Effects of Operational Parameters on the Decolourisation of Reactive Red 195 Dye from Aqueous Solutions by Electrochemical Treatment

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One of the most polluting factors in the environment is the textile industries’ wastewaters since they notably have complex ingredients and occurs in large volume. Moreover its effluents are in need of advanced treatment to be able to smoothly discharge to the receiving media. This study investigated the decolourisation efficiency of electrocoagulation process using three different electrodes, aluminum, zinc and iron, in Reactive Red 195 dye removal from model solutions. Effect of major operational parameters such as current density, pH, sacrificial electrode materials and operation time was followed for percentage decolourisation efficiency. The performance of the process was found to be maximum with iron electrode for Reactive Red 195 dye, but aluminum electrode was the best one for the real textile wastewater that is the mixture of textile dyes. Decolourisation efficiency reached to 98% employing current density of 40 mA cm\(^{-2}\) and iron electrode for the real effluent containing the dye, and COD was eliminated 74% employing aluminum electrode at the same current density. As a conclusion electrocoagulation was found to be efficient in treating and decolorizing the textile effluents and model solutions.

Keywords: Electrochemical treatment; Reactive red 195; COD and color removal; Metal electrode; Textile wastewater

1. INTRODUCTION

Throughout history, textile industry has been one of the largest revenue generating sectors in the world. However as a consequence of the large worldwide production, dye-containing effluents remains an important ecological issue due to stability of the compounds, their low biodegradability, lethality to certain forms of marine life and carcinogenic character. The contamination of natural streams and aesthetic problems motivate the scientific community to search for novel effective and inexpensive
strategies to treat this kind of industrial effluents [1]. Some conventional treatment methods in order to depurate before discharge of wastewaters containing textile dyes are coagulation, flocculation, adsorption, biological and chemical oxidation. Coagulation is the addition of coagulating agents such as Fe\(^{3+}\) or Al\(^{3+}\) ions to the bulk and precipitation of pollutants generally in the form of chlorides for dyes. The electrochemical treatment can form the coagulating agents employing the EC method [2-4]. Electrocoagulation utilizes the electrical current to dissolve Fe (or steel) or Al sacrificial anodes dipped in the wastewater, causing to occur metal ions that yield several Fe(II) (and/or Fe(III)) or Al(III) combinations with hydroxide ion depending on the medium pH [5,6]. These derivatives function as coagulants or destabilization ingredients that implement charge neutralization for dyes’ separation from the wastewater. Coagulated species can also be moved away by electroflotation when they are adsorbed to the bubbles of H\(_2\) gas grew at the cathode and carried over the solution where they can be cleaned.


Nowadays electrocoagulation (EC) has been designated in a succesful manner to treat dissimilar wastewaters such as; landfill leachate [11], restaurant wastewater [12], salina wastewater [13], tar sand and oil shale wastewater [14], urban wastewater [15], laundry wastewater [16], nitrate and arsenic bearing wastewater [17], chemical mechanical polishing wastewater [18] and textile wastewater [19]. The leading contaminants in textile wastewater are notably the organic and inorganic chemicals such as chemical finishing agents, surface active agents, inhibitor materials, active substances, chlorinated compounds, salts, dyestuff, total phosphate, dissolved solids and total solids. Coloring matter is the main contaminant in the textile wastewater because of 10-50% of the dyes are lost in the effluent [20].

Commonplace wastewater treatment methods fail to satisfy in the treatment efficiency of textile effluents due to chemical resistance of synthetic dyes [21]. Biological methods are taking a long time and they are frequently insufficient in depurating of dyes which are highly structured polymers with slight biodegradability and cannot be employed for big masses of textile wastewaters due to the poisonousness of so many dyes to organisms employed in the process [22,23]. Adsorption on activated carbon is a costly process and its regeneration is difficult besides a huge waste disposal charge [19]. Chemical coagulation leads to excess contamination due to the undesired reactions in treated wastewater and produces large amounts of sludge [24]. Decolourisation of dye by chemical oxidation is the most important and effective method but it generates some toxic waste products such as organochlorine compounds [25]. Many advanced oxidation processes such as ozonation, UV, UV-assisted oxidation, photocatalysis, Fenton reactive and ultrasonic oxidation are not economically feasible [26]. So proposing a novel treatment technology has been required in recent years. Electrocoagulation is one of the latest emerging methods and has some major advantages such as simple equipment and easy operation and
automation, a shorter retention time, high sedimentation velocities, more easily dewatered, reduced amount of sludge due to lower water content [27].

Today two major interaction mechanisms have been considered during decolourisation process by EC: precipitation and adsorption, each one develops in a different pH range. Flocculation occurs in the low pH range and is explained as precipitation, while the other one occurs in the higher pH range (> 6.5) and is explained as adsorption.

Precipitation:
\[ \text{dye} + \text{monomeric Al} \rightarrow [\text{dye monomeric Al}] (s) \quad \text{pH 4.0} - 5.0 \quad (1) \]
\[ \text{dye} + \text{polymeric Al} \rightarrow [\text{dye polymeric Al}] (s) \quad \text{pH 5.0} - 6.0 \quad (2) \]

Adsorption:
\[ \text{dye} + \text{Al(OH)}_3 (s) \rightarrow [\text{particle}] \quad (3) \]
\[ [\text{dye polymeric Al}] (s) + \text{Al(OH)}_3 (s) \rightarrow [\text{particle}] \quad (4) \]

Al(OH)\text{$_3$}$ is also present at alkali pH values above 9. New amorphous Al(OH)$_3$ “sweep flocs” have great surface areas, which is advantageous for a quick adsorption of soluble organic compounds and capturing of colloidal particles. These fresh flocs polymerize as
\[ n\text{Al(OH)}_3 \rightarrow \text{Al}_n(\text{OH})_{3n} \quad (5) \]
and they are removed easily from the aqueous medium by sedimentation and H$_2$ flotation [28].

Synthetic dye solutions and wastewater samples have been achieved carrying out electrocoagulation process on a laboratory scale and good performances of COD removal color, turbidity and dissolves solids have been obtained at gradient application conditions [28-32]. Nonetheless, a detailed literature review showed that not enough attempts were reported about electrocoagulation of textile dye the Reactive Red 195 comparing the type of electrode on the EC treatment performance. Therefore, this work is for the first time focused on the comparison of different electrode types (iron, aluminum and zinc) to remove Reactive Red 195 dye from model solutions and textile effluents applying electrocoagulation process. The effect of current density, initial pH, time and electrode type was also evaluated on decolourisation performance using sacrificial electrodes.

2. MATERIALS and METHOD

2.1 Materials

The chemical reagents and dyestuff used in the tests were of analytical grade and utilized without further purification in order to represent actual dyeing conditions. Reactive Red 195 (commercially named as Jakofix Red ME4BL) was kindly supplied from a local dyehouse located in Manisa. Its chemical formula is C$_{31}$H$_{19}$ClN$_7$Na$_5$O$_{21}$S$_6$ [33]. The test solutions were prepared by dissolving acquired amount of the Reactive Red 195 in deionized water. Stock solution with 1000 mg/L concentration and
test solution with 100 mg/L were used in the tests. Some characteristics of the reactive dyestuff is summarized in Table 1. pH regulation of the solutions was performed by adding NaOH or H₂SO₄ before experiments. Real textile effluent has been collected from an exhaust tank containing a mixture of dyeing solutions at a textile factory in Manisa (Turkey). The average, natural pH of it was 10 and its COD content was 1680 mg/L.

**Table 1.** Characteristics and chemical structure of the Reactive Red 195 dye

<table>
<thead>
<tr>
<th>Colour index name</th>
<th>M (g mol⁻¹)</th>
<th>λ_{max} (nm)</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Red 195</td>
<td>1168.28</td>
<td>540</td>
<td><img src="image" alt="Chemical structure of Reactive Red 195" /></td>
</tr>
</tbody>
</table>

### 2.2 Experimental Set Up

Fig. 1 illustrates the schematic image of the experimental apparatus. The operation was actioned in a batch-stirred electrochemical reactor under atmospheric pressure at room temperature. In each experiment, the reactor consisting of 0.6 L glass beaker was filled with 0.5 L of the treatment dye solution and, it was stirred with a magnetic stirrer at 200 rpm using a stirr plate Yellowline MST Basic during the process. Two uniform metal electrodes made of iron, zinc or aluminum with dimensions of 20cmX6cmX0.2cm were employed as anode and cathode for the tests. The distance between vertical and parallel electrodes influencing the amount of energy was 5.5 cm. The electroactive area of electrode is calculated approximately to be (8.3cmx6cm) 50 cm². Test solution was transferred into the reactor and electrodes were dipped in the electrochemical reactor containing the dye solution. The electrodes were connected to a DC power supply (SUNLINE SL-3010D) with galvanostatic operational options to control current density. Somayajula studied the effect of different supporting electrolytes on the electrochemical treatment of Reactive Red 195 dye and found that the best color removal could be achieved using NaCl agent [33]. Based on that result, the electrical conductivity of the dye solution was insufficient for electrocoagulation, and it was adjusted to an operational value with NaCl. The pH and conductivity of the samples were followed with a HANNA edge apparatus but not adjusted to a certain value during the treatment time. As electrocoagulation process continues, absorbance was measured over time on aliquots taken from reactor at regular intervals. After each experimental run, the electrodes and EC cell were thoroughly pured with HCl aqueous solution and deionized water prior the subsequent application to get rid of passivation. A spectrophotometer (DR-LANGE CADAS 30 S) was employed to find out the decolourisation efficiency of each sample via the decrease in absorbance at the maximum wavelength (λ_{max}= 540 nm for Reactive Red 195). Measurements of COD values of samples were taken with a Spectroquant Pharo 300 spectrophotometer.
2.3 Experimental Variables

Process parameters were designated as the effects of the current density and initial pH and electrode type in order to explore optimum working conditions. The experiments were implemented with values of applied current density ($j$) of 10, 20 and 40 mA/cm$^2$. Initial pH of the electrochemical treatment medium was examined for acidic (pH=4) and basic (pH=8) conditions of solution. The effect of electrode type was studied with aluminum, zinc and iron electrode.

2.4 Analytical Procedures

The wavelength of the dye which is the maximum value was chosen as 540 nm and decolourisation efficiency was calculated for absorbance values at this wavelength so it was not made a duplication and facilitated the data displays [34]. The calculation of Decolourisation Efficiency (DE%) after electrocoagulation treatment was performed using this formula:

$$\text{DE} \% = \left[ \frac{\text{Co} - \text{C}}{\text{Co}} \right] \times 100$$  \hspace{1cm} (6)

where Co and C are the light absorbance of dye before and after electrocoagulation process, respectively. The concentration of residual dye was constituted from its absorbance in the UV–Vis range (200–800 nm) by applying the calibration method of Beer–Lambert’s law. The Beer-Lambert’s law denotes the connection between concentration and absorbance as indicated at Eq. (7):

$$A=\varepsilon b C$$  \hspace{1cm} (7)

where $A$, $\varepsilon$, $b$ and $C$ correspond to absorbance ($A=\log_{10} \frac{I}{I_0}$), molar extinction coefficient, the path length of the sample in cm and the concentration of the compound in solution, respectively. The linear
relationship (Absorbance versus Concentration) was smoothly obtained. COD of the original and treated wastewater was measured using standard closed reflux colorimetric method.

3. RESULTS and DISCUSSION

Some fundamental factors such as initial pH, initial dye concentration, operation time, electrode material, current density and electrical conductivity have an effect upon the efficiency of electrocoagulation process. This study investigates the effects of variation of operating time, current density and electrode type on the performance of electrochemical process. Comparative results were shown in figures generated according to the results of tests.

3.1 Effect of Current Density

![Figure 2. Effect of current density on decolorization efficiency over time for different electrodes (initial pH=4).](image-url)
In order to remove the dye at initial concentration of 100 mgL⁻¹ of Reactive Red 195, selected values of applied current density were performed for 10, 20 and 40 mA cm⁻² keeping constant another operating conditions. The effect of the parameter on the treatment was investigated for initial pH value of 4 and 8. Figs. 2 and 3 depict the effect of current density on the percentage of decolorization after operating time of 45 min sampling at the 5 min intervals and using three different electrode materials at initial pH value of 4 and 8, respectively.

Current density is one of the major parameters in all electrochemical treatment processes because the rate of coagulant dosage and bubble production, magnitude and improvement of the flocs are assigned on the basis of this parameter, which can have an effect upon the efficiency of the electrocoagulation [20].

Current density speeds obviously up the anode dissolution rate. The higher the current density, the faster the metal ion generation. This causes to an enhancement in the number of metal hydroxide flocs and overall the pollutant removal becomes greater in efficiency. An increase in current density
above the optimum current density value does not result with increase in pollutant removal efficiency because sufficient number of metal hydroxide flocs are available for the sedimentation of the pollutant [20].

The decolourisation efficiency increased with the current density and electrolysis time but in different proportions depending on the nature of the electrodes and pH of the aqueous media. Employing aluminum electrodes, the removal yields of 97%, 91% and 99% in aqueous acidic medium (initial pH=4) and removal yields of 95%, 98% and 99% in aqueous basic medium (initial pH=8) were achieved after 45 min at current densities of 10, 20 and 40 mA cm\(^{-2}\), respectively. Both Fig.2 and Fig.3 show clearly that the best current density value was 40 mA cm\(^{-2}\) and it was a suitable choice to get the best decolourisation efficiency at studied operation parameters. For zinc electrodes, in acidic solution the removal yields of 64%, 72% and 97% and in basic solution the removal yields of 64%, 70% and 96% were scored after 45 min of process time at current densities of 10, 20 and 40 mA cm\(^{-2}\), respectively. For iron electrodes, in acidic solution the removal efficiency reached to 98%, 95% and 97% and in basic solution the removal efficiency reached to 99%, 99% and 96% in ten minutes at current densities of 10, 20 and 40 mA cm\(^{-2}\), respectively.

![Conductivity over time for different electrodes](image)

**Figure 4.** Effect of the current density on conductivity over time for different electrodes (initial pH=4)
Additionally decolorization efficiency was found to be 100% for 40 mA cm\(^{-2}\) with iron electrode. It was clearly inferred from the figures that acidic or basic initial pH values were resulted in pretty close yields. Hence pH arrangement is non-essential before the electrochemical process of Reactive Red 195 dye solution. Decolourisation efficiency values show the superior performance of iron electrode over the aluminum and zinc electrodes at studied current densities. Besides a notable decolourisation was achieved within 5 min reaction time at all investigated current densities when implemented iron electrodes into the discontinuous EC cell. The design of the applied current density is also crucial in that the electrical energy saving of the process. It affects directly electrical energy requirements of the process and hence needs to be carefully optimized to achieve high treatment efficiencies at low cell current [34].

Fig. 4(a)-(c) illustrates the influence of the current density on the electrical conductivity of the solution treated electrochemically in acidic initial pH values of solution.

**Figure 5.** Effect of the current density on conductivity over time for different electrodes (initial pH=8)

Fig. 5(a)-(c) displays the effect of the current density on the electrical conductivity of the solution treated electrochemically in basic initial pH values of solution. Both of them demonstrate that increase
in current density results in a significant increase in conductivity of the solution. Pajootan et al. investigated the relation between electrical energy consumption and solution conductivity, and found a decrease in power consumption while conductivity increased. Besides, employing of high current density leads to extra use of electrical energy and heats the dye solution in the event. [35].

3.2 Effect of pH

The efficiency of the electrocoagulation process can be affected by the pH of the effluent, since metal ions at suitable pH values can form wide ranges of coagulated species and metal hydroxides that precipitate and adsorb dissolved contaminants or destabilise and aggregate suspended particles [36]. Also pH leads to the $\text{Fe}^{3+}$ formation from $\text{Fe}^{2+}$, and pH of the treatment medium imposes on the surface charge of coagulating particles [37]. To make a detailed research associated with the effect of the initial pH on the decolourisation efficiency, this parameter was assessed at two different initial values of pH 4 and 8 which were adjusted with $\text{H}_2\text{SO}_4$ or NaOH. The consequences of pH alteration can be followed from Fig.2 and Fig. 3. It is clear from the figures that there is very little difference in the final values of removal efficiency between asidic and basic initial pH conditions. For this reason it be said that the electrochemical process does not need pH setting before the operation. As is obvious from the Fig.5, dye removal process was complete in large part at first ten minutes. Fig.6 and Fig.7 represent changes in pH with time at studied current densities for aluminum, zinc and iron electrodes. According to the reactions substantiated in the bulk, pH of the solution tends to increase during the process. At the end of the process, final pH of all tests tends to reach over 10. Reaction steps of electrochemical process generated in the solution is quite complex. However, decolourisation process may involve the dye molecule adsorbing by both electrostatic attraction and physical entrapment. The insoluble metal hydroxides of iron can remove dye molecules by surface complexation, it is assumed that the dye molecule can draw attention as a ligand character to bind a hydrous moiety with precipitation and adsorption mechanisms [27, 38].

![Graphs showing pH change with time for different current densities and electrodes](image_url)
Figure 6. Effect of the current density on pH over time for different electrodes (initial pH=4)

Figure 7. Effect of the current density on pH over time for different electrodes (initial pH=8)
The effect of pH on the performance of electrocoagulation process is described in the following way: the dominant aluminum species evolve according to the solution pH; $\text{Al}^{3+}$ and $\text{Al(OH)}^{2+}$ are seen intensively in pH 2–3, and with pH between 4 and 9, various polymeric species such as $\text{Al}_{13}\text{O}_{4}\text{(OH)}_{24}^{7+}$ are produced and precipitated as $\text{Al(OH)}_3(s)$ [32].

### 3.3 Effect of the Operation Time

Reaction time influences the treatment efficiency of the electrocoagulation process, because it determines the rate of production of $\text{Al}^{3+}$ and hydroxyl ions produced on the electrode [39]. It is provided to the process in order to generate metal hydroxides and to complete coagulation of the impurities [40]. So operation time was selected as one of the experimental performance parameters in electrochemical process. Process time was selected from 1 min to 45 min and decolourisation efficiency reached to above 95% at all cell current values and even 5 min could be enough for the degradation of the dye with iron electrode. Best percentage for removal efficiencies (99% for Al, 97% for Zn and 100% for Fe electrodes) has been obtained at 45 min. The effect of the electrolysis time can be followed from all figures in the paper because in general graphics were drawn for decolourisation efficiency versus electrolysis time.

### 3.4 Effect of the Electrode Material

Electrode configuration is regarded as another important parameter since it has profound effects on the electrochemical action generated in the effluent. Appropriate selection of electrode material is closely related with yield of electrocoagulation process. The nature of electrode material specifies the pollutant separation/precipitation mechanisms [41]. On this basis, aluminum, zinc and iron plates were fixed as electrodes and compared for decolourisation efficiency of the process within the scope of this study. Fig.8(a-c) and Fig.9(a-c) show time dependence of decolourisation efficiency for different electrode materials at constant current density.
Figure 8. Effect of electrode material on decolorization efficiency over time for different values of current density (initial pH=4).

Figure 9. Effect of electrode material on decolorization efficiency over time for different values of current density (initial pH=8).
As can be observed from the Fig.8c and Fig.9c, color removal was quickly ensured after 5 min of treatment yielding above 95% with iron electrode at even lowest value of current density.

A significant difference in the performance between three electrode materials was observed in that the removal of Reactive Red 195 dye. Comparing three electrode materials in terms of color removal capacity, iron electrode was found to have a higher decolorization efficiency than the other two electrodes.

The comparison of our experiments’ performance with the results for some recently noted studies concerning the removal of Reactive Red 195 and some another dyes by electrocoagulation process are presented in Table 2. When the table is examined in detail, various combinations of the operation parameters can be produced for different dyes and electrode types.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Electrode Type</th>
<th>Electrolysis Time (min)</th>
<th>% Decolourisation Efficiency</th>
<th>Reference No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive Red 195</td>
<td>MMO (Mixed Metal Oxide)</td>
<td>50.3</td>
<td>100</td>
<td>[33]</td>
</tr>
<tr>
<td>Reactive Red 195</td>
<td>Fe, Al</td>
<td>60</td>
<td>&gt;90</td>
<td>[42]</td>
</tr>
<tr>
<td>Reactive Red 195</td>
<td>Fe-Al</td>
<td>18</td>
<td>100</td>
<td>[43]</td>
</tr>
<tr>
<td>Reactive Red 195</td>
<td>Fe-Steel</td>
<td>5</td>
<td>100</td>
<td>[44]</td>
</tr>
<tr>
<td>Acid Yellow 220</td>
<td>Al, Fe</td>
<td>7.5</td>
<td>97</td>
<td>[45]</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>Ti/(RuO$<em>2$)$</em>{0.8-}$</td>
<td>180</td>
<td>100</td>
<td>[46]</td>
</tr>
<tr>
<td>Coomassie Brilliant</td>
<td>Fe-Fe</td>
<td>60</td>
<td>94</td>
<td>[47]</td>
</tr>
<tr>
<td>Blue R250</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive Red 223</td>
<td>Al-Al</td>
<td>60</td>
<td>89</td>
<td>[47]</td>
</tr>
<tr>
<td>Levafix Brilliant</td>
<td>Al, Fe</td>
<td>20</td>
<td>99</td>
<td>[48]</td>
</tr>
<tr>
<td>Blue E-B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive Red 195</td>
<td>Fe, Al</td>
<td>10</td>
<td>99</td>
<td>This work</td>
</tr>
</tbody>
</table>

### 3.4 Treatment of the Real Wastewater

Fig.10 and Fig.11 point out the results obtained with aluminum, zinc and iron electrodes for COD and % COD removal efficiency, respectively.
Different from the model solution experiments, aluminum electrode was observed to be more effective in reducing COD of real textile effluent containing Reactive Red 195 dye compared with iron and zinc electrode. So aluminum electrode can be preferred considering the treatment efficiency of real wastewater mixture.

The effect of the electrode type on the removal of Reactive Red 195 dye in the real textile wastewater could be seen in Fig.12.

These differences between iron and aluminum electrodes were explained by Raschitor in terms of the evolution of the dissolved metals, related with pH changes [49]. To reach the yield of 98% for decolorization efficiency of real textile effluent, current density of 40 mA cm$^{-2}$ and iron electrode was required for 30 minutes. To achieve 74% COD removal percentage, aluminum electrode could be employed at the same current density.
Figure 12. Effect of the electrode type on the removal of Reaktif Red 195 dye in the real textile wastewater.

4. CONCLUSIONS

The removal of Reactive Red 195 dye from model solutions by electrocoagulation process has been reported employing iron, aluminum and zinc electrodes during 45 min operation time in the present work. In this study, removal efficiency was reached to 99% in just 10 min for current density of 10 mA/cm² using iron electrode in the process. These parameters of the electrochemical process could be set as optimum operation conditions for decolorization. This study also showed that zinc electrode might be used in the electrocoagulation process even if its efficiency is lower than aluminum and iron.

Complete removal of Reactive Red 195 dye and partial COD removal of wastewater were achieved by electrocoagulation. Best results of decolourisation efficiency was obviously achieved employing iron electrode in comparison with aluminum and zinc at natural pH of reactive dye solution. However in the case of real textile wastewater containing the mixture of reactive and disperse dyes, aluminum electrode was more yielding. The results of this study was confirmed that electrocoagulation is a cost-effective, useful and simple process at dye removal without utilizing high current density values. In other words, this electrochemical process can be implemented as a treatment method in the decolourisation of wastewater containing Reactive Red 195 dye.

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References

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