Color Removal from Simulated Textile Effluents Using Clean Electrocoagulation Technique

Elham Keshmirizadeh*, Roya Khosravi, Sabereh Mahdifar

1Department of Applied Chemistry, Karaj Branch, Islamic Azad University, Karaj, Iran.
(Received 26 Apr. 2012; Final version received 28 Sep. 2012)

Abstract
The present work was directed toward the successful ability of electerocoagulation to remove color from synthetic and simulated textile effluent by aluminum/iron electrodes. Two representative reactive dyes were selected for the synthetic dye system, a black dye alone and mixed dye (black, blue, red, 1:1:1 vol/vol). Several important operating parameters such as electrode material, initial pH(3-9), current density(60-120 A/m²), operating time (6-40), initial dye concentration (100-1200 mg/L) and solution conductivity (applied conductivity is better than literature) were studied in an attempt to reach higher color removal efficiency (%98). The chemical oxygen demand decreased by more than %87. The results of this work are comparable with those of recent studies. The electrical energy consumption in the above conditions was on order of 1.2-3.2 kWh/m³ of wastewater and the water recovery was 0.97m³ /m³ of wastewater, in this research “water recovery” was introduced and calculated in order to show the more economically feasible recycling of treated water. However the operating parameters used for the synthetic dye were less effective for treatment of simulated textile wastewater.

Keywords: Electerocoagulation (EC), Textile effluents, Black dye, Mixed dye, Aluminum electrodes, Iron electrodes.

Introduction
The electrocoagulation technique is potentially considered to be an effective tool for the treatment of textile wastewater with high removal efficiency [1-2]. In the recent past, problems involving water contamination have called the attention to the necessity of removing toxic organic compounds from industrial aqueous effluents [3]. Dye effluents from printing, dyeing and textile industries may contain chemicals that exhibit carcinogenicity, reproductive and developmental toxicity and chronic toxicity toward humans and animals [4]. Dye compounds are found in high concentrations in the residual waters of paint, paper and textile industries. The textile industry actually represents a range of industries with operations and processes as

*Corresponding author: Dr. Elham Keshmirizadeh, Assistant Prof., Department of Applied Chemistry, Karaj Branch, Islamic Azad University, POBOX: 31485-313, Karaj-Iran. Email: ekeshmirizadeh@yahoo.com, Tel: 0261-4182764, Fax: 0261-4418156.
diverse as its products. It is almost impossible to describe a “typical” textile effluent because of such diversity [5].

Conventional wastewater treatment system is inefficient because of the recalcitrant nature of dyes. Existing physical and chemical technologies are expensive, time consuming and produce a large amount of sludge or cause secondary pollution [6]. EC requires simple equipment and is easy to operate [7]. The EC cell is controlled electrically and has no moving parts, thus requires less maintenance, also the EC process avoids uses of chemicals and so there is no problem of neutralizing excess chemicals [8]. EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. The ability of EC to carry out decolorization has recently achieved very much attention [9, 10].

The present work on decolorization of mixed dyes is a step toward an effective treatment of textile wastewater. In this study, a wide range of initial black dye concentrations (10-100) mg/L alone and initial mixed dye concentrations (100, 300, 500, 1000, 1200) mg/L were investigated, whereas most of other studies worked on initial dye concentrations up to 100 mg/L [11]. Some important operating parameters were optimized for the efficient degradation, analysis of dye removal and the exploitation of the EC for dye removal from dye mixtures. These parameters included electrode type, current density, time of EC, energy consumption, pH, on the process efficiency and COD removal of the synthetic wastewater. The parameters that were found to be suitable for the EC treatment of the synthetic wastewater were then tested in an EC treatment of simulated wastewater from a textile dyeing factory. Two processes can interfere with the electrolytic process: polarization or passivity and mass transport control [12-14]. It should be noted that, in this investigation, the influences of various supporting electrolytes were studied to avoid electrode passivity. However, in this research “water recovery” was introduced and calculated in order to show the more economically feasible recycling of treated water.

A Brief Description of EC

EC involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions in aluminum or iron electrodes, respectively. The anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals [1]. If iron or aluminum electrodes are used, the generated Fe(aq)³⁺ or Al(aq)³⁺ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides [15]. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials [16].

EC of wastewater using iron electrodes takes
place according to the following reactions: the following mechanism is involved for the production of Fe(OH)$_m$ typically, where $m=2$ or 3 [17]:

- **Anodic reactions:**
  
  $$\text{Fe(s)} \rightarrow \text{Fe}^{2+} (\text{aq}) + 2e^- \quad (1)$$
  
  $$\text{Fe}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Fe(OH)}_2 (\text{s}) \quad (2)$$

- **Cathodic reaction:**
  
  $$2\text{H}_2\text{O (l)} + 2e^- \rightarrow 2\text{OH}^- (\text{aq}) + \text{H}_2 (\text{g}) \quad (3)$$

- **Overall reaction:**
  
  $$\text{Fe(s)} + 2\text{H}_2\text{O (l)} \rightarrow \text{Fe(OH)}_2 (\text{s}) + \text{H}_2 (\text{g}) \quad (4)$$

The insoluble metal hydroxides of iron can remove dye molecules by surface complexation or electrostatic attraction. In surface complexation, it is assumed that the pollutant can act as a ligand to bind a hydrous iron moiety with precipitation and adsorption mechanisms [16]:

**Precipitation:**

Dye + monomeric (or polymeric) Fe$\rightarrow$ [Dye-monomeric(or polymeric) Fe]$_{(S)}$ \hspace{1cm} (5)

**Adsorption:**

Dye + Fe(OH)$_n$$_{(S)}$ $\rightarrow$ [Sludge] \hspace{1cm} (6)

**Experimental**

**Materials**

All chemicals used were of analytical grade. Two representative dye molecules were selected for the synthetic dye wastewater, a black reactive dye alone and mixed dye (containing reactive black, reactive blue, reactive red, 1:1:1vol/vol) see Table1. All organic dyes, kindly provided by Ghazvin Textile Processing industry, Ghazvin, Iran.

**Sampling and Preparation**

The dye wastewater was synthesized with a certain amount of mixed dye (or black dye) after pH adjustment (sulfuric acid solution and sodium hydroxide (0.1M) were used). Original pH of the solution was 5. The composition of simulated industrial textile wastewater was represented in Table1. In order to standardize the textile wastewater in the runs, the industrial textile wastewater was synthetically prepared based on real process information of pretreatment and dyeing stages [18].

**Experimental Set-up**

The EC experiments were conducted in an undivided electrochemical cell (net volume reactor was 0.7 L) (Figure 1), using a batch mode with a sufficient magnetic stirring (200rpm). The cell contained two parallel planar electrodes with an inter-electrode distance of 1.5 cm, using iron or aluminum electrode as anode or cathode (6×6 cm$^2$) as reported in our previous work [14]. The degradation started when the electricity was switched on and the current was set at the desired value. One DC power supply package having an input of 220V and variable output of
0–30 V, with variable current 0–4 A was used.

Methods of Analysis and Measurements
In all experiments [19] (APPA - AWWA 2005), the pH was measured with a Metrohm pH meter (Model No. 827), the conductivity was measured with an Hach/Lange conductivity meter (method 2510-B), COD, dye concentrations were determined from their absorbance characteristics in the UV–vis range (200–800 nm) with the calibration method from standard methods (method 2120-C), using an UV-vis spectrophotometer (Hach/Lange (DR/2800)) was used. Upon completion of the process, the test samples were filtered before dye analysis. Samples were taken at given time intervals for analysis. All experiments were repeated twice, and the experimental error of 4% was observed. The calculation of dye removal efficiency after EC process was performed using this formula:

\[
\text{Dye removal efficiency (\%)} = \frac{100 \left(ABS_0^M - ABS^M\right)}{ABS_0^M} \tag{7}
\]

where \(ABS_0^M\) is the average of absorbance values as it is maximum absorbency visible wavelength, \(ABS^M\): the value after EC, \(ABS_0^M\): the value before EC, \(\lambda_{\text{max}}\) (black dye)=600nm, \(\lambda_{\text{max}}\) (red dye)=571nm, \(\lambda_{\text{max}}\) (blue dye)=571nm, \(\lambda_{\text{max}}\) (mixed dye)=597nm. Power consumption or electrical energy consumption (EEC) was determined as follows:

\[
\text{EEC (kWh/m}^3 \text{ wastewater)} = \frac{VIt}{v} \tag{8}
\]

where \(V\) is the operating voltage (volt), \(I\) is the operating current (ampere), \(t\) (or \(t_{\text{EC}}\)) is the time of reaction (hr) and \(v\) is the volume of wastewater (m\(^3\)).

Figure1. Schematic diagram of the electrocoagulation reactor [14].
Table 1. The composition of simulated textile wastewater [19], and synthetic mixed dye (in this study).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration (simulated textile wastewater)</th>
<th>Concentration (synthetic mixed dye, in this study)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cottoclarin F(mg/L)</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Dextrin(mg/L)</td>
<td>1600</td>
<td>-</td>
</tr>
<tr>
<td>Sucrose(mg/L)</td>
<td>640</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen peroxide (35-40%, d=1.133(mL/L)</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Sodium hydroxide(mg/L)</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>Acetic acid(mg/L)</td>
<td>165</td>
<td>-</td>
</tr>
<tr>
<td>Reactive dye(mg/L)</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Sodium carbonate(mg/L)</td>
<td>700</td>
<td>-</td>
</tr>
<tr>
<td>Sodium chloride(mg/L)</td>
<td>5000</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene dinitro tetra acetic acid(EDTA)(mg/L)</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>Detergent(mg/L)</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>Silicon oil(mg/L)</td>
<td>20</td>
<td>-</td>
</tr>
</tbody>
</table>

The current density (CD) was measured according to equation (9):

$$ CD = \frac{I(A)}{2S_{\text{electrode}}(m^2)} \quad (9) $$

The water recovery was measured according to equation (10) [14]:

$$ Water \ recovery = \frac{\text{volume of product water (after EC)}}{\text{initial volume of wastewater (before EC)}} \quad (10) $$

Indeed the clear supernatant is product water or treated water; however, highly dense (or dewatered) sludge remained at the reactor bottom after EC.

Results and discussion

The optimum operating conditions are described below and the EC process was controlled by several operational parameters, such as follows:

**Effect of Current Density on the Black Dye Removal Efficiency**

In all electrochemical processes, current density (CD) is the most important parameter for reaction controlling in the reactors. According to Faraday’s law [20] CD determines the coagulant production rate and regulates the rate and size of the bubbles and growth of flocs. A series of EC tests were carried out by solutions containing constant initial dye concentrations with CD varied from 60 to 120 A/m². It is obvious that the dye removal efficiency increases at higher CD. Figure 2 shows the black dye removal efficiency versus different CD (for example...
black dye alone: 100 mg/L, treatment time: 6min). The optimum CD of 100 Am\(^{-2}\) was used for the decolorization from dye solution containing black dye. The results show some improvement over previous attempts [9]. It should be noted that an increase in current density from 100 to 120 A/m\(^{2}\) yielded an increase in the efficiency of color removal from 98 to 99%, which was not a significant change. As a result of increasing the CD, the applied potential increased. Thus, it is advisable to limit the CD in order to avoid excessive oxygen evolution as well as to eliminate other adverse effects, like heat generation [1]. Therefore, 100A/m\(^{2}\) was a reasonable CD in our experiments. In this study, the CD that was found to be suitable for the EC treatment of black dye was then tested in EC treatment of mixed dye and also simulated textile effluent.

![Figure 2](image)

**Figure 2.** Effect of current density on the black dye removal efficiency. Conditions: Black dye concentration: 100 mg/L, pH\(_{\text{initial}}\): 5.5, Initial conductivity: 2.75 mS/cm, Initial volume of wastewater: 700mL, Electrode: Fe/Fe, Electrolyte: NaCl.

**Effect of Initial pH on the Black Dye Removal Efficiency**

It has been established that the pH is an important parameter influencing the performance of the electrochemical process [21]. The dependence of EC time on initial pH values in black dye and mixed dye were investigated over pH range of 3-9, see Figure 3. If pH is 3 or 9 efficiency decreases to below 20%. 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 [22]. At lower pH the protons in the solution are reduced to H\(_2\) at the cathode and the same proportion of hydroxide ions can not be produced [23]. According to Figure 3, the maximum removal efficiency was 98% in pH=5.5 for black dye, similar effects were reported by song [21] and 98% in pH=7 for mixed dye (also 95% in pH=5.5). The form of Fe-species formed in the wastewater could not explain the observed pH effect because the data in the literature on the ferric-hydroxy complexes concentration – pH diagram actually show the cationic ferric-hydroxy complexes that are expected to be favorable for dye coagulation are predominant at low or neutral pH [24]. Since the initial pH value of the black dye solutions was near 5.5, no change in the pH of the solution was needed and all later experiments were done at this initial pH.
Figure 3. The influence of initial pH on the time of EC for black and mixed dye. Conditions: Initial dye concentration: 100 mg/L, Dye removal efficiency: 98% Initial conductivity: 2.75 mS/cm, CD: 100A/m², Initial volume of wastewater: 700mL, Electrolyte: NaCl.

Effect of Electrode Type on the Black Dye and Mixed Dye Removal Efficiency

To examine the effect of electrode type in more detail, the anodes were changed between Fe, Al and combined Fe/Al. Figure 4 shows the electrode type as a function of EC time for the 3 electrode types, also the detailed conditions are represented in Table 2. Even though sharp increases of removal efficiencies could be observed with 6 min EC time for Fe/Fe and Fe/Al in black dye and for mixed dye in Fe/Al electrode. The iron type resulted in higher removal efficiency at shorter EC times than the other electrode types. Table 2 compares the energy consumption and water recovery for each electrode type. The iron anode required the lowest energy ranging between 1.238-1.338kWh/m³ of wastewater for black dye and between 1.234-1.278kWh/m³ of wastewater for mixed dye even though the resistance of iron material is higher than that of aluminum (iron:10⁻⁷Ω.m, aluminum:2.82×10⁻⁸Ω.m) [25]. A possible explanation is based on the difference in physical characterization of the particles in the treated wastewater.

As observed from the experiment, the characteristics of the particles formed by the Al anode were different from those formed by the Fe. The particles from the Al looked puffy and fluffy and had bad settling characteristics, while those from the Fe were dense and settled down quickly. The aluminum hydroxide flocks resulting in higher resistance and increased energy consumption. The Fe was ranked over the Al and combined Fe/Al electrodes in treating black dye, because the Fe resulted in better dye removal efficiency and lower consumption of electrical energy.

Figure 4. Effect of electrode material on the EC time for the treatment of black dye and mixed dye. Conditions: Initial dye concentration: 100 mg/L, Dye removal efficiency: 98% Initial conductivity: 2.75 mS/cm, CD: 100A/m², Initial volume of wastewater: 700mL, Electrolyte: NaCl.
Table 2. Optimized operational parameters for various electrodes.

<table>
<thead>
<tr>
<th>Type of electrode [Anode/Cathod]</th>
<th>Operating time (min)</th>
<th>Energy consumption (kWh/m³ of wastewater) Eq.(8)</th>
<th>Water recovery (m³/m³ of wastewater) Eq. (10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Black dye</td>
<td>Mixed dye</td>
<td>Black dye</td>
</tr>
<tr>
<td>Fe/Fe</td>
<td>6</td>
<td>6.3</td>
<td>1.238</td>
</tr>
<tr>
<td>Fe/Al</td>
<td>6</td>
<td>6</td>
<td>1.331</td>
</tr>
<tr>
<td>Al/Al</td>
<td>&gt;30</td>
<td>10</td>
<td>1.731</td>
</tr>
</tbody>
</table>

Conditions: Initial dye concentration: 100 mg/L, Dye removal efficiency: 98%. Initial conductivity: 2.75 mS/cm, CD: 100A/m², Initial volume of wastewater: 700mL, Electrolyte: NaCl.

Effect of Initial Concentration on Mixed Dye Removal Efficiency

Dye solutions with different initial concentrations in the range of 100–1200 mg/L were treated; however, other studies worked on initial dye concentrations up to 200 [17] and [9] or 400 mg/L [21]. Consequently, optimized operational parameters such as CD, EC time and EEC values are represented based on various initial mixed dye concentrations in Table 3. According to the results, at high initial mixed dye concentrations, the removal efficiency was near 98% while time, voltage and the energy consumption increased, [21] reported similar results for the removal of dye solutions up to 400 mg/L; however, [17] and [16] obtained different results.

Table 3. Optimized operational parameters for various mixed dye initial concentrations.

<table>
<thead>
<tr>
<th>Initial mixed dye concentration (mg/L)</th>
<th>Operating time (min)</th>
<th>Energy consumption (kWh/m³ of wastewater) Eq.(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>6</td>
<td>1.234</td>
</tr>
<tr>
<td>300</td>
<td>6</td>
<td>1.728</td>
</tr>
<tr>
<td>500</td>
<td>6</td>
<td>1.810</td>
</tr>
<tr>
<td>1000</td>
<td>6</td>
<td>1.892</td>
</tr>
<tr>
<td>1200</td>
<td>10</td>
<td>3.291</td>
</tr>
</tbody>
</table>

Conditions: pH_{initial}: 7, Electrode: Fe/Al, Electrolyte: NaCl, Dye removal efficiency: 98%, Initial conductivity: 2.75 mS/cm, CD: 100A/m², Initial volume of wastewater: 700mL.

Effect of Electrolyte Dosage and Type of Supporting Electrolyte

In this research, two tasks were investigated: (1) access to maximum dye removal efficiency and (2) a study on water recovery reuse. If the conductivity of water recovery is near 2.75 mS/cm or less, recycling is more economically feasible. In this study, electrolyte consumption for enhancement of EC was optimized at 2.75 mS/cm, and other operational parameters are reported based on this conductivity level (Tables 3, 4). However, other authors [21] and
[17] reported a conductivity level of up to 15 mS/cm. Thus electrolyte consumption in the highest dye concentration (1200 mg/L) was 1.5 g/L in this study; see Figure 5, whereas in previous research values up to 10 g/L were reported.

Textile wastewaters have a broad variation in conductivity. Higher conductivity decreases the potential for the same current density. In order to reduce the IR-drop or solution resistance potential, conductivity of the solution should be sufficient. Most EC studies have used chloride as anion to enhance the conductivity of the solution [15] and some of them have utilized sulfate as the electrolyte [21]. To study the effect of electrolyte type on the removal efficiency of black dye and mixed dye by EC in the presence of different supporting electrolytes including NaCl, KCl, Na₂SO₄, K₂SO₄, MgSO₄ and NaNO₃ was studied. Current density of 100 A/m² and initial conductivity of 2.75 mS/cm were uniformly applied to the experiments. It can be seen from Figure 6 that in the presence of NaCl the removal efficiency of black dye and mixed dye were 0.98 at the time of 6 min. This is compared with the EC time of 7 to 20 min for the same experiments performed in the presence of other electrolytes. The difference could be attributed to the passivity of electrodes. However in the presence of chloride ion, the passivity is curtailed since the adsorbed chloride ion promotes the dissolution of iron [26]. Comparison of EC time revealed that sulfate and nitrate ions have less influence on corrosion of iron than chloride (Figure 6).

**Treatment of Synthetic Mixed Dyes and Simulated Textile Wastewater**

When reactive blue and reactive red and reactive black were mixed, the synthetic
mixed dye turned black. Figure 3 to 5 and Table 2 show that the same set of design parameters effective for treating black dye individually may also treat the mixed dyes effectively. The set of parameters that were effective for both dyes was further employed to treat the simulated textile wastewater. Table 1 compares the properties of the synthetic mixed dye wastewater and simulated textile wastewater before electrochemical treatment in this study. Table 4 shows that removal of dye from simulated textile wastewater is expected to be more difficult than from synthetic mixed dye wastewater. The simulated textile wastewater might contain some components which interfere with the curtailed mechanism.

**Table 4.** Optimized operational parameters for mixed dye and simulated wastewater.

<table>
<thead>
<tr>
<th>Initial dye concentration (mg/L)</th>
<th>Operating time (min)</th>
<th>Water recovery (m^3/m^3 of wastewater)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed dye</td>
<td>1200</td>
<td>10</td>
</tr>
<tr>
<td>Simulated textile effluent</td>
<td>1200</td>
<td>40</td>
</tr>
</tbody>
</table>

| Conditions: pH_{initial}: 7, Electrode: Fe/Al, Electrolyte: NaCl, Dye removal efficiency: 98%, Initial conductivity: 2.75 mS/cm, CD: 100A/m^2, Initial volume of wastewater: 700mL. |

**Conclusion**

The study on decolorization of mixed dye is a step toward an effective treatment of textile wastewater. Overall, the EC process has the potential to treat the textile wastewater and thus to reduce the contamination of the environment by the dye molecules. In this research, although suitable choices of values of some parameters were different for each dye, a set of optimum operating parameters that could be used to treat black dye separately and a mixture of three dyes by electerocoagulation technique were proposed as follows:

(i) The optimum operating conditions in dye solutions containing initial black dye and mixed dye concentrations within 100-1200 mg/L were obtained to achieve a higher removal capacity (98%). Optimized range of electrical energy consumption (EEC): 1.2-3.2 kWh/m^3 of wastewater, optimized current density: 100A/m^2, operating EC time: 6–10 min, pH_{optimum}: 5.5, 7 (in addition, this study showed that the influence of initial pH was different for each dye), applied electrical potential: 12–15 V, the “water recovery” was very significant, measuring as high as 0.97 m^3/m^3 of wastewater. However, in this research “water recovery” was introduced and calculated in order to show the more economically feasible recycling of treated water, also Fe/Fe and Fe/Al electrodes were superior in treating black dye and mixed dye.
respectively. (ii) In this investigation, it should be noted that the influences of various supporting electrolytes were studied to avoid electrode passivity. The role of NaCl, KCl, Na₂SO₄, K₂SO₄, MgSO₄ and NaNO₃ as supporting electrolyte were evaluated. NaCl as superior could remove dye from wastewaters with the best performance in every aspect. In this study, the electrolyte consumption for enhancement of EC is optimized at 2.75 mS/cm (or 1.5 gr/L NaCl) for low to high concentration of dye, this applied conductivity is better than literature. (iii) The parameters that were found to be suitable for the EC treatment of the synthetic wastewater were then tested in an EC treatment of simulated wastewater from a textile dyeing factory, the results show that removal of dye from simulated textile wastewater was found to be more complicated than from synthetic mixed dye wastewater for several reasons. The real textile wastewater might contain other dye molecules that could not be removed by the electrocoagulation process with the design parameters that were used. Another possible explanation was that the real textile wastewater might contain some components which interfere with the electrocoagulation mechanism.

References


