REMOVAL OF REACTIVE BLACK DYE RB-5 FROM SYNTHETIC WASTEWATER BY ELECTROCOAGULATION TECHNIQUE

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Abstract: Decolonization of azo dye Reactive Black 5 (RB-5) from synthetic wastewater was studied using Electrocoagulation (EC) technique. The effect of operating parameters such as initial pH, conductivity, inter electrode distance, current density, and time of electrolysis was studied in an attempt to reach higher removal efficiency. Initially, a simple electrochemical cell was prepared with an anode and a cathode made from iron. Then the effect of each variable was studied separately using synthetic wastewater in a batch mode. Under the conditions of an initial dye concentration of 100 mg/L, initial pH of 4, current density of 250 A/cm^2, conductivity 6 ms/cm, temperature of 25±2 ^{o}C, interelectrode distance of 0.6 cm, and time of electrolysis 10 min the color removal efficiency reached 99.4%. Electrical energy consumption in the above conditions for the decolorization of the black dye was 0.75 kWh/m^3.

Keywords: *Electrocoagulation,black color, Iron electrode, current density, energy consumption*

ازالة الصبغة السوداء الفعالة (RB-5) من المياه الملوثة المصنعة باستخدام تقنية التخثير الكهربائي

الخلاصة: تم في هذه الدراسة بحث امكانية استخدام تقنية التخثير الكهربائي في ازالة الصبغة السوداء الفعالة (RB-5) من المياه الملوثة المصنعة. تم دراسة تأثير كل من الرقم الهيدروجيني الأولي ،التوصيل الكهربائي، البعد بين الأقطاب، كثافة التيار و زمن التحليل الكهربائي من اجل الوصول إلى الظروف المثلى لعملية الأزالة. تم أولا تركيب الخلية الكهربائية المكونة من الانود والكاثون وهما مصنوعان من الحديد وبعدها تم دراسة هذه المتغيرات بصورة منفصلة على عملية الإزالة باستخدام المياه العادمة المصنعة في النظام الدفعي. وتحت ظروف تركيز أولي للصبغة السوداء بلغ ١٠٠ ملغرام/لتر، رقم هيدروجيني أولي مقداره ٤، كثافة التيار مقدارها ٢٥٠ أمبير/سم٢، التوصيل الكهربائي مقدارها ٦ ملسمنز/سم، درجة حرارة مقدارها ٢٥ ±٢ درجة مئوية، مسافة بين الأقطاب مقدارها ٠,٦ سم، وزمن تحليل كهربائي مقداره ١٠ دقائق بلغت نسبة إزالة الصبغة السوداء من المحلول ٩٩,٤ %. إما كمية الطاقة المصروفة للحصول على نسبة الإزالة السابقة في تلك الظروف فبلغت ٠,٧٥ كيلو واط. ساعة / م٣.

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1. Introduction

The environmental impact of the textile industries is associated with its high water consumption as well as by the color, variety and amount of chemicals which are released to the wastewater [1]. Wastewaters from dyeing and finishing operations in the textile industry are generally high in color and organic content. The wastewater from the textile industry is known to be strongly colored. Color is the first contamination to be recognized in this wastewater. A very small amount of dye in water is highly visible and reduces penetration of light in water systems, thus causing a negative effect on photosynthesis [2]. Color removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to its visibility problems [3, 4].

There are several methods for color removal such as biological treatment, oxidation, coagulation and flocculation and adsorption. One of the most commonly used techniques is coagulation. Lime and salts of iron, magnesium and aluminum have been used over many years as effective coagulants. In coagulation processes, the coagulant is added to an organic colloidal suspension to cause its unstable by the reducing of the forces that maintain them individual. It includes the reduction of responsible surface charges for particle repulsions. This reduction in electrical charge causes agglomeration. Flocks of larger size are then settled and a purified effluent is achieved. However, this technique produces a huge volume of sludge [5, 6]. Wastewater treatments based on the electrocoagulation processes have been recently proved to circumvent most of these problems, while being also economically attractive [7].

Electrocoagulation (EC) can be specified as an electrochemical technique used for treating wastewater whereby using sacrificial anodes such as aluminum or iron electrodes corrode to release active coagulant precursors into the solution. These coagulants produce insoluble metallic hydroxide flocks which had the ability to remove a wide range of contaminants by surface complexation or/and electrostatic attraction [8]. The function of EC for the handling of effluent has been described by several sources. A literature survey indicated that electrocoagulation is an effective process for different cases of industrial wastewater, e.g. Food processing industries, textile industries and paper mill industry [9, 10]. EC is an efficient method for wastewater treatment, by merit of various benefits including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenable to automation and cost effectiveness [11, 12, 13]. This operation is characterized by simple equipment, gentle functioning, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals and decreasing amounts of precipitate or sludge which rapidly forms sediments.

In this study, operational parameters were investigated that are suitable for treating synthetic wastewater containing a black dye. These parameters included initial PH, conductivity, electrode distance, current density, electrocoagulation time and energy consumed.

2. Electro-coagulation (EC) Process Description

The process of destabilizing suspended particles, emulsifier, or dissolved pollutants in an aqueous medium by presenting an electric current into the spiritualist is called electrocoagulation. The easiest form to of electrocoagulation reactor can be made from electrolytic cell with one cathode and one anode [14]. The cell metal plates used as conductor are known as 'sacrificial electrodes' and could be of the same or different materials. This technique was used by many researchers and proven very effective in wastewater treatment. The EC is characterized by reducing sludge production, ease of operation and no use of aggressive chemicals, and [15]. In the EC process, the colloid – destabilizing agents that affect the charge neutralization are produced by electrolysis. Iron anodes are used to produce iron captions which have the same result when Fe-based salt was added as a coagulant in conventional treatment plants.

The main mechanisms of the electro-coagulation process: (1) electrolytic reactions at the surfaces of electrode, (2) Coagulants formation in the aqueous solution, (3) adsorption of suspended and soluble pollutants on coagulants surfaces, and sedimentation or flotation removal [16, 17].

Iron hydroxide, Fe $(OH)_n$ produces from oxidation process in an electrolytic system when iron is used as anodes where n = 2 or 3. The main reactions that occur at the electrodes are shown in Eqs. (1) through (7) [18]:
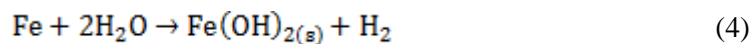
When n = 2
Anode:

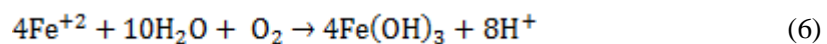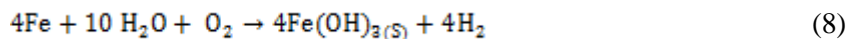$$Fe \rightarrow Fe^{+2} + 2e^- \tag{1}$$

$$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2 \tag{2}$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

Overall:

$$Fe + 2H_2O \rightarrow Fe(OH)_{2(s)} + H_2 \tag{4}$$

When n = 3
Anode:

$$4Fe \rightarrow 4Fe^{+2} + 8e^- \tag{5}$$

$$4Fe^{+2} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+ \tag{6}$$

Cathode:

$$8H^+ + 8e^- \rightarrow 4H_2 \tag{7}$$

Overall:

$$4Fe + 10\ H_2O + O_2 \rightarrow 4Fe(OH)_{a\,(S)} + 4H_2 \tag{8}$$

Monomeric ions and polymeric hydroxyl complexes including: $Fe(H_2O)_6^{+3}$, $Fe(H_2O)_5(OH)^{+2}$, $Fe(H_2O)_4(OH)^{+2}$, $Fe_2(H_2O)_8(OH)_2^{+4}$ and $Fe_2(H_2O)_6(OH)_4^{+4}$ may generated by electro-chemical oxidation of the iron electrode depending on the pH of the aqueous solution [19].

3. Materials and methods

3.1. *Preparation of synthetic wastewater*

The dye used in this study was reactive black-5 dye (RB-5), the Molecular formula is $C_{26}H_{21}N_5Na_4O_{19}S_6$, molecular weight is 991.82 g/mol and the absorbance is λmax: 595 nm supplied by (Dura color industries, India). The chemical structure is shown in Fig. 1 The synthetic wastewater was prepared by dissolving 100mg /L of the dye with deionized water and the dye solutions pH for each experiment were adjusted by adding 0.1M sodium hydroxide or 0.1M hydrochloric acid solutions. While 1M NaCl was used to adjust the conductivity to the desired value.
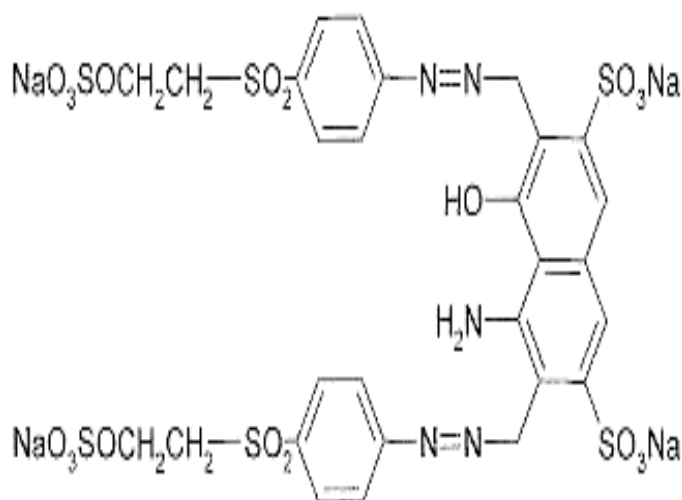

Figure 1. Chemical structure of the Reactive Black 5 dyes (RB-5)

3.2. *Experimental apparatus and procedure*

The equipment's used were a DC voltage power supply (Farnell L30E, UK), magnetic stirrer (gallenhamp, UK), pH meter (WTW 3110, Germany), Conductivity meter (WTW 3110, Germany), and spectrophotometer (Genesys 10, Thermo Scientific, USA). The experiments were performed in a batch reactor consisting of a 0.6 L glass beaker equipped with a cathode and an anode, both made of iron (stainless steel 306) and installed in parallel. The distance between the anode and cathode was varied from 0.6 cm to 2 cm. The entire electrode assembly was fitted with non-conducting wedges and hanged from the top of the glass beaker. The dimensions of the electrodes were 0.07cm × 5.0 cm×11. 0 cm.

The total effective electrode area is calculated to be (5 cm×6 cm) 30 cm^2. The electrodes were dipped into the beaker containing the dye solution with a 0.5 L working volume. The experimental setup used in the present study is presented in Fig. 2.

The experiments were carried out with the synthetic wastewater at room temperature (25±2°C) and with constant agitation speed (approximately 200 RPM). To control the current density , a DC power supply with galvanostatic operational options was used to connect the electrodes. The reactor content was filtered and analyzed after the electrolysis process was finished.
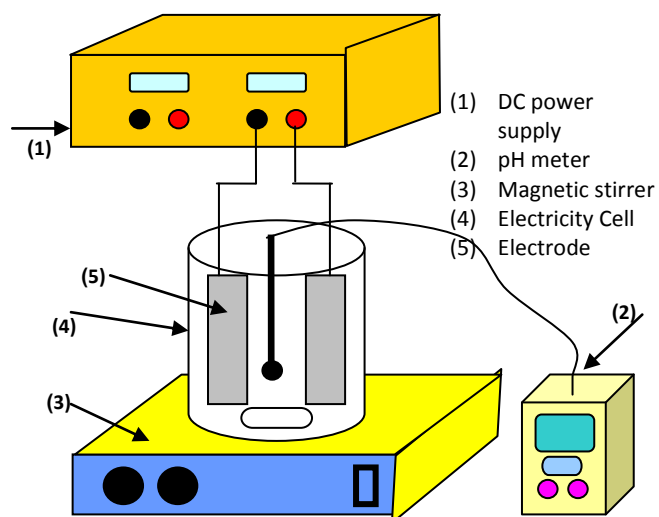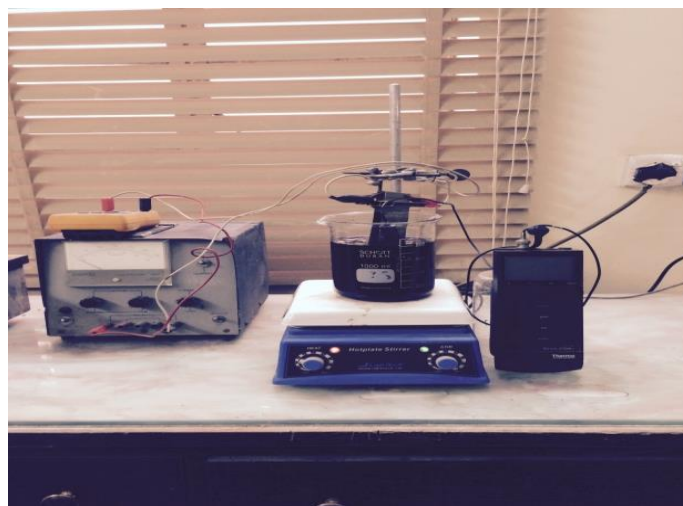

Figure 2a. Schemetaic diagram of treatment system

(1) DC power supply
(2) pH meter
(3) Magnetic stirrer
(4) Electricity Cell
(5) Electrode

Figure 2b. Photo of treatment system

3.3. Analytical method

AUV-Vis spectrophotometer was used for measuring dye concentration using at 595 nm. Equation 7 was used to calculate the dye removal efficiency.

$$\text{Color removal efficiency} \ (\%) = \left(\frac{Co - C}{Co} \right) \times 100 \qquad (9)$$

Where C_o and C are the concentration of the dye before and after electrocoagulation, respectively.

Wastewater treated energy consumption has calculated as follows:

$$E = \frac{U \times I \times t \times 1000}{V} \qquad (10)$$

Where:

E: Energy Consumption (kWh/m^3)

U: Cell voltage (v)

I : Current (A)

t: Time (h)

V: Volume of wastewater (m^3)

In this study, each treatment was repeated twice and the absorbance concentration of each sample was repeated three times.

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4. Results and discussion

4.1. Effect of initial pH

RB-5 dye removal efficiency, as a function of pH within the range of 2–10, is shown in Fig. 3 and the operational conductions of the pH effect in the experiments are listed in Table (1). It can be seen that, dye removal efficiency significantly affected by the initial pH. The removal efficiency increases with increasing pH from 2 to 4 and decreasing at pH > 4. From Fig. 3 it is seen that for 100 mg/L of dye the removal is almost 98% at pH 4 and decreases to value 50.8% at pH 5. Therefore, the desired pH of the black color degradation by EC process should be 4. This was because at high pH some of the hydroxide ions are probably oxidized at the anode. This action prevents the production of the same proportion of iron ions and, therefore, the dye removal efficiency of black dye is decreased. At lower pH the protons in the solution are reduced to H_2 at the cathode and the same proportion of hydroxide ions cannot be produced. These results coincide with those obtained by other researchers [19, 20, 21, 22, 23]. In Fig. 4, test runs with raw effluent are shown for iron electrode with different pH values.

Table 1. Operating conditions of pH effect experiment

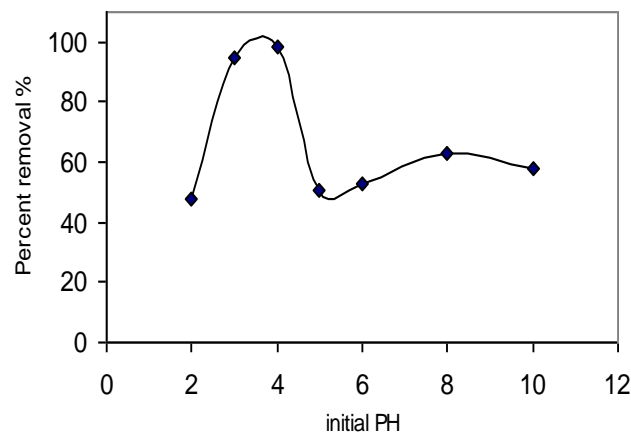| Parameter	Value
Conductivity (ms/cm)	3
Inter-electrode distance (cm)	1.2
Current density (A/m^2)	200
Electrolysis time (min)	10
Initial concentration of dye (mg/L)	100

Figure 3. Effect of initial pH on the percent removal of RB-5 dye

Figure 4. Effect of pH variation (from left to right - raw effluent; treated effluent with pH value, 2; 3; 4; 5; 6; 8; and 10, respectively)

4.2. Effect of conductivity

Effluents from textile industry have a wide variation in ionic strength due to high chemicals concentration added from finishing and dyeing processes in this manufacture. When the ionic strength high, this will generally cause an increase in current density in the same cell voltage, or the cell voltage decreases with increasing effluent conductivity at a constant current density [23]. Thus, the effect of effluent conductivity on electrocoagulation performance in terms of dye removal must be investigated. The wastewater conductivity is adjusted to the desired level by adding an appropriate amount of NaCl. The effect of conductivity on the removal efficiency,   voltage used and the energy consumption is shown in Figs.5 to 7 and the operational conductions of conductivity effect are shown in Table (2). From Fig. 5, it was found that raising the conductivity of the solutions from 1 to 8 ms/cm did not have a considerable effect on RB-5 dye removal as also reported by Lin and Peng (1994) [24].

Figs. 6 and 7 show that, as the conductivity of solution raising from 1 to 6 ms/cm, the voltage used to decrease from 15 to 3.5 V and energy consumed decreased from 3 to 0.6 KWh/m^3. Conductivity above 6 ms/cm did not have a considerable effect on the

voltage used and energy consumed. Therefore, for 100 mg/L of dye solution, optimum conductivity is 6 mS/cm^3.

Table 2. Operating conditions of conductivity experiments

Parameter	Value
pH	4
Inter-electrode distance (cm)	1.2
Current density (A/m^2)	200
Electrolysis time (min)	10
Initial concentration of dye (mg/L)	100
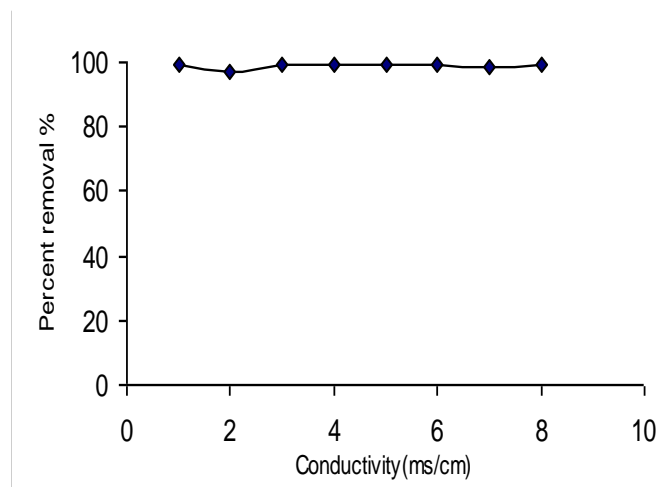
Figure 5. Effect of conductivity on the percent removal of RB-5 dye
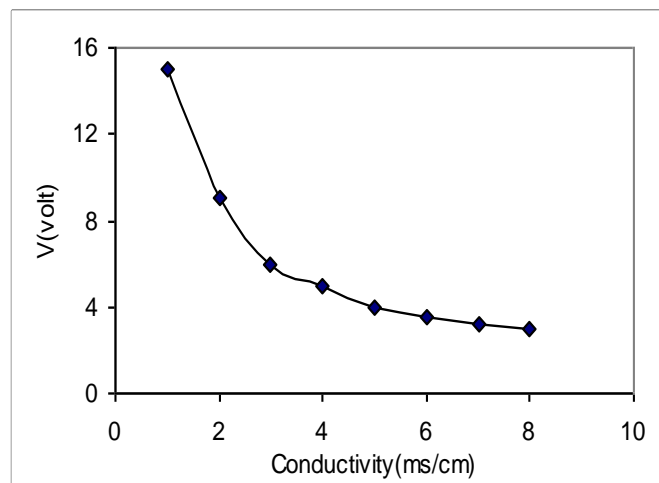

Figure 6. Effect of conductivity on the volt consumed
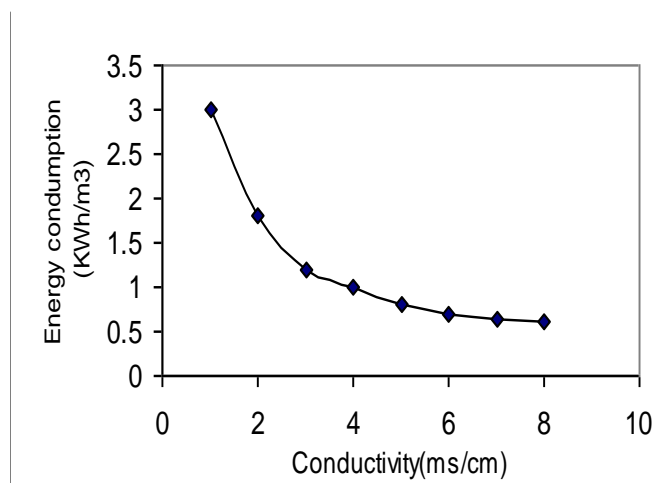
Figure 7. Effect of conductivity on the energy consumption

4.3. Effect of inter electrode distance

The process percentage removal efficiency can be enhanced by varying the distance between the electrodes [25]. It is recommended that, greater inter electrode distance should be used in the case of high values of effluent conductivity. In the case of moderate values, it is recommended to use a smaller distance, as this will reduce the energy consumption. The operational conductions to test the inter electrode distance is shown in Table (3). In the present experiment, the variation of the inter electrode distance was increased from 0.6 to 2 cm as shown in Fig. 8 where the removal efficiency of RB-5 dye did not significantly changed. Fig. 9 shows that, increasing inter electrode distance from 0.6 to 2 cm, the voltage used to obtain a current density of 200 A/m^2 increased from 2.5 to 5.3 V. Also, as shown in Fig.10.The inter electrode distance varying from 0.6 to 2 cm increased the power consumption in the cell from 0.5 to 1.05 KWh/m^3, respectively, and this was attributed to the high current flowing through the system. Therefore, for 100 mg/L of dye solution optimum inter electrode distance to give minimum energy consumed is 0.6 cm.

Table 3. Operating conditions of inter electrode distances experiment**s**

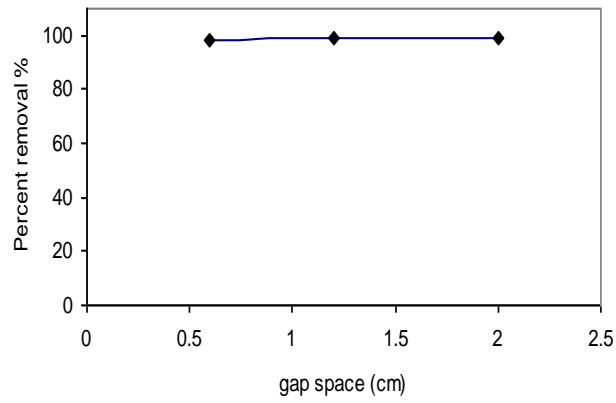| Parameter	Value
pH	4
Conductivity (ms/cm)	6
Current density (A/m^2)	200
	10
Electrolysis time (min)	100
Initial concentration of dye (mg/L)	

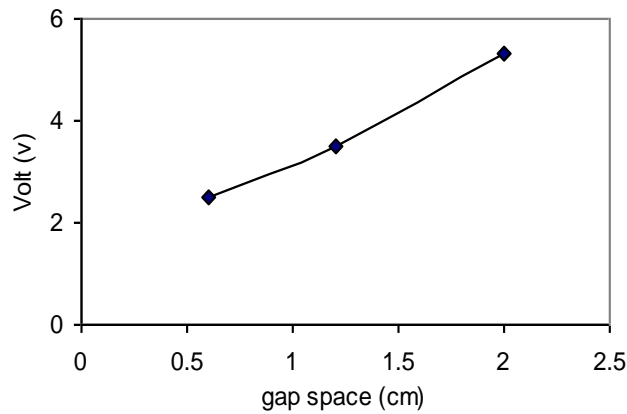Figure 8. Effect of gap space on the percent removal of RB-5 dye

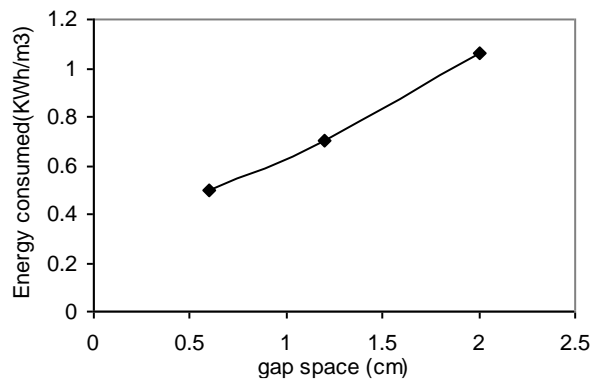Figure 9. Effect of gap space on the volt consumed

Figure 10. Effect of gap space on the energy consumption

4.4. Effect of current density

When the EC process is applied, the optimum current density will depend on the economic status and geographical situation. The operation conductions of current density experiment are listed in Table (4). Fig. 11 shows that, the efficiency of RB-5 dye removal from 84.71 to 99.53% and hold constant above this value when the current

density increased from 100 to 250 A/m^2. Ions production efficiency on the anode and cathode increases as the current density increases; thus, there is an increase in the floc production and this will improve the dye removal. The same conclusion had been mentioned by Kashefialasl et al., 2006 [26]. Parallel to the applied current, voltage and energy consumed increased immensely from 2 V and 0.2 KWh/m^3 at 100 A/cm^2 up to 4.5 V and 1.8 KWh/m^3 for 400 A/cm^2, respectively as shown in Figs. 12 and 13. Supplied current density increased from 100 to 400 A/m^2 led to better dye removal, but this is not economically interesting due to the high voltage and energy consumption. In Fig.14, test runs with raw effluent are shown for iron electrode with different current density. The optimum current density for dye concentration solution of 100 mg/L was 250 A/m^2 and energy consumed at this value was 0.75 KWh/m^3.

Table 4. Operating conditions of current density experiment

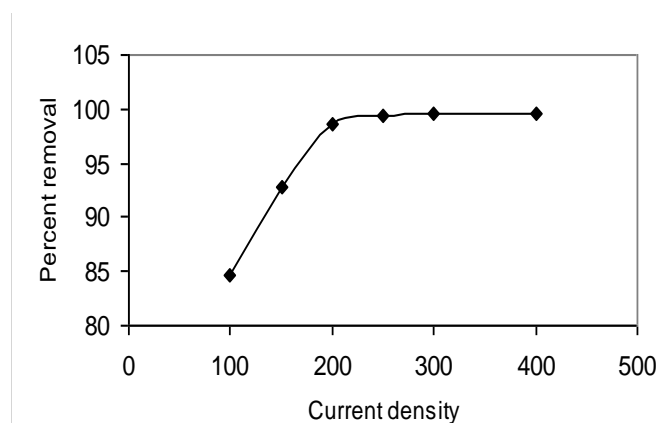| Parameter	Value
pH	4
Conductivity (ms/cm)	6
Inter-electrode distance (cm)	0.6
Electrolysis time (min)	10
Initial concentration of dye (mg/L)	100

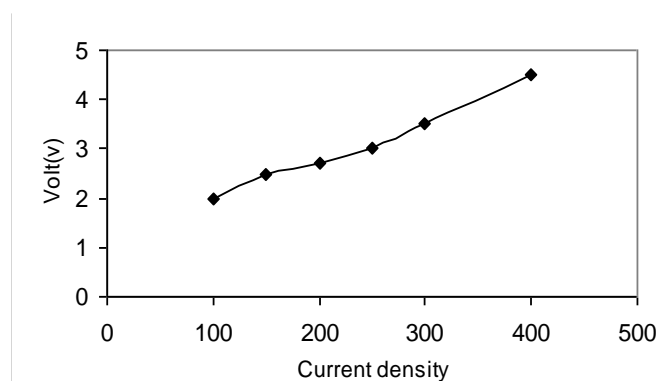Figure 11. Effect of current density on percent removal of RB-5 dye

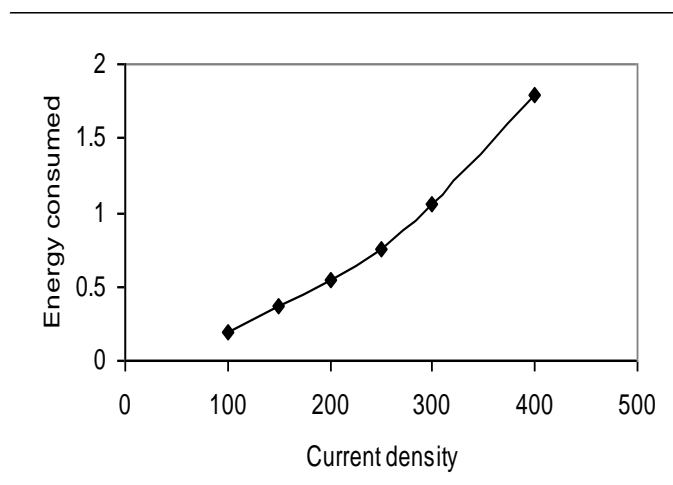Figure 12. Effect of current density on voltage consumed

Figure 13. Effect of current density on energy consumed

Figure 14. Effect of the variation of the current density (from left to right - raw effluent; treated effluent with 100; 150; 200; 250; 300 and 400 A/m², respectively)

4.5. Effect of electrolysis time

The effect of electrolysis time on the EC process was also performed. The operation conductions of electrolysis time experiment are shown in Table (5). Fig.15 illustrates the removal of RB-5 dye as a function of the operating time. It is clearly seen from Fig.15 that, the operating time has a significant effect on the dye removal. When the operating time increases from 2 to 10 minutes, the removal efficiency, increase from 23.7 to 99.4 % and held constant after this time. This increase in removal efficiency of color attributes to increasing of producing hydroxyl and metal ions on the electrodes with time. In Fig.16, test runs with raw effluent are shown for iron electrode with different time.

Table 5. Operation condition of electrolysis time experiment

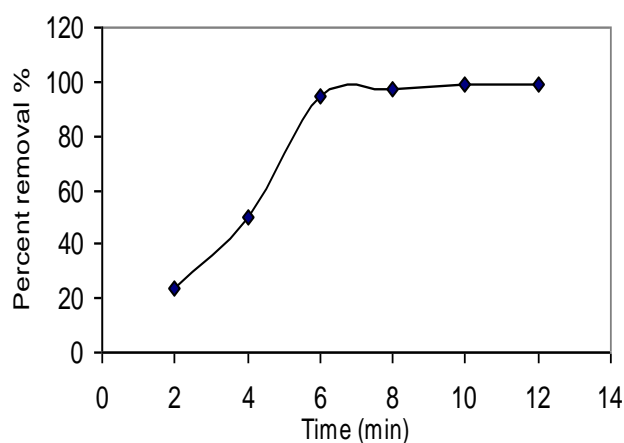| Parameter	Value
pH	4
Conductivity (ms/cm)	6
Inter-electrode distance (cm)	0.6
Current density (A/m^2)	250
Initial concentration of dye (mg/L)	100

Figure 15. Effect of electrolysis time on RB-5 dye percentage removal

Figure 16. Effect of the variation of time of electrolysis (from left to right – raw effluent; treated effluent with 2; 4; 6; 8; 10 and 12 min, respectively)

5. Conclusions

The results showed that the decolorization of a dye solution by the Electrocoagulation was affected by initial pH, conductivity, inter electrode distance, current density, and electrolysis time. The optimum conditions to reach 99.4 % of black color removal efficiency by electrocoagulation process were pH 4, conductivity

6ms/cm, inter electrode distance 0.6cm, current density 250 A/cm^2, and 10 min electrolysis time. The energy consumed at the optimum condition was 0.7 KWh/m^3.

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