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Evaluation of electro-coagulation method for decolorization and degradation of organic dyes in aqueous solutions

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Abstract−This research has two parts: at first part electro coagulation (EC) method was used to remove the dye Direct Black 22 (DB22 (in aqueous media. All experiments were done in a 2 liter reactor with two electrodes made of steel (SS-304) as cathodes and one aluminum electrode as anode. Parameters affecting the process, such as anode material, electrolyte concentration, current density, initial pH of solution and the initial dye concentration, were investigated. Total amount of consumed energy was used for determination of optimal conditions. According to the results obtained for DB22 at optimized conditions, color and COD removal percentage were 92% and 85%, respectively. In addition, the current efficiency for aluminum anode in removal of DB22 was 90%. At the second part of the research work, color removal by EC for six different dyes was evaluated. The results showed that dye structure and anode type are very important factors on performance of the process.

Key words: Direct Black 22, Electro Coagulation, Organic Dyes, Removal, Water Treatment

INTRODUCTION

Dye and textile manufacturing processes introduce a large amount of wastewater containing dyestuffs with intensive color and toxicity into the environment and aquatic systems [1]. Considerable quantity of toxic aromatic dyes, especially azo dyes, are known to be present in the wastewater generated by dye and textile industries [2]. The major characteristics of the wastewater generated by these industries, in many areas, are strong color, variable pH and temperature, high COD and low biodegradability. These cause some serious problems for aquatic life and human health disorders [3,4].

Various processes are applied for treatment and color removal from dye-contaminated effluents. The most common methods are biological treatment, chemical coagulation, activated carbon adsorption, ultra filtration, advanced oxidation processes (AOPs), ozonation and EC [5-7]. Biological methods are not applicable for most textile wastewaters due to the toxicity of most commercial dyes to the organisms used in the process [8]. The costs of treatment process for adsorption, ultra filtration and ozonation are higher in comparison with chemical coagulation [5]. Large volume of sludge is generated by chemical coagulation and may release secondary pollutants [9]. EC process provides a cost-effective, simple and reliable method for the treatment of wastewater without using any additional chemicals, thus producing the secondary pollution. It also reduces the amount of sludge, which needs to be disposed [10,11]. This process produces by anodic dissolution followed by hydrolysis, aluminum or iron hydroxide flocks which destabilize and aggregate the suspended particles or precipitates and absorbs dissolved contaminants. Aluminum and iron are the most common anode materials for EC method. These materials have low price, readily available, and proven effective [12]. For aluminum, the main reactions during EC are [12,13]:

At the cathode:

$$3H_2O+3e^- \rightarrow 3/2H_{2\,(g)}+3OH^- \quad (1)$$

At the anode:

$$Al \rightarrow Al^{3+}+3e \quad (2)$$

In the solution:

$$Al^{3+}_{(aq)}+3H_2O \rightarrow Al(OH)_3+3H^+_{(aq)} \quad (3)$$

EC has been successfully used to treat various wastewaters such as decolorization of dye solutions and textile wastewaters [14-18], potato chip manufacturing wastewater [19], removal of fluoride ions from industrial wastewater [2,21], heavy metal removal from wastewater [22,23], vegetable oil refinery wastewater [24], tannery wastewater [25], electroplating wastewater [26], removal of phosphate [27], and petrochemical wastewater treatment [28]. In this paper the EC process is used for removal of a poly azo dye, DB22 in aqueous solutions by an aluminum sacrificial anode, so the influence of operating variables such as current density, pH, conductivity, initial dye concentration, and structure of dye molecular was investigated. DB22 was selected because it is extensively used in textiles, printing and leather industry [29].

EXPERIMENTAL

1. Materials and Methods

The dye solution was prepared using DB22 provided by AlvanSabet Company (Iran). Its structure and characteristics are given in Table 1. The batch experimental cell is shown in Fig. 1. The synthetic wastewater containing the direct dye was prepared using distilled water. Sodium chloride, used as supporting electrolyte, was a product of Merck Company with purity of more than 99.5%. Concentration of the dye in each sample was analyzed with a UV-vis spectrophotometer (PG Instrument LTD Model T80), measuring

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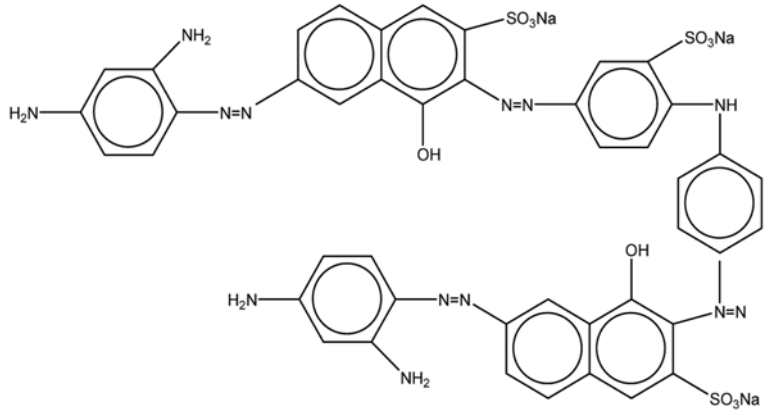
Table 1. Characteristics of the DB22 dye

Structure	
Chemical class	Azo
Color index number	C. I- 35435
λ_{max} (nm)	480
Mw (g/mol)	1083.99
Molecular formula	$C_{44}H_{32}N_{13}Na_3O_{11}S_3$

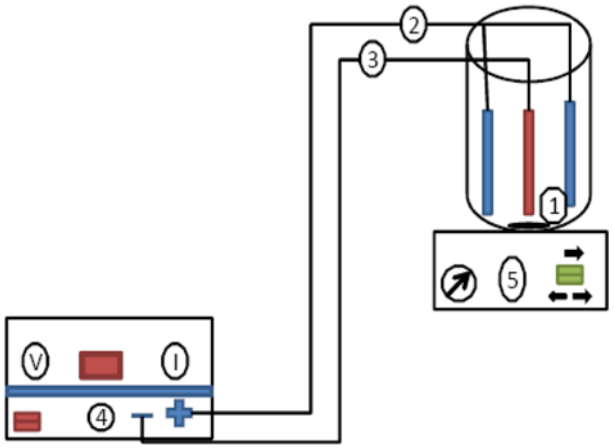


Fig. 1. Apparatus of the EC reactor.
1. Electrochemical cell
2. Cathodes (SS-304)
3. Anode (Aluminum)
4. DC power supply
5. Magnetic stirring

the absorbance at λ_{max}=480 nm using the appropriate calibration curve. The pH of the solutions was measured by pH meter (Jenway, UK-3010) and adjusted by adding NaOH or H_2SO_4 solutions (Merck, Germany). Steel plates (SS-304) were used as cathodes and aluminum plate was used as anode; also, we used iron (ST37-2) as anode. Dimensions of electrodes were 0.14 m×0.025 m×0.001 m and the distance between two electrodes in EC cell was 0.02 m in all experiments. The electrodes were connected to a DC power supply (Adak, PS-405, Iran). All the runs were performed at room temperature. In each run, 2 L of the dye solution was decanted into the electrolytic cell. All experiments were repeated twice.

2. Chemical Analysis

The dye concentration was estimated from its absorbance characteristics in the UV-vis range (200-800 nm) at maximum wavelength (λ_{max}=480 nm) with the calibration method. The color removal efficiency (X) after EC treatment was calculated by using this formula:

$$X = \frac{C_0 - C}{C_0} \quad (4)$$

Where C_0 and C are concentrations of dye before and after EC in mg/L, respectively. Energy consumption (E_{con}) was also calculated by using the commonly used equation:

$$E_{con} = VI\, t_{EC} \quad (5)$$

Where E_{con} is the electrical energy in Wh, V the cell voltage in volt (V), I the current in ampere (A) and t_{EC} is the time of EC process (hour). In this research criterion, E_{con}, which indicates the needed energy for almost perfect removing of the dye, was used for the evaluation of influence of the operational parameters on the EC. In this regard for all experiments X=0.9 was chosen as the desired point from treatment.

The chemical oxygen demand (COD) of the dye solutions was measured using open reflux method, according to the standard method procedure [33].

RESULTS AND DISCUSSION

1. Effect of Anode Material on EC Process

Electrode material has a significant effect on the treatment efficiency in any electrochemical process. Therefore, appropriate selection of the electrode material is important [2]. First, decolorization of solutions containing DB22, by using iron and aluminum materials, was investigated.

Results indicated that in pH=4 iron electrode removed DB22 effectively, but in neutral pH it could not; this is due to the fact that in pH=4 hydroxide surface has positive charge and absorbs DB22 which is anionic dye and removes it from solution [30], while aluminum electrode has a good performance in DB22 removal.

2. Effect of Electrolyte Concentration

Sodium chloride is usually employed for increasing the conduc-

tivity of water or wastewater in treatment processes [11]. Besides ionic contribution of sodium chloride in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions, such as HCO_3^- and SO_4^{2-}; for instance, by avoiding the precipitation of calcium carbonate in hard water that could form a protecting layer on the surface of the electrodes and increasing the ohmic resistance of the electrochemical cell. At very high current density, chloride anions can also be oxidized to active chlorine forms, such as hypochlorite anions, that can oxidize dyes [11,31].

The conductivity of the dye solutions was adjusted using NaCl. The experimental conditions were: initial pH of 6.8, current density J=25.71 A/m^2 and EC was conducted for X=0.9. NaCl in six different concentrations is used for determination of electrolyte effect on electrical energy consumption.

According to Fig. 2, increase in electrolyte concentration from 0.125 to 4 g/L causes an increase in electrical energy consumption which is due to more current. 0.125 g/L has the lowest energy consumption, but because the decolorization time is longer, 0.25 g/L is selected as a optimal concentration.

3. Effect of Initial pH

As reported by other investigators, it has been established that the pH of solution is an important operating factor influencing the performance of electrochemical process [27,32]. To examine its effect, the sample was adjusted to the desired pH for each experiment by adding sodium hydroxide or sulfuric acid solutions. Fig. 3 shows E_{con} as a function of the initial pH. Minimum E_{con} were observed at pH around 4. So initial pH of 4, can be introduced as optimum. In pH=2 there is high removal efficiency, because monomeric cations of aluminum bond to negative charge groups of dye and form insoluble species in solution. During experiments pH values have not changed considerably.

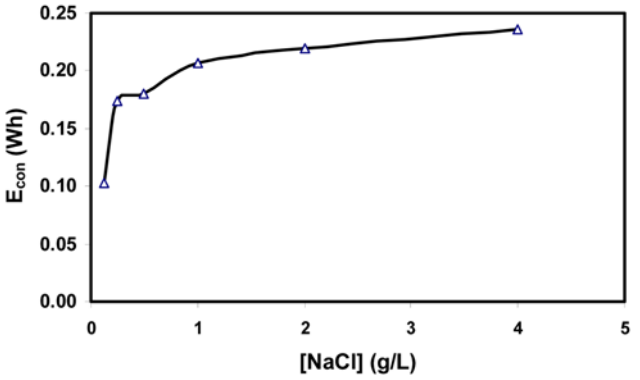


Fig. 2. The effect of consumed electrolyte on the energy consumption; C_{DB22}=50 mg/L, J=25.71 A/m^2, pH=6.8.

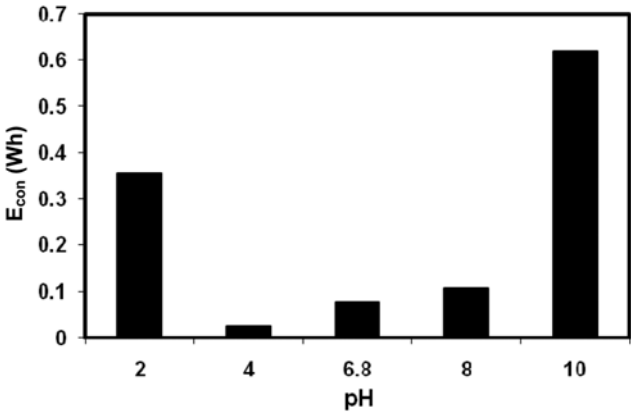


Fig. 3. Effect of initial pH on the energy consumption; C_{DB22}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2.

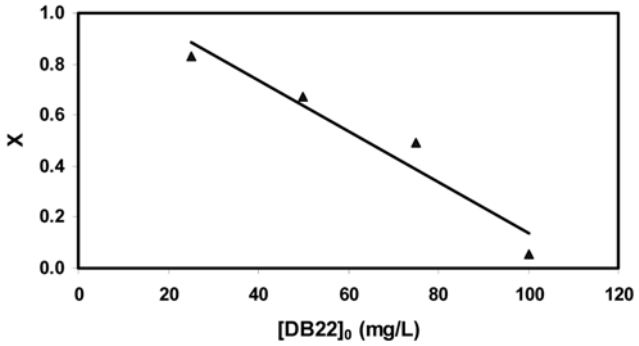


Fig. 4. Effect of initial concentration of dye in EC efficiency of DB22; C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=4.

4. Effect of Initial Concentration on the Efficiency of Dye Removal

The variation of rate of color removal for four different initial dye concentrations is shown in Fig. 4. It can be seen in Fig. 4 that with increasing initial concentration, removal efficiency of dye decreases linearly. The reason for this is the lack of flocs for adsorption of excess dye in high concentrations. It is necessary to mention that the total amount of flocs is constant for all concentrations.

5. Effect of Current Density and Current Efficiency

The effect of current density on the removal efficiency is calculated according to the following equation:

$$J = \frac{I}{A} \tag{6}$$

Where J is the current density (A/m^2), I is the current (A), and A is the active surface area of anode electrodes (m^2).

To determine the effect of J on the rate and energy consumption, experiments were performed with J values of 5.71, 11.42, 17.14 and 25.71 A/m^2, while maintaining the rest of the investigated parameters: d=0.02 m, C_{NaCl}=0.25 g/L and pH=6.8.

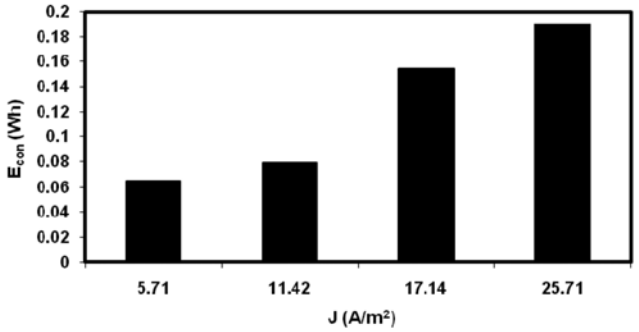


Fig. 5. Effect of current density on the energy consumption; C_{DB22} =50 mg/L, C_{NaCl}=0.25 g/L, pH=6.8.

As shown in Fig. 5, in J of 5.71 A/m^2 the E_{con} is lowest, but the time required for efficient removal will be longer 11.42 A/m^2. This difference is about 123 min.; therefore, 11.42 A/m^2 as optimal current density is selected.

Like all other electrolytic processes, current efficiency and electrical energy consumption are very important economical parameters in the EC process [11].

The current efficiency (□) of EC process was calculated (Eq. (7)).

$$\Phi=\left[\frac{\Delta M_{exp}}{\Delta M_{theo}}\right]\times 100 \quad (7)$$

In this equation ΔM_{exp} is the actual amount of aluminum dissolved in the solution due to oxidation of anode which was measured via back titration of EDTA by $ZnCl_2$ according with the standard method [33]. Also ΔM_{theo} is the theoretical amount of aluminum that should be dissolved in the solution by induced current in the electrolysis cell and can be calculated according to the Faraday law:

$$\Delta M_{theo.}=\frac{MIt_{EC}}{nF} \quad (8)$$

That M_{theo} is of the metal dissolved (g), I is the current (A), t is the time of EC process (hour), M is molecular weight of the metal (g/mol), n is the number of electrons involved in the redox reaction (for the Aluminum n=3) and F is the Faraday constant (96,487 C/mol) [6,10,11].

These calculations were carried out after optimizing the operational parameters in EC process. The calculated values are shown in Table 2.

6. COD Reduction of the DB22 Dye in Solution

The COD of dye solution was measured according to the standard methods for the examination of water and wastewater. Then, subsequent to decolorization in the optimized conditions (C_0=50 mg/L, J=11.42 A/m^2 and t_{EC}=16 min for DB22), the COD of the treated solution was measured. The COD was reduced more than 85% in solution Fig. 6.

Table 2. Current efficiency of aluminum electrode in EC process: C_{DB22}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=4

	V_{ZnCl2}	ΔM_{theo} (g)	ΔM_{exp} (g)	E (Wh)	X	I (A)	t_{EC} (min)
0.90	27.6	0.003579	0.003237	0.0232	0.92	0.04	16

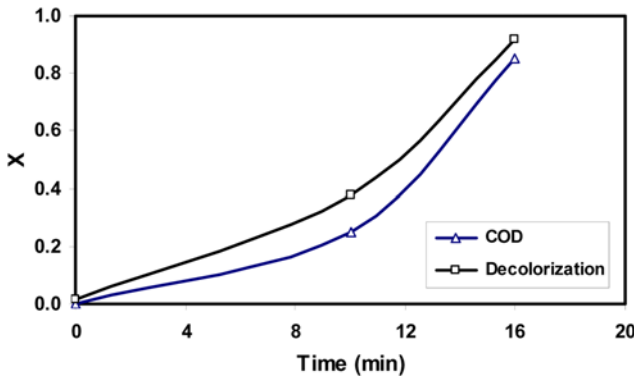


Fig. 6. Color and COD removal of DB22 in EC efficiency of DB22; C_{DB22}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=4.

7. Kinetics Study of DB22 Removal

The rate of removal of DB22 can be represented by the following first-order mechanism:

$$\ln\frac{C}{C_0}=-Kt \quad (9)$$

Where C_0 is the initial dye concentration (mg/L), k is the rate constant (min^{-1}) and t is the time (min). According to the above equation, a plot of $\ln(C_0/C)$ against t will yield a straight line with a slope of K. Fig. 7 reveals reasonably good fit of first-order kinetic model to the observed data. The rate coefficient for the first-order removal rate of DB22 can be obtained from Fig. 7.

8. Performance of EC Method on Color Removal

For comparison the effect of dyes type on color removal six different organic dyes as shown in Table 3 was selected and some experiments by iron or aluminum electrode as anode in neutral pH of each dye and C_{dye}=50 mg/L, J=11.42 A/m^2, C_{Nacl}=0.25 g/L were done.

As indicated in Figs. 8, 9, 10 and Table 4, the EC method by using aluminum as anode is an efficient process for removal of these six mentioned dyes; however, in removal of Bismarck brown 1 and acidic dyes iron anode is more effective than aluminum.

But as mentioned in part (3.1), iron anode is not able to remove DB22 in its neutral pH.

According to the results, the effect of dye type on performance showed that color removal with aluminum anode in comparison with iron anode is quite different. It means that adsorbent type is very important in the EC process. Dye type is also a main parame-

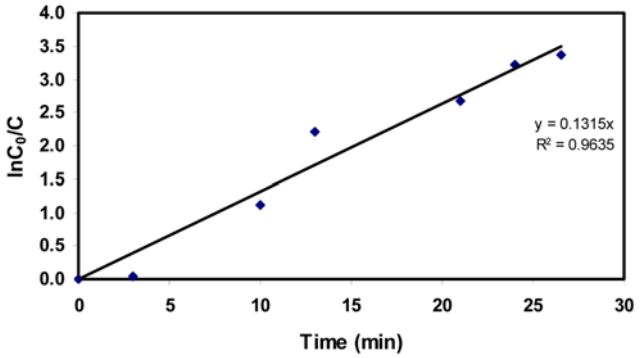


Fig. 7. Kinetic removal of DB22; C_{DB22}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=4.

Table 3. Characteristics of selected dyes

Chemical formula	λ_{max} (nm)	Mw (g/mol)	Dye
$C_{23}H_{13}C_{12}N_6O_8S_2$	596	637.43	C. I. Reactive Blue 4 (RB4)
$C_{26}H_{16}N_3Na_3O_{10}S_3$	568	695.58	C. I. Acid Blue 92 (AB92)
$C_{44}H_{32}N_{13}Na_3O_{11}S_3$	480	1083.969	C. I. Direct Black 22 (DB22)
$C_{16}H_{13}N_3O_7S_2Na_2$	530	467.38	C. I. Acid Red 33 (AR33)
$C_{18}H_{20}C_{12}N_8$	456	419.31	C. I. Bismarck Brown 1(BB1)
$C_{26}H_{17}N_5Na_2O_8S_2$	526	637.26	C. I. Direct Red 16 (DR16)

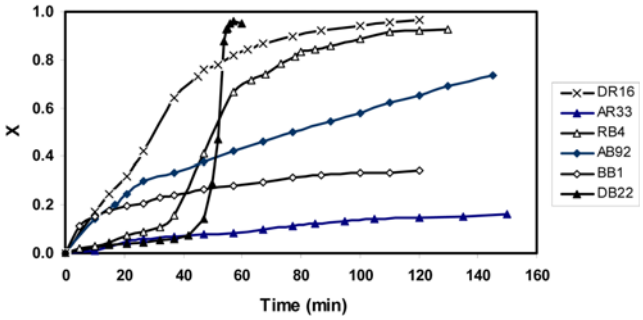


Fig. 8. The effect of dye type on EC efficiency by aluminum anode; C_{dye}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=Natural.

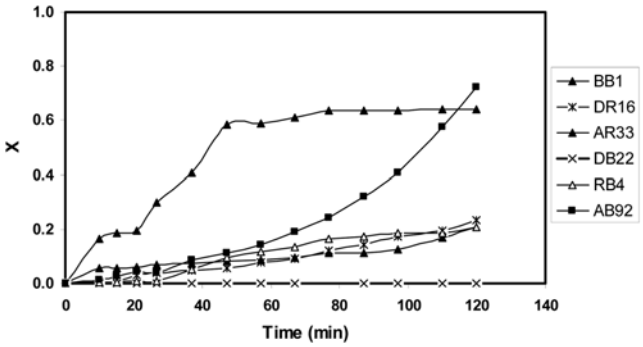


Fig. 9. Dye type investigation in EC process by iron anode; C_{dye}= 50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=Natural.

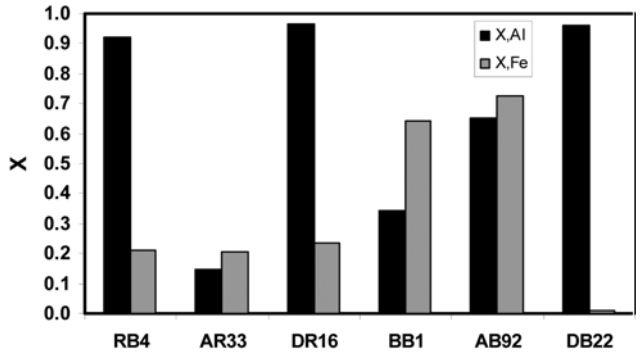


Fig. 10. Dye removal efficiency in EC process by aluminum and iron anodes; C_{dye}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=Natural.

Table 4. Dye removal efficiency in EC process by aluminum and iron anodes: C_{dye}=50 mg/L, C_{NaCl}=0.25 g/L, J=11.42 A/m^2, pH=Natural

Dye	t_{EC} (min)	X (aluminum anode)	X (iron anode)
C. I. Reactive Blue 4 (RB4)	120	0.88	0.18
C. I. Acid Blue 92 (AB92)	120	0.65	0.72
C. I. Direct Black 22 (DB22)	54.5	0.92	0.00
C. I. Acid Red 33 (AR33)	120	0.14	0.20
C. I. Bismarck Brown 1(BB1)	120	0.34	0.63
C. I. Direct Red 16 (DR16)	120	0.95	0.23

ter too, because different dyes have different removal efficiency based on their molecular weight, structure, solubility and type of intermediate products from electrochemical decomposition.

CONCLUSIONS

In this study the EC process is used for removal of dyes and the results showed that this method is very effective for removal of dyes like DB22. The effect of various operational parameters on color removal efficiency was investigated and optimized. The decolorization of the reactive dye using aluminum sacrificial anode was affected by the initial pH, the current density, the amount of NaCl and the initial dye concentration. The removal efficiency of DB22 and COD of the sample were 92% and 85%, respectively, when aluminum was used as a sacrificial anode under the conditions of initial pH 4, initial dye concentration 50 mg/L, current density 11.42 A/m^2, salt concentration 0.25 g/L, temperature 300 K, centrifuge time 5 min, electrolysis time 16 min, and distance between the electrodes 0.02 m. At above optimal conditions the current efficiency for aluminum anode in removal DB22 was 90%. The results showed that first-order kinetic model was found to be in good agreement with the experimental results. Finally, the effect of dye structure on performance showed that dye removal with aluminum anode in comparison with iron anode is quite different.

ACKNOWLEDGEMENTS

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NOMENCLATURE

EC : electrocoagulation
DB22 : direct Black 22
COD : chemical oxygen demand
X : color removal efficiency [%]
C_0 : the concentration of the dye (mg L^{-1}) before of EC process
C : the concentration of the dye after EC process
E_{con} : electrical energy consumed [Wh]
V : voltage [V]
I : current [A]
T_{EC} : time of EC process [hour]
J : current density [A/m^2]
A : the active surface area of anode electrode [m^2]
Φ : current efficiency of EC process
ΔM_{exp}: the actual amount of aluminum dissolved in the solution due to oxidation of anode
ΔM_{theo}: the theoretical amount of aluminum that should be dissolved in the solution
M : molecular weight of the metal [g/mol]
N : the number of electron moles
F : faraday s constant [96,487 C]

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