Simultaneous decolorization of binary mixture of Reactive Yellow and Acid Violet from wastewaters by electrocoagulation
Can Serkan Keskin, Abdil Özdemir and I. Ayhan Şengil

ABSTRACT
Dyes are common pollutants in a large variety of industrial wastewaters, and the treatment of these wastes has been extensively studied by coagulation. For the removal of pollutants from the wastewaters, different techniques have been used and electrocoagulation is one of the widely used methods. This process is very effective in removing organic pollutants including dyestuff wastewater. The purposes of this study were to investigate the effects of the operating parameters, such as current density, electrolyte concentration, dyestuff concentration, and pH of solution on decolorization and chemical oxygen demand (COD) removal of wastewater containing two different dyes in same solution by direct current electrocoagulation. The amount of dye removed was found by application of first derivative spectrophotometric method to the synthetic dye mixtures. In this work synthetic dye mixture which include C.I. Reactive Yellow 145 (RY145) and C.I. Acid Violet 90 (AV 90) were used for electrocoagulation (EC) process with iron electrodes. In the presence of both dye molecules, the optimum pH was found to be 4, optimum NaCl concentration was 3000 mg/L and optimum current density was 5.56 mA/cm². Under these conditions in the case of 100 mg/L each dye concentration at 20°C and 3 cm interelectro distance the color removal efficiency was reached 97.7% for AV 90 and 97.1% for RY145 in 10 minutes time duration. Dye concentration dependent highest COD removal efficiency was measured as 82% around at 100 mg/L dye concentration.

Key words | C.I. Acid Violet 90, C.I. Reactive Yellow 145, COD, derivative, electrocoagulation

INTRODUCTION
Removal of organic matters from wastewater is an important application to protect spring and surface waters. Different agents such as vegetable oils, textile dyes, lignins, surfactants, pharmaceuticals etc. create organic pollution issued from industry, agricultural or urban areas. The most widely used methods to remove pollutants are adsorption (Froehner et al. 2009), chemical and electro coagulation (Quinones et al. 2009; El-Gohary & Tawfik 2009), flotation (Senaa et al. 2009), filtration (Cha et al. 2010), ion exchange (Li et al. 2010), membrane separation (Damodar & You 2010), biological methods (Cheng et al. 2010) etc. Removal of dyes from wastewaters by EC is a popular method because of the high efficiency of the decolorization. EC process was based on formation of coagulants via electrolytic reactions at electrode surfaces. In the comparison of electrocoagulation with the other methods, it has some advantages including simple equipment requirement, easy automation of process (Mollah et al. 2001) and no chemical requirements. The dosing of coagulant reagents depends directly on the cell potential or current density. Electrocoagulation process also helps the flocculation by the turbulence generated by oxygen and hydrogen evolution at the cathode and anode electrodes. By the gas evolution, particles are destabilized and they start attracting each other and generate bigger particles. The gas evolution inside the solution helps the separation of particles from the solution and carries the particles to top of the
solution to be removed easily (electrofloation). The most widely used electrodes are both iron (Sengil & Özacar 2009), both aluminum (Merzouka et al. 2009), one is iron (anode) and the other one is aluminum (cathode) (Chou et al. 2009) and carbon steel as anode and stainless steel as cathode (Zhang et al. 2009). The similar events formation of metal hydroxide and hydrogen gas occur with all these electrodes. Electrocoagulation strongly depends on pH, particle size, concentrations, and conductivity of the continuous phase. Electrocoagulation of wastewater using iron electrodes takes place according to the following reactions: the following mechanism is involved (Huitle & Brillas 2009) for the production of Fe(OH)$_n$, where n = 2 or 5.

Mechanism 1

Anode: $4\text{Fe}(s) \rightarrow 4\text{Fe}_{(aq)}^{2+} + 8e^-$  

Bulk of solution: $4\text{Fe}_{(aq)}^{2+} + 10\text{H}_2\text{O}_{(l)} + O_{(aq)}^{2-} \rightarrow 4\text{Fe}(	ext{OH})_{3(s)} + 10\text{H}^+(aq) + 8e^-$  

Cathode: $8\text{H}^+(aq) + 8e^- \rightarrow 4\text{H}_2(g)$  

Overall: $4\text{Fe}(s) + 10\text{H}_2\text{O}_{(l)} + O_{(aq)}^{2-} \rightarrow 4\text{Fe}(	ext{OH})_{3(s)} + 10\text{H}^+(aq) + 8\text{H}_2(g)$

Mechanism 2

Anode: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^-$  

Bulk of solution: $\text{Fe}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)} \rightarrow \text{Fe}(	ext{OH})_{2(s)}$  

Cathode: $2\text{H}_2\text{O}_{(l)} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^{-}_{(aq)}$  

Overall: $\text{Fe}(s) + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{Fe}(	ext{OH})_{2(s)} + \text{H}_2(g)$

UV-VIS spectrometers are used for concentration calculations which based on measurement at a wavelength corresponding to maximum absorbance of dye. When more than one dye was analyzed in a mixture, their spectra will most probably overlap in a certain wavelength region. Chromometric and graphical calibration techniques (Kramer 1998) in spectral analysis can be used to solve this problem without any separation procedure before determination step. In this study, due to the spectral overlap, graphical solution was applied to determine the remaining dye amount in the solution. The utilized method to calculate the amount of dye in solution is a derivative spectrophotometric method. In this study, a first-order derivative method was developed and validated for determination of remaining dyes in solution. The method based on formation of calibration equations for both dyes and application of them to the samples. The objective of the present study is to investigate the simultaneous removal of Reactive Yellow 145 (RY 145) and Acid Violet 90 (AC90) and also COD from aqueous solution via electrocoagulation using iron as an electrode material. The effects of several parameters including initial pH, applied voltage, initial dye concentration, and electrolysis time were investigated to measure the dyes removal efficiency of electrocoagulation process.

MATERIALS AND METHODS

Materials

The structures of dyes used in the experiments are shown in Figure 1. RY145 and AV 90 were provided from Aldrich Chemical Compan. In order to measure dye concentrations, the solutions were analyzed by UV-Vis spectrometer (Schimadzu UV-Vis 160) by measuring the full absorption spectrum of mixtures in the range of 200–800 nm (Figure 2). Data treatments, regressions and statistical analysis were performed by using the EXCEL software. The calibration procedure was carried out by using 14 calibration standards prepared using different concentration of each dye. RY145 and AV 90 concentrations were varied between 0.4 to 24 mg/L. COD removal experiments were carried out by using standard procedures (APHA 1992). COD was spectrophotometrically determined by using an Hach DR/4000 spectrophotometer.

![Figure 1](https://iwaponline.com/wst/article-pdf/63/8/1644/444843/1644.pdf)
Design and method

The experiments were carried out in a batch reactor which consists of a D.C. power supply and iron electrodes in a beaker having capacity of 1000 ml. There were two electrodes and the distance between the electrodes was 3 cm and the immersed dimensions of the electrodes were 9 cm \( \times \) 5 cm \( \times \) 0.2 cm. The stirrer was used during the electrocoagulation. The electrodes were washed before every experiment with dilute HCl and distilled water. For pH adjustment HCl and NaOH were used. Solutions conductivity was changed by using different amount of NaCl varying between 500–3000 mg/L. The applied current density between 0.5–4 A range was measured by an ammeter. Binary systems were prepared by mixing 50:50 from each dye solution in the concentrations of 25, 50, 75, 100, 150 and 200 mg/L from each dye in the mixture. Experiments were conducted at 20°C.

The particulates of colloidal ferric oxyhydroxides gave yellow-brown colour into the solution after EC. All the suspended solids were removed by electrocoagulation and electrolytic flotation. Thus, during electrolysis, the clear solution was obtained. All the samples were santrifuged (5000 rpm) to remove the particles in the solution and samples were analysed by taking clear part of samples We did not used a filter paper to eliminate any interference that might come form filter papers to measure the remaining dye concentrationa and COD.

RESULTS AND DISCUSSION

First derivative of the spectra was calculated by \( \Delta \lambda = 6 \) nm intervals and resulting spectra are shown in Figure 3. After derivation of absorption spectra of compounds, zero crossing points were determined to establish two different calibration equations. For each compound a graph was plotted by using concentration versus absorption values. The amounts of RY145 and AV 90 in the binary mixture were found to be proportional to the signals and statistical parameters of their calibration equations are summarized in Table 1. The validity of the calibrating method was tested by preparing various binary mixtures containing 0.4–24 mg/L RY145 and AV 90 in water. Mean recoveries and the relative standard deviations were calculated and their results were given in Table 2. The relative standard deviation (RSD) was used to express the precision of experiments. The following equation was used to calculate the RSD values of results.

\[
RSD = \frac{SD}{\bar{x}} \times 100
\]

where \( SD \) is standard deviation and \( \bar{x} \) is mean value.

<table>
<thead>
<tr>
<th>Method</th>
<th>Regression Equation</th>
<th>( r )</th>
<th>SE(m)</th>
<th>SE(n)</th>
<th>( S ) (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RY145</td>
<td>( A = -5.6 \times 10^{-5} C_{RY145} - 1.8 \times 10^{-5} )</td>
<td>0.9993</td>
<td>9.18 ( \times ) ( 10^{-7} )</td>
<td>1.32 ( \times ) ( 10^{-5} )</td>
<td>1.92 ( \times ) ( 10^{-5} )</td>
</tr>
<tr>
<td>AV90</td>
<td>( A = -0.00027 C_{AV90} + 2.13 \times 10^{-5} )</td>
<td>0.9999</td>
<td>5.73 ( \times ) ( 10^{-7} )</td>
<td>5.38 ( \times ) ( 10^{-6} )</td>
<td>7.82 ( \times ) ( 10^{-6} )</td>
</tr>
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Dye removal efficiency depends on electrochemical reactions at the cathode. Hydrogen gas is evolved at the cathode and rate of reaction completely depends on the removal of H⁺ via H₂ evolution. If the solution pH is low, EC process is fast, after consumption of H⁺ in the solution, as it is shown in Equation (2), hydrogen ions will be provided by hydrolysis of iron. This process also explains that dye removal efficiency will be higher at high pH values by iron hydroxides. To examine pH effect, the dye solution was adjusted to the desired pH for each experiment by adding sodium hydroxide or hydrochloric acid solution. Hector et al. (Moreno et al. 2009) explained the whole electrochemical process of electrocoagulation and depending on their findings, Fe(III) hydroxide formation is the highest between pH 4 and 10. Dissolution process of iron is one of the important parameters for the removal of wastes in water. Lorenz et al. (Lorenz et al. 2002) also reported that one of the important parameters for the dissolution and passivation rate of iron is the pH of solution. The optimum pH must be chosen in order to achieve best coagulation conditions. The effect of initial pH on the removal efficiency of both dyes is presented in Figure 4. The experimental results showed that when pH of the dye solution was around 4, there was maximum color removal efficiency. Inset of Figure 4 shows the pH change of dye solutions during electrocoagulation process. At low pH values, electrocoagulation process increases the pH of solution. Chen et al. (Chen et al. 2000) and Renu et al. (Ahlawat et al. 2008) mention that at high pH above 9, EC process acts as a neutralizer, we saw the similar trends at high pH values. Although the optimization experiments showed that the maximum removal efficiency was reached 99.3% at pH 8 for AV 90 and 97.1% at pH 4 for RY145. The maximum removal efficiency of both dyes was observed between the pH values of 4–10, in 10 min time interval and at 5,556 mA cm⁻² current density. Results demonstrated that removal of dyes was remained between 97–99% for AV 90 and 72–97% for RY145.

The salt concentration of a solution directly affects the conductivity of solution. Changing the conductivity affects the current efficiency, cell voltage and consumption of electrical energy. The effect of conductivity on dye removal was investigated by addition of NaCl in different amounts. Figure 5 shows the effect of NaCl as an electrolyte on removal of both dyes. The presence of chloride ions in the solution increases the iron dissolution in water (Arroyo et al. 2009). Electrolytes increase the conductivity of the solution and decrease the cell voltage for the necessary current density. Although electrolyte concentration helps to increase the conductivity, results show that color removal efficiency of electrocoagulation did not change considerably for both dyes in water. Removal percentages are between 96–98% for AV 90 and 94–97% for RY145. For the lowest cost of electrocoagulation process during both dye removal, the determined optimum amount of NaCl is 3 g L⁻¹.

In all electrochemical process, one of the most important parameters is the current density that determines the coagulant production rate and size of the bubble production and size of the bubble production and
hence effects the growth of flocs (Daneshvar et al. 2003, 2004; Mollah et al. 2004). The effect of current density on the efficiency of color removal was investigated by carrying out the experiments at different current densities. Figure 6 shows the effect of current density and energy consumption for the simultaneous removal of both dyes in water. The removal efficiency of AV 90 increased from 35.8% to 97.7% by increasing the current density from 2.778 mA/cm² to 5.556 mA/cm² and 64.6% to 97.1% for RY145 in 10 min electrocoagulation time period. In the case of shorter time period and higher current densities, the removal efficiency did not show too much difference. The removal percentage raised 66.3% to 96.8% for AV 90 and 54.3% to 95.7% for RY145 in 5 min electrocoagulation time period when the current density was increased from 5.556 to 11.111.

Electrolysis time influence the treatment efficiency of the electrochemical process. Electrolysis time determines the iron ion production in the solution. Figure 7 shows the effect of time on the simultaneous color removal efficiency for both dyes in water. Efficiency is increased with the time because of hydroxyl and iron ion production on the electrodes. Removal percent of dyes were 97.7% and 97.1% in 10 min, respectively for AC90 and RY145. Results show that the color removal efficiency was not affected considerably after 10 min electrocoagulation time.

The dye solutions with different initial concretions were investigated in the range of 25–100 ppm. By keeping all other parameters, initial dye concentrations were changed and removal efficiencies were calculated. Figure 8 shows the effect of initial dye concentrations on removal efficiencies of both dyes. As it is expected, at low concentration ranges, removal efficiency was higher than the high initial dye concentrations. Removal percentages were 99.6%–97.7% for AV 90, 98.6%–97.1% for RY145 in the concentration range of 25 to 100 ppm in 10 min. When the initial concentration was increased to 200 ppm, the removal efficiency was decreased to 96.7% for AV 90 and 72.0% for RY145.

Figure 9 shows the correlation between dye mixture COD removal efficiency. COD removal efficiency after EC process was calculated using the formula below,

\[ R(\%) = \frac{COD_0 - COD_t}{COD_0} \times 100 \]
where COD₀ is the initial concentration in mg/L and CODᵣ is the concentration after EC process in mg/L. The COD removal experiments were carried out under the conditions of 25–200 ppm concentration range of each dye, initial pH of 4, current density 5.556 mA cm⁻², concentration of salt 3,000 mg L⁻¹, and distance between the electrodes 3 cm, in 10 min electrocoagulation time period and the result presented in a figure below. Figure shows the percentages of COD removal with various concentrations. It can be seen that from figure the percentage of COD removal increased from 35% to 82.37% in the 25–100 ppm concentration range and decreased to 78.09% and 72.44% with 150 and 200 ppm concentrations respectively. The decreasing trend of COD removal with increased dye concentration reveals that residual dye or dye metabolites caused to increase the effluent COD. (Wijetunga et al. 2008) also reported similar trends with the dye concentration increase.

CONCLUSIONS

High levels of COD will be generated during the dyeing methods employed in textile industries. Electrocoagulation method is employed in the laboratory to the synthetic dye mixtures and reming dye amounts and COD levels were analysed. EC has been evaluated as a tool for Reactive Yellow 145 (RY145) and C.I. Acid Violet 90 (AC90) dyes and COD removal from aqueous solutions in an EC reactor with iron electrodes. The effect of various operational parameters on color removal efficiency was investigated and optimized. The simultaneous removal of both dyes was found to be affected by the initial pH of the solution, electrolysis time, initial dye concentration, current density and electrolyte concentration. The color removal efficiencies for AV 90 and RY145 were 97.7% and 97.1%, respectively under the conditions of initial pH of 4, initial concentration 100 mg L⁻¹, current density 5.556 mA cm⁻², concentration of salt 3,000 mg L⁻¹ and distance between the electrodes 3 cm. It was found that the proper electrolysis time for the removal of color from this dye solution was 10 min. Color removal efficiency by EC decreased when the initial dye concentration was more than 200 mg. It can be noticed from the results that, a high COD removal efficiency of 82% is recorded for the dye mixture. The process of bringing down the dye concentrations and COD levels of waste below the acceptable values before discharging into surface water sources is studied in detail in the present work and this method can be use for the removal of dye mixtures from the wastewaters.

REFERENCES


