Journal of Hazardous Materials B112 (2004) 55–62

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections

N. Daneshvar [a,*], H. Ashassi Sorkhabi [b,1], M.B. Kasiri [a,2]

[a] *Water and Wastewater Treatment Research Laboratory, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*
[b] *Electrochemical Research Laboratory, Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*

Received 31 December 2002; received in revised form 19 March 2004; accepted 20 March 2004

Available online 4 June 2004

Abstract

This study was performed to investigate the variables that influence the efficiency of decolorization of a solution containing an azo dye (Acid Red 14) by electrocoagulation (EC) in order to compare the efficiency of different electrode connections for color removal. Current density, time of electrolysis, interelectrode distance, and pH of the solution were the variables that most influenced color removal. Initially, a simple electrochemical cell was prepared with an anode and a cathode. Then the effect of each variable was studied separately using synthetic wastewater in a batch mode. The efficiency of the method tested was determined by measurement of color removal and reduction of Chemical Oxygen Demand (COD). For dye solutions with COD of approximately 30 ppm and dye concentrations less than 150 ppm, high color removal (93%) was obtained when the pH ranged from 6 to 9, time of electrolysis was approximately 4 min, current density was approximately 80 A/m^2, the temperature was approximately 300 K, and interelectrode distance was 1 cm. During the EC process under these conditions, the COD decreased by more than 85%. In the second series of experiment, the efficiency of EC cells with monopolar electrodes in series and parallel connections and an EC cell with bipolar electrodes were compared with results using a simple electrochemical cell. The experimental results showed that an EC cell with several electrodes was more effective than a simple electrochemical cell in color removal. The results also showed that an EC cell with monopolar electrodes had a higher color removal efficiency than an EC cell with bipolar electrodes. Furthermore, within an EC cell, the series connection of the monopolar electrodes was more effective for the treatment process than the parallel connection in color removal.

Keywords: Electrocoagulation; Wastewater treatment; Azo dye; Color removal; Bipolar electrodes

1. Introduction

Fiber dyeing produces a great deal of wastewater. The effluent from the dyeing process is colorful and its decolorization is very important before discharge to the environment.

Traditional biochemical and coagulation processes are inadequate for the treatment of solutions containing biorefractory and soluble dyes. The cost of treatment by activated carbon adsorption is high. Oxidation using ozone or hypochlorite is an efficient decolorization method, but the operating and equipment costs are relatively high. Moreover, the presence of residual chlorine produces a secondary pollutant [1].

Treatment of wastewater by electrocoagulation (EC) has been practiced for most of the 20th century with limited success. In the last decade, this technology has been increasingly used in South America and Europe for treatment of many kinds of wastewater, by allowing the particles to react with: (i) an ion having an opposite charge; or (ii) a floc of metallic hydroxides generated within the effluent [2].

The EC process is highly dependent on the chemistry of the wastewater, especially its conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent influence the process. The mechanism of removal of pollutants by EC process with iron electrodes is shown below [2].

* Corresponding author. Tel.: +98-411-5275825/5212096/3393146; fax: +98-411-3340191.

E-mail addresses: nezam_daneshvar@yahoo.com (N. Daneshvar), ashassi@tabrizu.ac.ir (H. Ashassi Sorkhabi), kasiri54@yahoo.com (M.B. Kasiri).

[1] Tel.: +98-411-3355998.

[2] Tel.: +98-411-4776665.

0304-3894/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2004.03.021

Iron upon oxidation in an electrolytic system produces iron hydroxide, $Fe(OH)_n$ where $n = 2$ or 3. Two mechanisms have been proposed for the production of $Fe(OH)_n$:

(a) Mechanism 1:

- Anode:

$$4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^- \quad (1)$$

$$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^+(aq) \quad (2)$$

- Cathode:

$$8H^+(aq) + 8e^- \rightarrow 4H_2(g) \quad (3)$$

- Overall:

$$4Fe(s) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g) \quad (4)$$

(b) Mechanism 2:

- Anode:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad (5)$$

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) \quad (6)$$

- Cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (7)$$

- Overall:

$$Fe(s) + 2H_2O(l) \rightarrow Fe(OH)_2(s) + H_2(l) \quad (8)$$

The $Fe(OH)_n(s)$ remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from the wastewater by either complexation or electrostatic attraction followed by coagulation. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:

$$L\text{–}H(aq) + (OH)OFe(s) \rightarrow L\text{–}OFe(s) + H_2O(l) \quad (9)$$

The prehydrolysis of Fe^{3+}cations also leads to the formation of reactive clusters for wastewater treatment [2]. The EC process is characterized by a fast rate of pollutant removal, compact size of the equipment, simplicity in operation, and low operating and equipment costs [3]. The EC is a simple and efficient method for the treatment of water and many kinds of wastewater. It has been tested successfully in the separation of pollutants from restaurant wastewater [3], treatment of urban wastewater [4], degradation and decolorization of dye solution [1,5], defluoridation of water [6,7], separation of aqueous suspensions of ultrafine particles [8], and removal of nitrate from water [9]. Hence, it is expected that the electrocoagulation would be an ideal choice for decolorization of dye solutions [3].

One of the most important fibers, that are used in carpet industry is red fiber, and Acid Red 14 is the common dye for fiber dyeing, especially for woolen fiber dyeing. Hence, Acid Red 14 was chosen for this project.

2. Experimental

2.1. Materials and methods

The experimental equipment schematically is shown in Figs. 1–4. The electrocoagulation unit consisted of an 0.5-L electrochemical reactor with iron (ST 37-2) anode and steel (grade 304) cathode. The electrodes were 50 mm×50 mm or 40 mm×40 mm. The current density was maintained constant by means of a precision DC power supply (ADAK-PS 808).

The dye solution was prepared using Acid Red 14 provided by Aldrich company (Chromotrope FB). The structure of Acid Red 14 is shown in Fig. 5. All samples were allowed to settle for 20 min in a 250-ml vessel before any analysis. Neither centrifuging nor filtration was performed. The conductivity of the dye solution was relatively low.

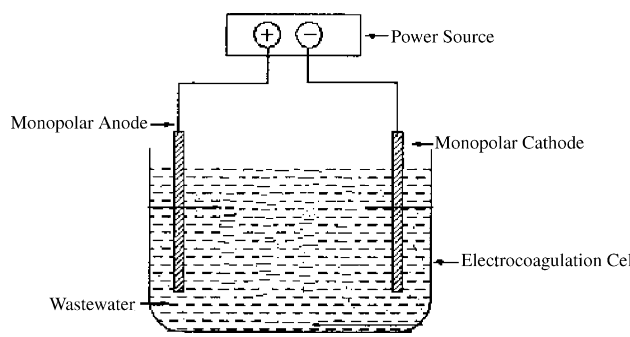

Fig. 1. Electrocoagulation apparatus.

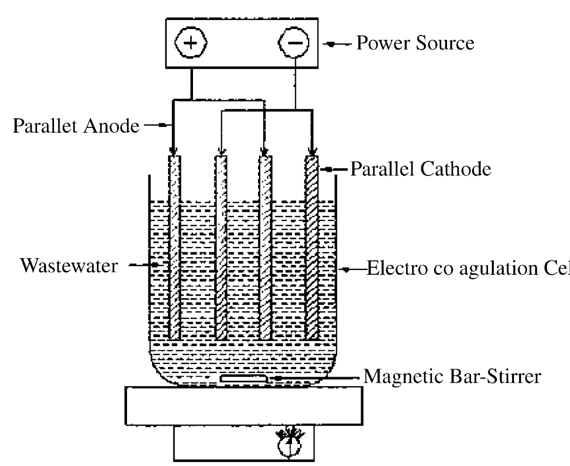

Fig. 2. Bench scale EC reactor with monopolar electrodes in parallel connection.

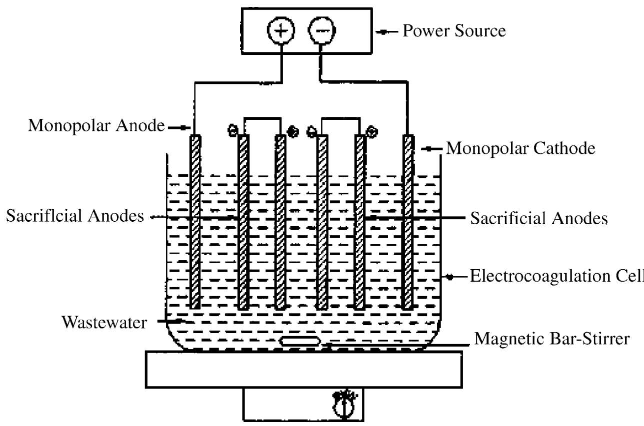

Fig. 3. Bench scale EC reactor with monopolar electrodes in series connection.

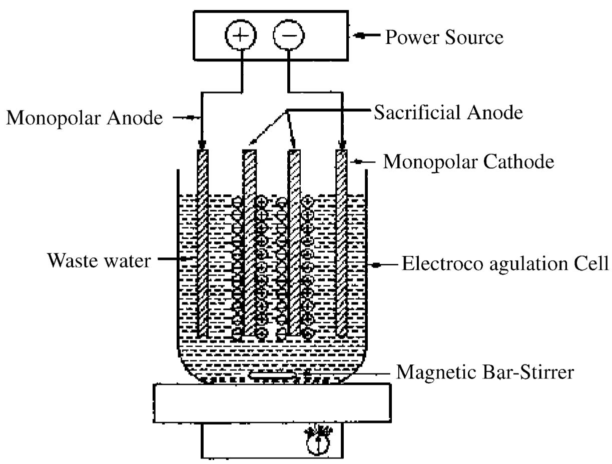

Fig. 4. Bench scale EC reactor with bipolar electrodes.

2.2. Chemical analysis

The dye concentration was determined using a UV-Vis spectrophotometer (Perkin-Elmer 550 SE) at 515 nm. The equation used to calculate the color removal efficiency in the treatment experiments was:

$$CR(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (10)$$

where C_0 and C were the initial and present concentrations of the dye in solution (mg/l), respectively.

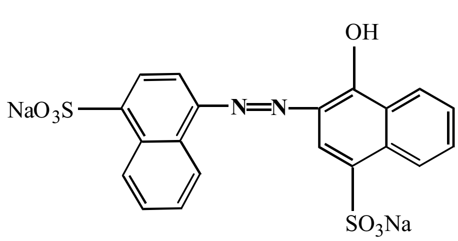

Fig. 5. Structure of Acid Red 14 (C.I. no. 14720).

The Chemical Oxygen Demand (COD) was measured by a volumetric method (closed reflux, titrimetric method) [10].

3. Results and discussion

3.1. Effect of current density on the efficiency of color removal

The exact range of the optimum current density will depend on the geographical as well as the economic situation where the EC process is utilized. As shown in Fig. 6, an increase in current density from 40 to 60 A/m^2 yields an increase in the efficiency of color removal from 52.10 to 91.12% because when the current density increases, the efficiency of ion production on the anode and cathode increases. Therefore, there is an increase in floc production in the solution and hence an improvement in the efficiency of color removal.

For a solution with a dye concentration of 50 ppm, the optimum current density was in the range of 60–80 A/m^2.

3.2. Effect of time of electrolysis on the efficiency of color removal

During electrolysis, the positive electrode undergoes anodic reactions while cathodic reactions occur on the negative electrode. The released ions neutralize the particle charges and thereby initiate coagulation.

The color-removal efficiency depends directly on the concentration of ions produced by the electrodes. When the electrolysis period increases, an increase occurs in concentration of ions and their hydroxide flocs. Accordingly, as shown in

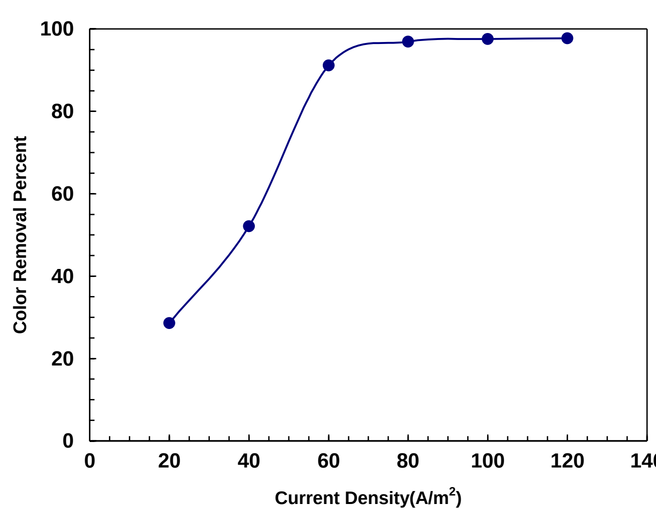

Fig. 6. Effect of current density on the efficiency of color removal from a solution with concentration of the dye = 50 ppm, volume of the solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, time of electrolysis = 4 min, retention time = 20 min, and dimension of the electrodes = 50 mm × 50 mm.

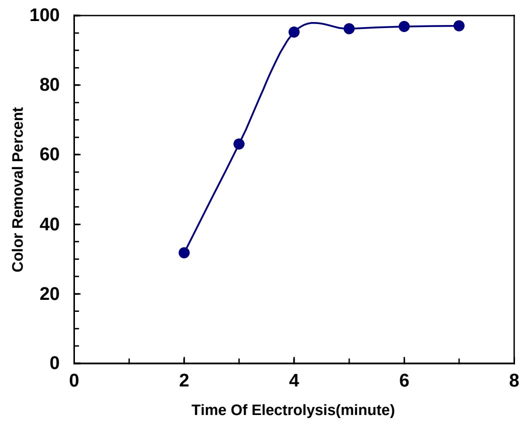

Fig. 7. Effect of time of electrolysis on the efficiency of color removal from a solution with concentration of the dye = 50 ppm, volume of the solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, current density = 80 A/m^2, retention time = 20 min, and dimension of the electrodes = 50 mm × 50 mm.

Fig. 7, an increase in the time of electrolysis from 2 to 4 min yields an increase in the efficiency of color removal from 31.76 to 95.24%.

For a solution having a dye concentration of 50 ppm, and a treatment unit with current density of approximately 80 A/m^2, the optimum time of electrolysis was 4 min.

3.3. Effect of interelectrode distance on the efficiency of color removal

Interelectrode distance does not have a significant effect on the efficiency of color removal. However, as shown in Fig. 8, when the interelectrode distance increases, the efficiency of color removal increases slightly. This change probably occurs because the electrostatic effects depend on the interelectrode distance, so when this distance increases, the movement of produced ions would be slower and they would have more opportunity to aggregate and produce flocs. Moreover, these flocs are able to adsorb more dye molecules.

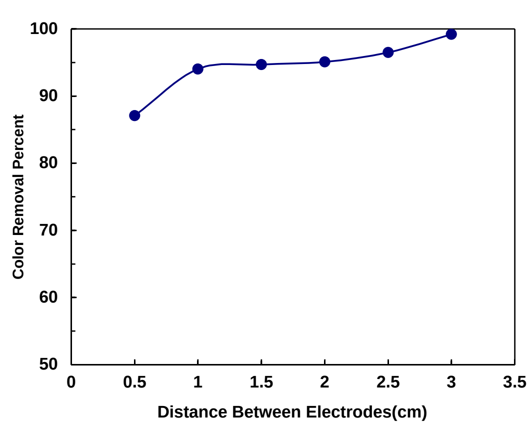

Fig. 8. Effect of interelectrode distance on the efficiency of color removal from a solution with concentration of the dye = 50 ppm, volume of the dye solution = 250 ml, C_{NaCl} = 10 g/l, current density = 80 A/m^2, time of electrolysis = 4 min, retention time = 20 min, and dimension of the electrodes = 50 mm × 50 mm.

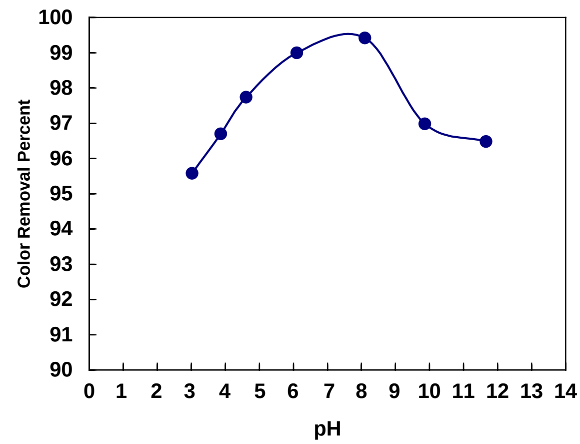

Fig. 9. Effect of initial pH on the efficiency of color removal from a solution with concentration of the dye = 50 ppm, volume of the dye solution = 250 ml, c_{NaCl} = 10 g/l, current density = 80 A/m^2, time of electrolysis = 4 min, retention time = 20 min, interelectrode distance = 1 cm, and dimension of the electrodes = 50 mm × 50 mm.

For a solution with a dye concentration of 50 ppm and a treatment unit with current density of 80 A/m^2, the optimum interelectrode distance was 1 cm.

3.4. Effect of initial pH on the efficiency of color removal

It has been established that the influent pH is an important operating factor influencing the performance of electrochemical process [3,11]. To examine its effect, the dye solution was adjusted to the desired pH for each experiment by adding sodium hydroxide or sulfuric acid. Fig. 9 demonstrates the efficiency of color removal as a function of the solution pH. The maximum efficiency of color removal was observed at pH in the range 6–9 as expected considering the nature of the reaction between ferrous and hydroxide ions. As observed by other investigators [3,12], a pH increase occurs when the solution pH is low. However, when the solution pH is above 9, a pH decrease occurs. In other words, electrocoagulation can act as a pH neutralizer [3].

3.5. Effect of temperature on the efficiency of color removal

The electrochemical reaction rate like any other chemical reactions rate increases when temperature of solution increases. As shown in Fig. 10, when the temperature increases, the efficiency of color removal increases slightly. However, when temperature of solution is higher than 300 K, the movement of the produced ions increases considerably and these ions have little opportunity to aggregate and produce metallic hydroxide flocs. As a result, the efficiency of color removal decreases.

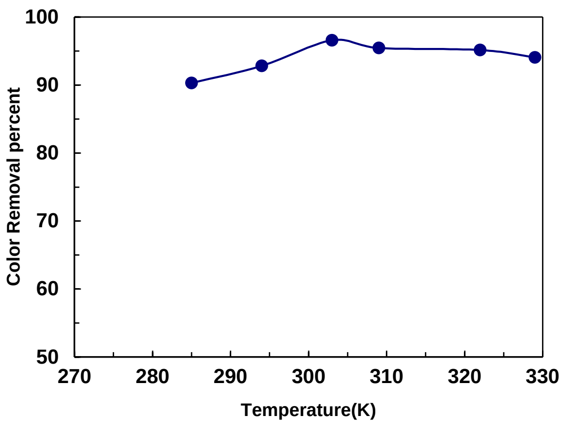

Fig. 10. Effect of temperature on the efficiency of color removal from a solution with concentration of the dye = 50 ppm, volume of the solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, current density = 80 A/m^2, time of electrolysis = 4 min, dimension of the electrodes = 50 mm × 50 mm, and retention time = 20 min.

3.6. *Effect of initial concentration of the dye on the rate of color removal and required power*

The variation of rate of color removal and required power for six different initial dye concentrations are shown in Figs. 11 and 12. It can be seen in Fig. 11 that the rate of color removal decreases considerably when the initial concentration of the dye is greater than 150 ppm. One of the most important pathways of color removal by EC process is adsorption on metallic hydroxide flocs. Up to a concentration of 150 ppm, the adsorption capacity of flocs is not exhausted and the rate of color removal is relatively constant. However, beyond this concentration, the adsorption capacity of flocs becomes exhausted. In other words, with an increase in the concentration of the dye, the rate of color removal decreases considerably.

As shown in Fig. 12, when the concentration of the dye solution was greater than 150 ppm, the power required for achieving a desired percentage of color removal increased. Therefore, the electrocoagulation process was more effective in decolorizing the dye solution when the concentration of the dye was less than 150 ppm.

3.7. *Effect of current density on the efficiency of color removal within an EC cell using monopolar electrodes in parallel connection*

An EC cell with a pair of anodes and a pair of cathodes in a parallel arrangement is shown in Fig. 2. Experiments showed that this cell was more effective than a simple electrochemical cell in color removal.

For a solution with a dye concentration of 50 ppm and interelectrode distance of 1 cm, the efficiency of color removal as a function of current density was determined (Fig. 13). The efficiency of color removal was greater than 90% when current density was approximately 30 A/m^2.

3.8. *Effect of current density on the efficiency of color removal within an EC cell using monopolar electrodes in series connection*

An EC cell with monopolar electrodes in series is shown in Fig. 3. Each pair of sacrificial electrodes is internally connected and has no interconnection with the outer electrodes. This arrangement of monopolar electrodes with cells in se-

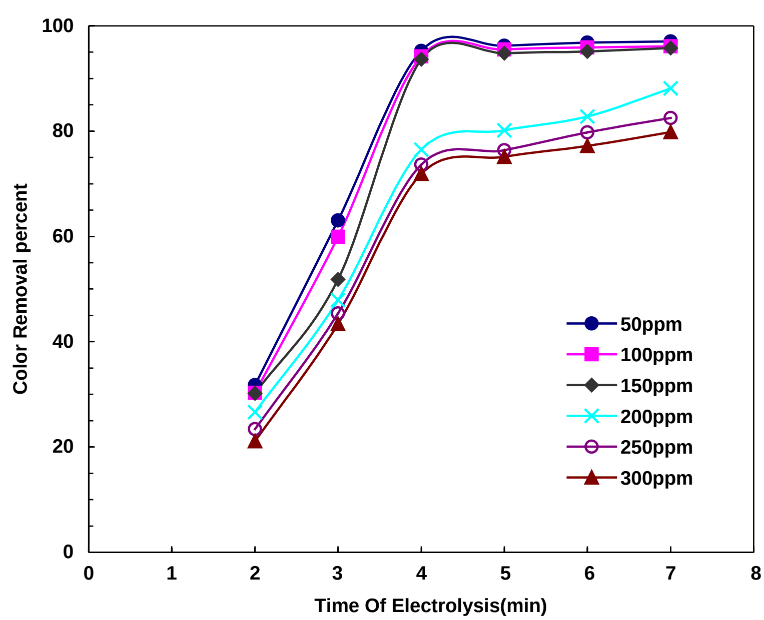

Fig. 11. Effect of initial concentration of the dye on the rate of color removal from a solution with volume = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, dimension of the electrodes = 50 mm × 50 mm, current density = 80 A/m^2, and retention time = 20 min.

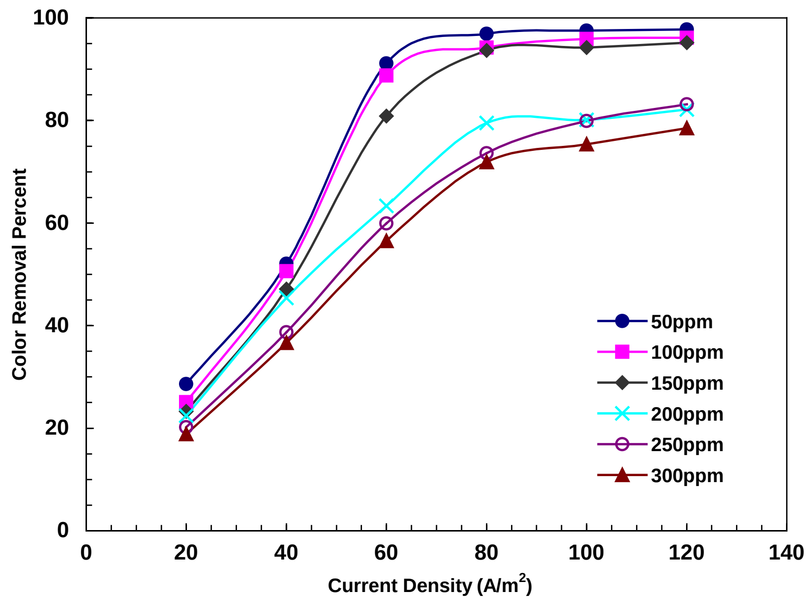

Fig. 12. Effect of initial concentration of the dye on power required for color removal from a solution with volume = 250 ml, C_{NaCl} = 10 g/l, interelectrode distance = 1 cm, dimension of the electrodes = 50 mm × 50 mm, time of electrolysis = 4 min, and retention time = 20 min.

ries is electrically similar to a single cell with many electrodes and inter connections [2].

Results showed that a cell with monopolar electrodes in series connection was more effective than a simple electrochemical cell for color removal.

As shown in Fig. 14, for a solution with a dye concentration of 50 ppm and interelectrode distance of 1 cm, the efficiency of color removal was greater than 90% when current density was approximately 20 A/m^2.

As shown in Fig. 15, an EC cell with electrodes in series connection was more effective in color removal than an EC cell with electrodes in parallel connection. This result is probably due to the higher potential required to achieve a certain current density in the series connection mode. Hence,

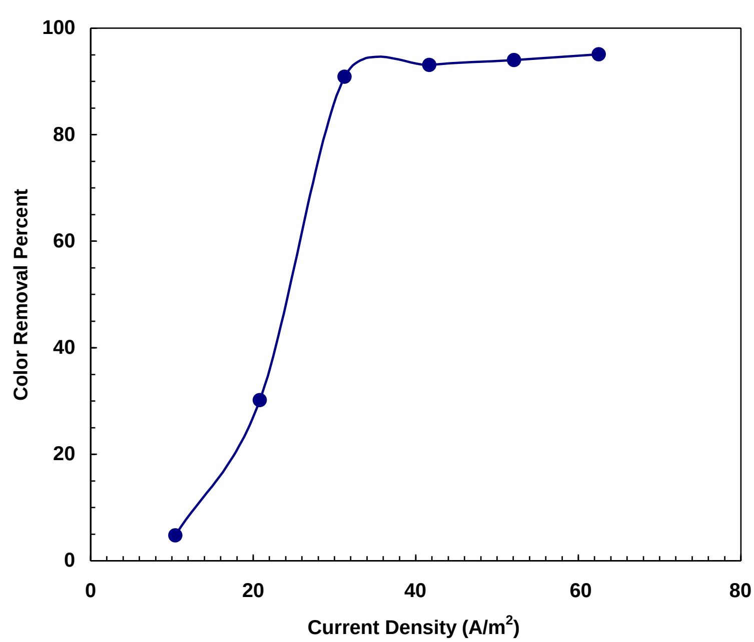

Fig. 13. Effect of current density on the efficiency of color removal within an EC cell using monopolar electrodes in parallel connection from a dye solution with concentration of the dye = 50 ppm, volume of the dye solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, time of electrolysis = 4 min, retention time = 20 min, and dimension of the electrodes = 40 mm × 40 mm.

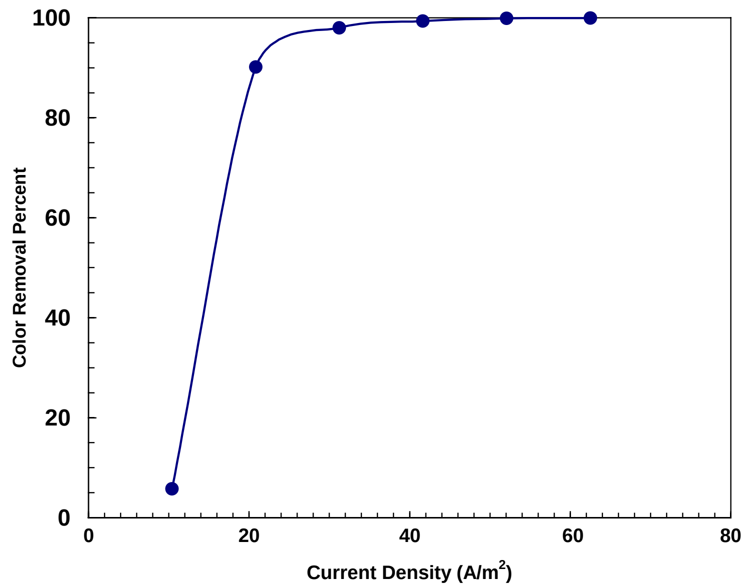

Fig. 14. Effect of current density on the efficiency of color removal within an EC cell using monopolar electrodes in series connection from a solution with concentration of the dye = 50 ppm, volume of the dye solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, time of electrolysis = 4 min, retention time = 20 min, and dimension of the electrodes = 40 mm × 40 mm.

this arrangement produces more flocs than the parallel connection mode, so the efficiency of color removal is higher.

3.9. Effect of current density on the efficiency of color removal within an EC reactor using bipolar electrodes

In this arrangement, the sacrificial iron electrodes were placed between the two parallel electrodes without any electrical connection (Fig. 4). Only the two monopolar electrodes were connected to the electric power source. When an electric current was passed through the two electrodes, the neutral side of the conductive plate was transformed to charged side, which had charges opposite to those on the parallel side. The sacrificial electrodes in this case are also known as bipolar electrodes. Thus, during electrolysis, the positive side undergoes anodic reactions, while on the negative side, cathodic reactions were encountered [2].

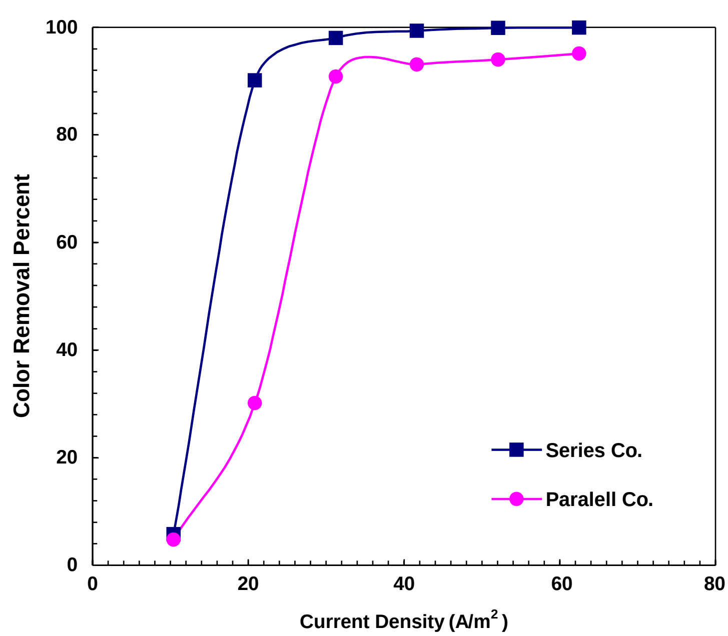

Fig. 15. Effect of current density on the efficiency of color removal within an EC cell using monopolar electrodes in: (a)series connection; b)parallel connection from a solution with concentration of the dye = 50 ppm, volume of the solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, time of electrolysis = 4 min, retention time = 20 min, and dimension of the electrodes = 40 mm × 40 mm.

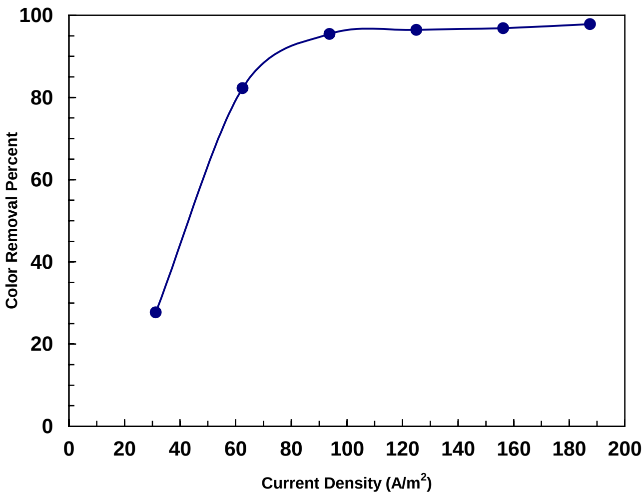

Fig. 16. Effect of current density on the efficiency of color removal within an EC cell using bipolar electrodes in parallel connection from a solution with concentration of the dye = 50 ppm, volume of the dye solution = 250 ml, c_{NaCl} = 10 g/l, interelectrode distance = 1 cm, time of electrolysis = 4 min, retention time = 20 min, and dimension of the electrodes = 40 mm × 40 mm.

The efficiency of color removal with different current density is shown in Fig. 16. The study showed that an EC cell with monopolar electrodes had a higher efficiency of dye removal than an EC cell with bipolar electrodes. For a dye solution with concentration of 50 ppm and interelectrode distance of 1 cm, the efficiency of color removal was greater than 90% when the current density was approximately 90 A/m^2.

3.10. COD of the dye solution

The COD of the initial dye solution was measured using a volumetric analytical method [10]. Then, subsequent to decolorization by a simple EC cell in optimized conditions (pH ranging from 6 to 9, time of electrolysis of approximately 4 min, current density of approximately 80 A/m^2, temperature approximately 300 K and interelectrode distance of 1 cm), the COD of the treated solution was measured again. The COD was reduced more than 85%.

4. Conclusions

The decolorization of dye solution (Acid Red 14) by means of electrocoagulation was affected by the current density, initial pH of the solution, interelectrode distance, and time of electrolysis. The results showed that when the initial concentration of the dye was less than 150 ppm, the dye was effectively removed (93%) at pH ranging from 6 to 9, time of electrolysis of approximately 4 min, current density of approximately 80 A/m^2, temperature approximately 300 K, and interelectrode distance of 1 cm. With the above conditions, the COD was reduced more than 85%. The experimental results showed that an EC cell with several electrodes was more effective than a simple electrochemical cell in color removal. The experiments also showed that an EC cell with monopolar electrodes had a higher color removal efficiency than an EC cell with bipolar electrodes. Moreover, within an EC cell, series connection of the monopolar electrodes was more effective than parallel connection in color removal.

Acknowledgements

The authors thank the University of Tabriz for financial and other supports provided.

References

[1] Z. Shen, W. Wang, J. Jia, J. Ye, X. Feng, A. Peng, J. Hazard. Mater. B84 (2001) 107–116.
[2] M. Yousuf, A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, J. Hazard. Mater. B84 (2001) 29–41.
[3] X. Chen, G. Chen, P.L. Yue, Seperation Purif. Technol. 19 (2000) 65–76.
[4] M.F. Pouet, A. Grasmick, Water Sci. Technol. 31 (3-4) (1995) 275–283.
[5] J.S. Do, M.L. Chen, J. Appl. Electrochemistry. 24 (1994) 785–790.
[6] N. Mameri, H. Lounici, D. Belhonice, H. Grib, D.L. Piron, Y. Yahiat, Seperation Purif. Technol. 24 (2001) 113–119.
[7] N. Mameri, A.R. Yeddou, H. Lounici, D. Belhonice, H. Grib, B. Bariou, Water Res. 32 (5) (1998) 1604–1612.
[8] M.J. Matteson, R.L. Dobson, R.W. Glenn Jr., N.S. Kukunoor, W.H. Waits III, E.J. Clayfield, Colloids Surf. A 104 (1995) 101–109.
[9] A.S. Koparal, U.B. Ogutveren, J. Hazard. Mater. B 89 (2002) 83–94.
[10] L.S. Clesceri, A.E. Greenberg, R.R. Trussell (Eds.), (Standard methods for the examination of water and wastewater, 17th edition, 1989, pp. 5-14.
[11] S.H. Lin, M.L. Chen, Water Res. 31 (4) (1997) 868–876.
[12] E.A. Vik, D.A. Carlson, A.S. Eikum, E.T. Gjessing, Water Res. 18 (1984) 1355.