food industries, cosmetics, paper mills and especially in textile industries which absorb alone more than 70% of the produced total quantity. The intense use of the synthetic dyes in these various industries generates sources of considerable pollution of the environment. Indeed, 10 to 15% of the quantity of dyes used is rejected into the natural environment. These dyes constitute because of their toxicity a potential danger to both Man and environment [1]. The presence of dyes in textile effluents is common and highly visible. Depending on the type of dyestuff used, the colour of the wastewater can change from day to day, or even several times a day because the dyestuff used in the dyeing process changes frequently due to customer's requirements. The large pH swing in the textile wastewater (can change from 2 to over 12) is another strong negative point. This variation is primarily caused by different kinds of dyestuff used in the dyeing process. As most dyes usually occur at low concentrations, it may be presumed that removing it from wastewater is not particularly difficult [2]. The research of powerful and practical treatments to decolorize and degrade dyeing wastewaters to decrease their environmental impact has then attracted increasing interest over the past two decades. An extensive literature reporting the characteristics and applications of most important conventional technologies developed for this purpose including physico-chemical and chemical methods, advanced oxidation processes (AOPs), microbiological treatments and enzymatic decomposition, has been collected in several critical reviews [3]. In contrast, only little information on the interest of electrochemical technologies for destroying dyes from wastewaters has been shown in some previous reviews [3], without considering the recent advances of these promising methods.

The electrochemical treatment has been receiving greater attention in recent years due to its unique features, such as versatility, energy efficiency, and automation and cost effectiveness [4]. The electrochemical treatment of textile dye wastewater has also been studied using cast iron , boron doped diamond (BDD), Pt/Ti , Ti/RuO2,Ti/Pt/Ir, active carbon fiber (ACF), stainless steel 304 and graphite carbon electrodes. Graphite was frequently used as an anode for the electrochemical degradation of textile wastewater as it is relatively cheaper and gives satisfactory results [4]. In an indirect electrochemical oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant [5]. In presence of chloride, oxidation of organic compounds is mediated by active chloro species. The main reactions at the electrodes are [5]:

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

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

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 aim of this work was to study the performance of a batch recycle electrochemical oxidation unit, a simple annular cell composed of a central graphite rod anode surrounded with a stainless steel screen cathode, to remove acid brown and reactive blue dyes from wastewater. The influence of the main operating parameters, such as current density, flow rate, dye concentration, NaCl concentration, initial pH on color removal and COD reduction has been investigated.

2. EXPERIMENTAL TECHNIQUE

Commercially available acid brown and reactive blue dyes were obtained from Isma dye company, Kafr El Dawar, Egypt. Its chemical structure are $C_{30}H_{20}N_8Na_2O_{12}S_2$ (M.wt = 794.63) and $C_{22}H_{16}$ N_2 $Na_2O_{11}S_3$ (M.wt = 626.56) for acid brown and reactive blue dyes respectively . Distilled water was used to prepare the desired concentration of dyestuff solution.

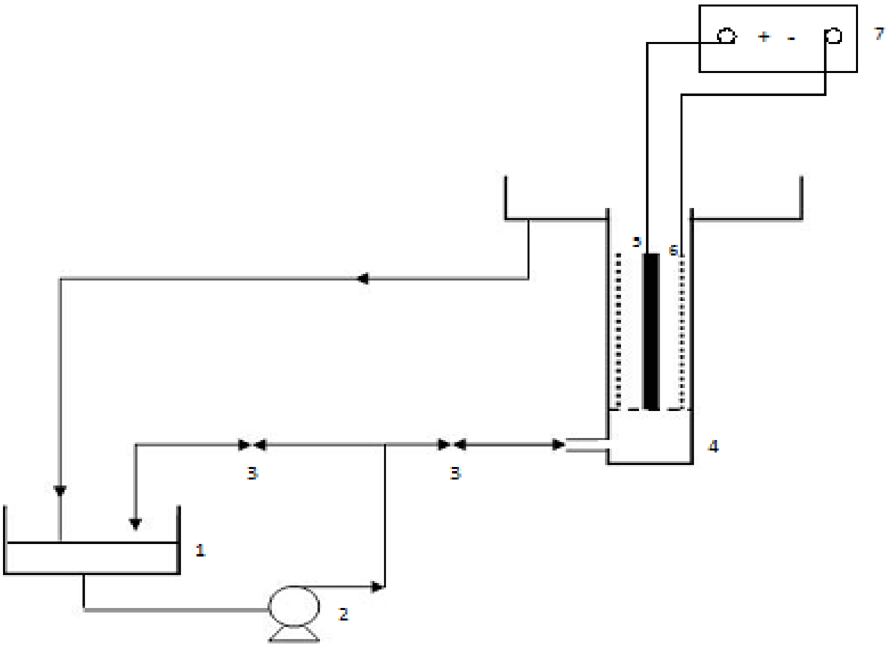

Figure 1. Electrochemical oxidation cell 1. Storage tank 2. Centrifugal pump 3. Valve 4. Cylindrical plexi glass column 5. Graphite rod anode 6. Stainless steel cathode 7. D.C.power supply

The experimental setup is shown in figure 1. It consisted of a vertical cylindrical column, flow circuit and electrical circuit. The column was a plexiglass cylinder of 7 cm inner diameter and 30 cm height. The bottom of the column was perforated plexiglass disc which acted as a flow distributor and support to the anode. A simple annular cell composed of a central graphite rod anode of 4 cm diameter and 24 cm height fixed to the bottom surrounded by a cylinder stainless steel screen cathode (mesh no10) placed at a distance 1 cm in front of the anode. Graphite was used as anode in view of the fact that O_2 overpotential is high on graphite while Cl_2 overpotential is low [6], this would increase current efficiency of Cl_2 evolution. Stainless steel was used as a cathode in view of its stability in the solution. Beside the simple costruction this geometry offers the following advantages: (i) the current and potential distribution are uniform all over the anode surface [6]. (ii) the screen cathode acts a turbulence promoter and improves the mixing efficiency inside 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 column. 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, 6 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 drawn at regular intervals of ten minutes during the experiment period using 10 ml pipette. All the experiments were performed at room temperature.

The decoloration was determined through absorbance at maximum wavelength (λ max = 440 and 620 nm for acid brown and reactive blue dyes respectively) using UV–visible spectrophotometer (Labomed, USA). The rate of color removal was calculated using the formula as given below.

$$\text{Color Removal } (\%) = \frac{ABS_0 - ABS_t}{ABS_0} \times 100 \quad (6)$$

Where ABS_0 is the initial absorbance value, whereas ABS_t is the absorbance value at time t.

Chemical oxygen demand was analyzed by open reflux method using the APHA standard method for wastewater analysis [7].

3. RESULTS AND DISCUSSION

Fig. (2 a and b) presents the color removal during the electrochemical oxidation at different current densities for acid brown and reactive blue dyes respectively. In agreement with previous studies increasing current density increases the rate of color removal due to increased generation of chlorine/hypochlorite under galvanostatic conditions [8]. Beyond a c.d of 6.63 mA/cm^2 there is no significant increase in the rate of colour removal, this may be attributed to the fact that the discharge potential Cl_2 increases with current density and becomes close to the discharge potential of O_2 [9]. Under such conditions simultaneous evolution of O_2 along with Cl_2 takes place with a consequent reduction in the current efficiency and the rate of Cl_2 generation. Also at high current densities NaOCl reduction at the cathode becomes more pronounced [6] according to the reaction:

$$ClO^- + H_2O + 2e \rightarrow Cl^- + 2OH^- \qquad (7)$$

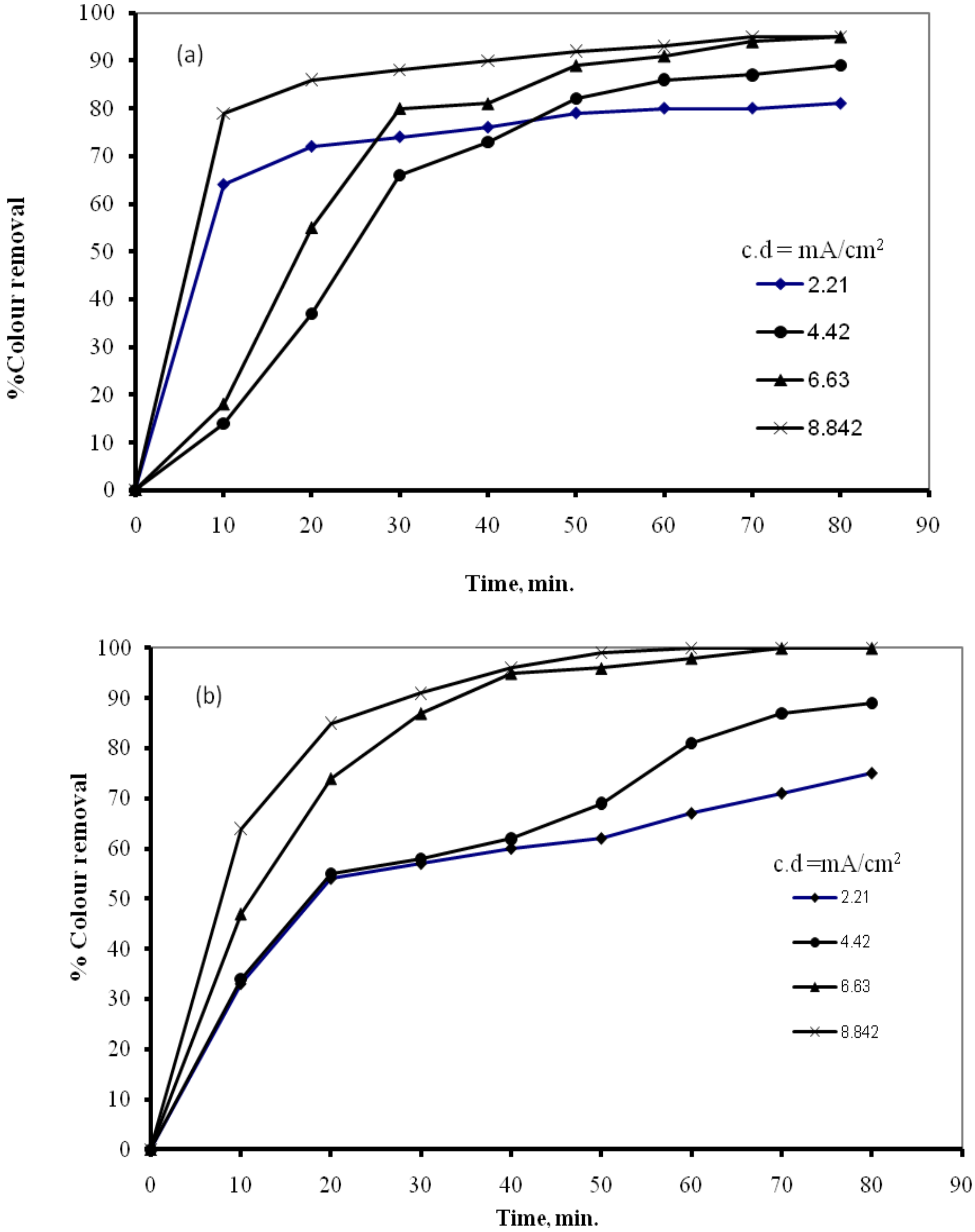

Figure 2. Effect of current density on efficiency of colour removal (C_0=100 mg/l, NaCl=15g/l, pH=7, flow rate= 765 cm^3/min, Temp. =25 °C) a. Acid brown b. Reactive blue

Fig.(3 a and b) shows the effect of NaCl concentration on color removal of acid brown and reactive blue dyes respectively. It is clear that increasing chloride concentration increases the percentage colour removal, this may be ascribed to the fact that increasing NaCl concentration lowers the discharge potential of Cl_2 according to Nernst equation [9] and therefore more current is consumed in Cl_2 and hypochlorite generation at the expense of O_2 evolution. Hence, the rate of colour removal increases. A further increase in NaCl concentration (> 15 g L^{-1}) there was a slight improvement in color removal, so the optimal concentration of NaCl used in the successive experiments was 15 g L^{-1}.

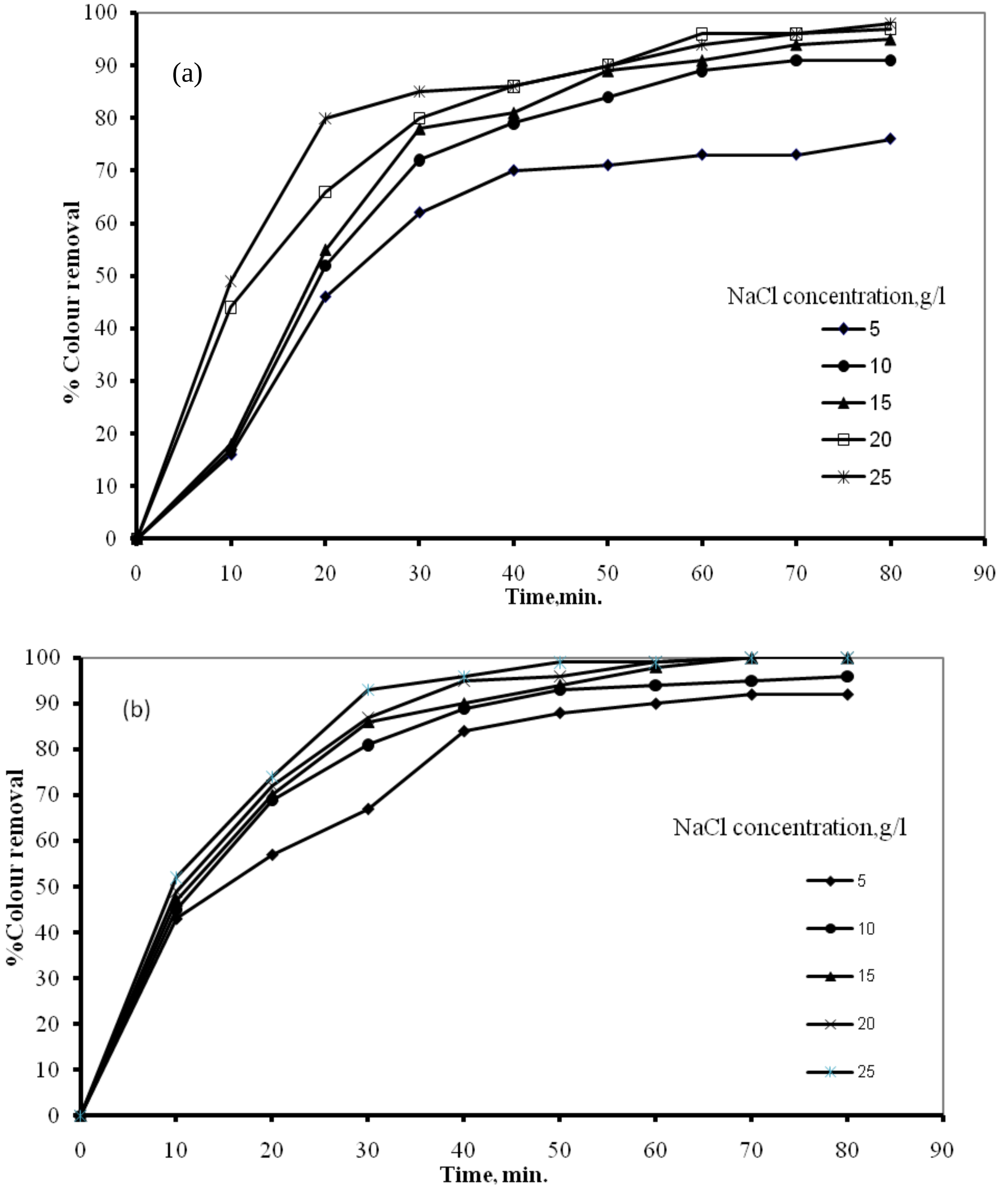

Figure 3. Effect of NaCl concentration on efficiency of colour removal (C_0=100 mg/l, c.d = 6.63 mA/cm^2, pH=7, flow rate= 765 cm^3/min, Temp. =25 °C) a. Acid brown b. Reactive blue

The initial dye concentration was varied in order to check its influence on the rate of color removal. The rate of removal decreased with increased in initial concentration as shown in Fig.(4 a and b). This may be explained by the fact that dye molecules tend to associate with increasing dye concentration to clusters of low diffusivity [10], this lowers the rate of dye diffusion to the anode surface with a consequent decrease in the rate of dye oxidation.

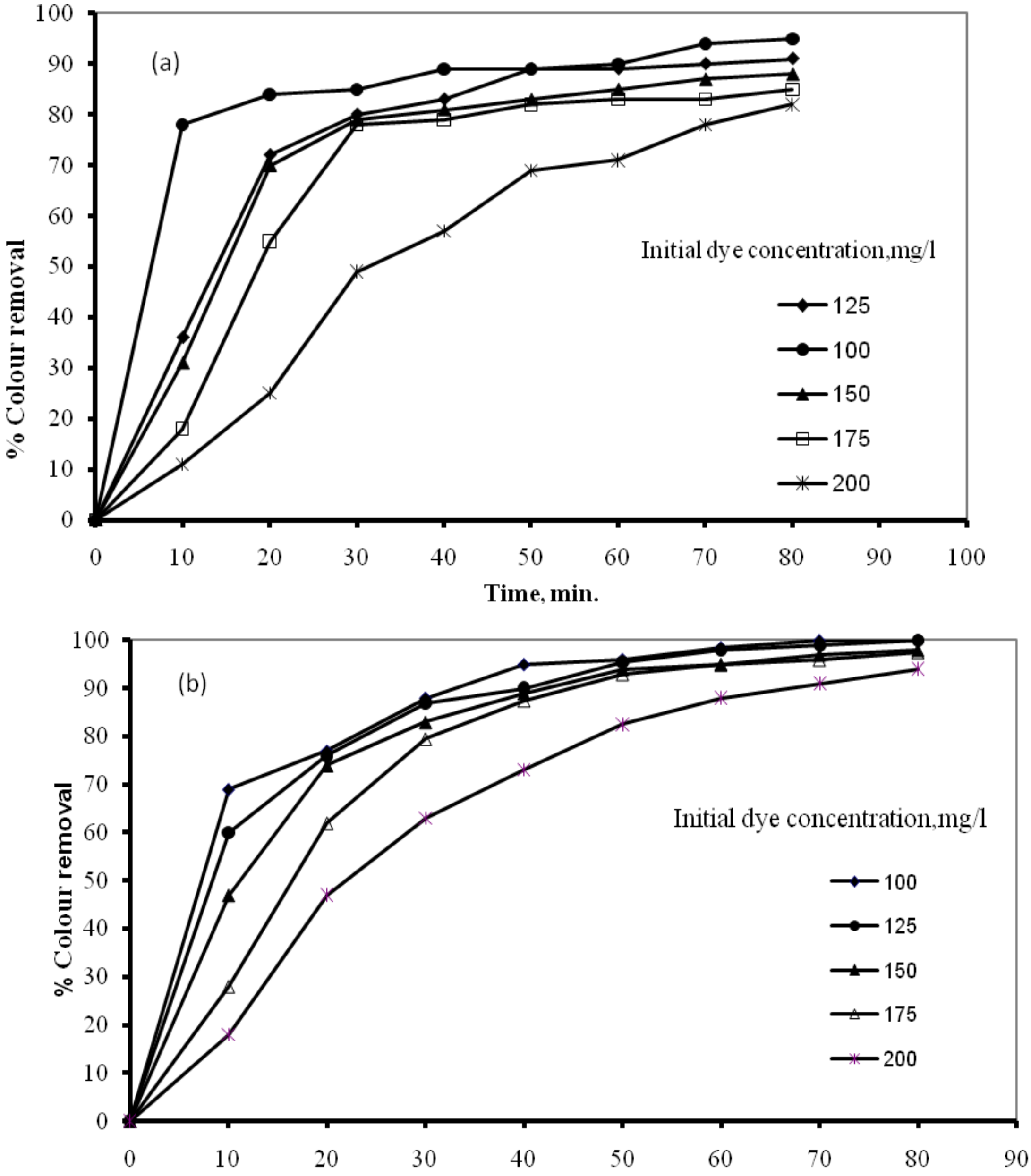

Figure 4. Effect of initial dye concentration on efficiency of colour removal (NaCl = 15 g/l, c.d = 6.63 mA/cm^2, pH=7, flow rate= 765 cm^3/min, Temp. =25 °C) a. Acid brown b. Reactive blue

The effect of initial pH on the color removal was presented in Fig. (5 a and b). It is clear that varying the initial pH from 3 to 9 does not have a significant influence on the color removal. This finding is consistent with previous studies where the system Cl_2/OCl^- was used to treat landfill leachate, tannery wastewater, textile wastewater, cresols and phenol [8]. The decerase in color removal at pH 11 may be attributed to the increased discharge of O_2 at the expense of Cl_2 evolution.

In order to investigate the effect of flow rate on the color removal, the inlet flow rate was varied from 311 to 1500 cm^3/min at fixed experimental conditions of pH = 7, current density = 6.63 mA/cm^2, NaCl concentration = 15 g/L, initial dye concentration = 100 mg/l, Temp.=25°C and for 80 min. Fig.(6 a and b) show that the flow rate has a little effect on color removal. This finding is consistent with previous study [11].

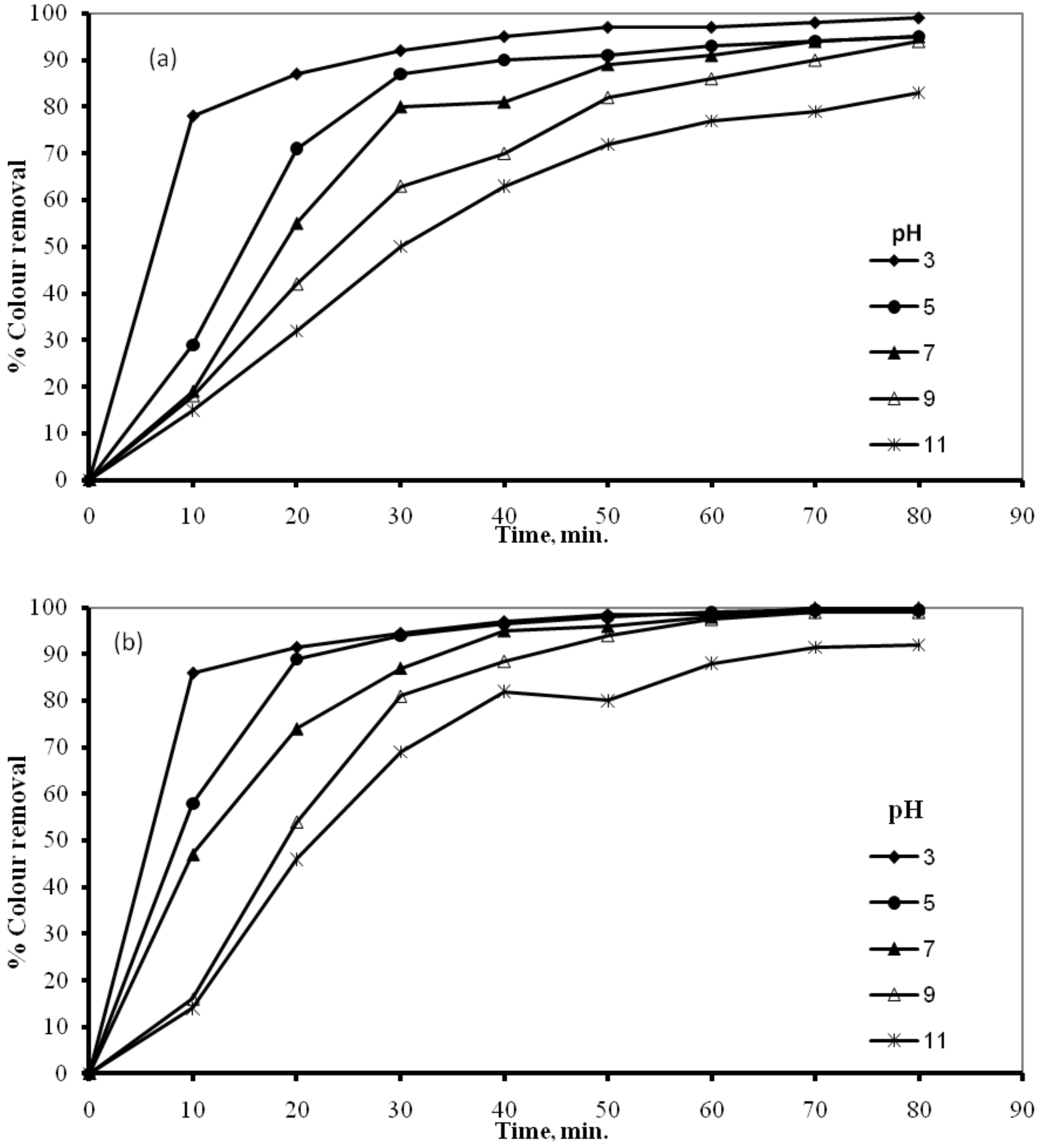

Figure 5. Effect of initial pH on efficiency of colour removal (NaCl = 15 g/l, c.d = 6.63 mA/cm^2, C_0= 100 mg/l, flow rate= 765 cm^3/min, Temp. =25 °C) a. Acid brown b. Reactive blue

The effect of flow rate may be explained by the fact that the cathodically generated H_2 bubbles and the anodically evolved Cl_2 bubbles enhances the rate of mass transfer and improve the mixing efficiency in the cell to a great extent which overshadows the role of solution flow. Gas bubbles induce micro-convection during detachment from the electrode surface and macro-convection as they rise along the electrode [12]. Besides, bubble collision and the subsequent bubble coalescence in the rising bubble swarm generates high intensity turbulence which enhance the rate of mass transfer of Cl_2 from the anode vicinity to the solution bulk [13,14].

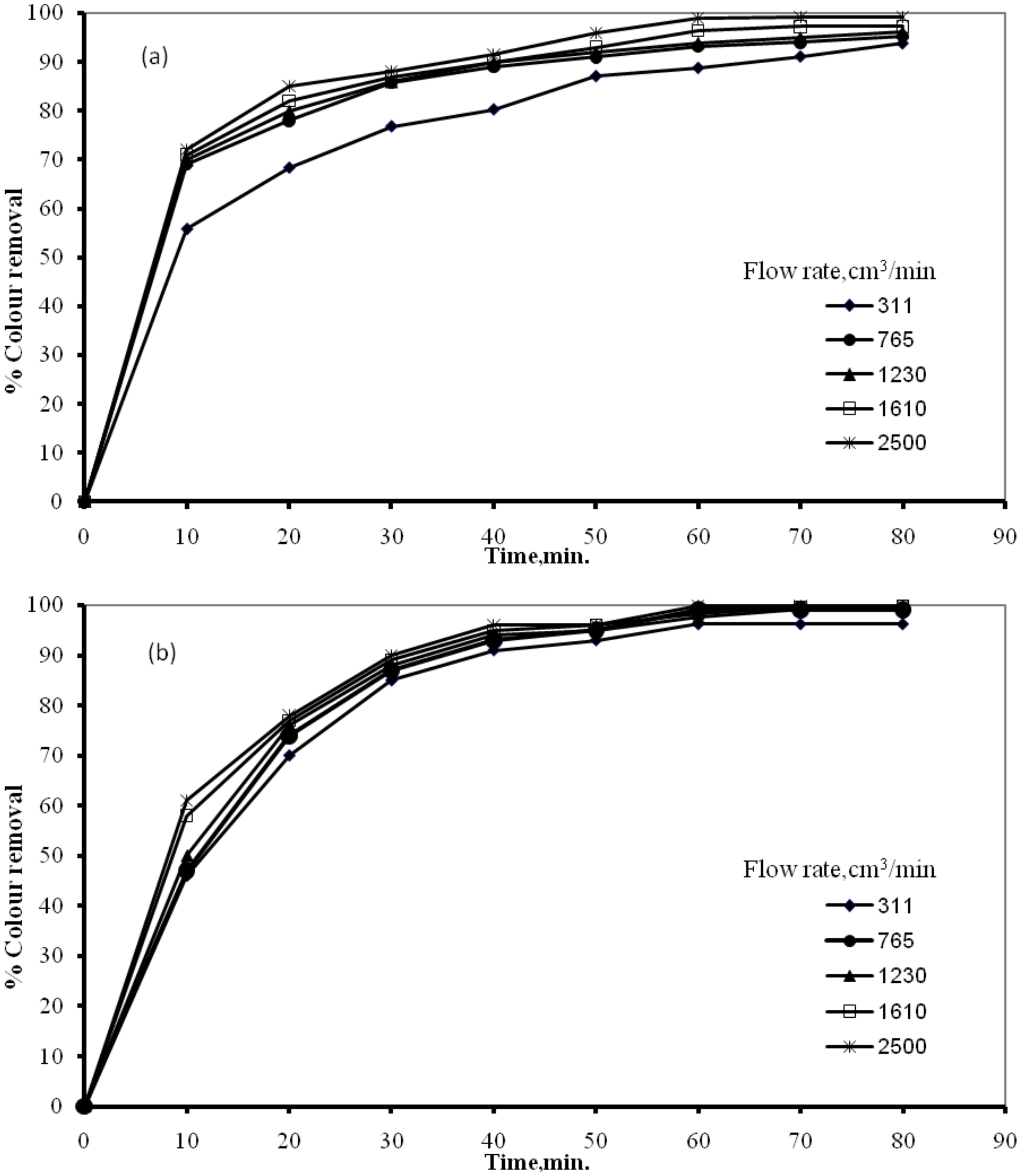

Figure 6. Effect of solution flow rate on efficiency of colour removal (NaCl = 15 g/l, c.d = 6.63 mA/cm^2, C_0= 100 mg/l, pH = 7, Temp. =25 °C) a. Acid brown b. Reactive blue

Mineralization of different dyes solutions were monitored by COD measurements before electrochemical oxidation and at the end of the run. The effect of operational parameters on COD reduction was shown in table 1. The percentage COD reduction decreases with the increase in initial dye concentration and increases with the increase in current density, solution flow rate and sodium chloride concentration.

Table 1. COD measurements

		c.d, mA/cm^2				NaCl,g/l					Dye concentration, mg/l				
		2.21	4.42	6.63	8.84	5	10	15	20	25	100	125	150	175	200
COD reduction,%	Acid brown	71	80	86	86	66	81	86	87	87	86	80	77	75	71
	Reactive blue	67	80	88	88	82	86	88	88	88	88	89	88	87	85

		pH					Flow rate,cm^3/min.				
		3	5	7	9	11	311	765	1230	1610	2500
COD reduction,%	Acid brown	89	86	86	87	74	82	86	87	87	89
	Reactive blue	89	88	88	88	82	88	88	88	88	89

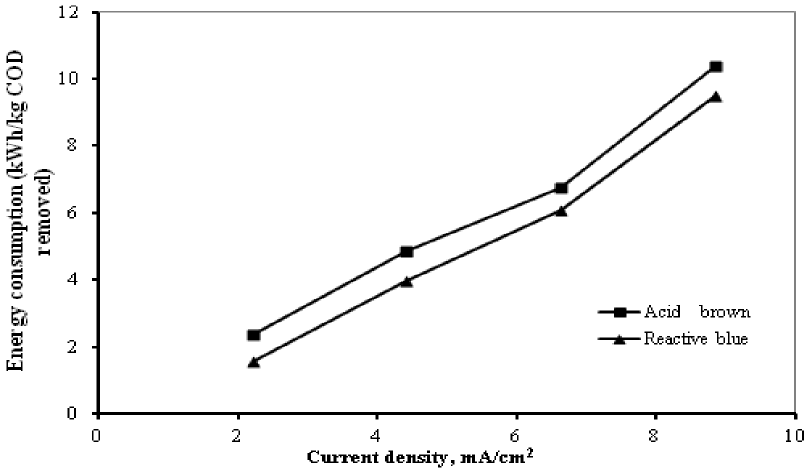

Figure 7. Effect of current density on energy consumption (NaCl = 15 g/l, flow rate = 765 cm^3/min, Time = 80 min., C_0= 100 mg/l, pH = 7, Temp. =25 °C)

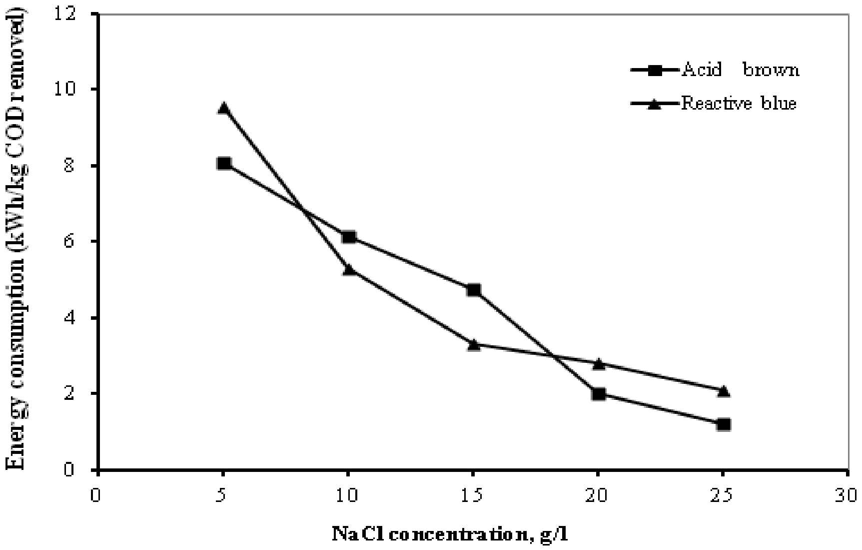

Figure 8. Effect of NaCl concentration on energy consumption (c.d = 6.63 mA/cm^2, flow rate = 765 cm^3/min, Time = 80 min., C_0= 100 mg/l, pH = 7, Temp. =25 °C)

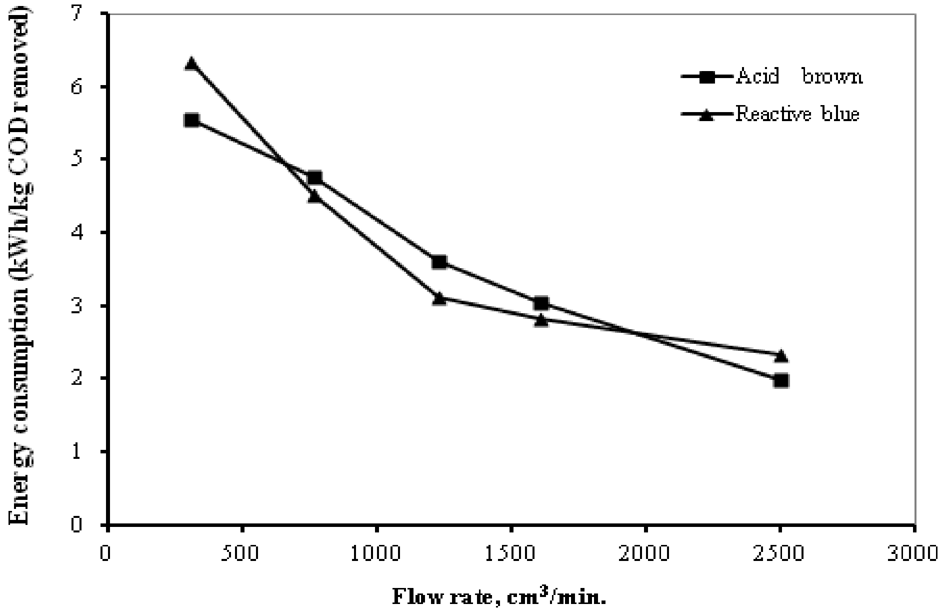

Figure 9. Effect of solution flow rate on energy consumption (c.d = 6.63 mA/cm^2, NaCl = 15 g/l, Time = 80 min., C_0= 100 mg/l, pH = 7, Temp. =25 °C)

To further assist in assessing the economic feasibility of electrochemical oxidation method in comparison with other methods, the energy consumption was calculated as follows [15]:

$$\text{Energy consumption (kWh/kgCOD removed)} = \frac{V\,I\,t \times 10^3}{60(COD_0 - COD_t) \times \text{treated volume (l)}} \qquad (7)$$

Where V is the cell voltage (V), I is the current (A), t is the electrolysis time (min.), COD_0 and COD_t are the initial chemical oxygen demands and chemical oxygen demands at time t (in mgO_2/l) respectively. Figures (7-9) show that energy consumption ranges from 1.2 to 10.4 kWh/kg COD removed depending on the operating conditions for electrochemical oxidation process.

4. CONCLUSIONS

In the present work the electrochemical oxidation of wastewater containing dyes was achieved. The effect of various operational parameters on the efficiency of color removal and COD reduction was investigated. The results showed that, the color removal and COD reduction increase with the increase in current density, NaCL concentration and flow rate while it were found to decrease with the increase in initial dye concentration. The pH was found to have no effect on the rate of electrochemical oxidation of the dye in the pH range from 3 to 9. From the economic point of view, the energy consumption based on kg COD removed was found to range from 1.2 to 10.4 kWh depending on the operating conditions.

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