Electrochemical Decolorization of Reactive Violet 5 Textile Dye using Pt/Ir Electrodes

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Abstract: Electrochemical decolorization of textile dyeing wastewater containing Reactive Violet 5 (RV5) were investigated at Pt/Ir electrodes in the presence of 75% NaCl + 25% Na₂CO₃ (w/w) supporting electrolyte mixture in a batch electrochemical reactor. Experimental parameters were operated in the range of 300-1500 mg/L textile dye concentration, 4-20 g/L 75% NaCl + 25% Na₂CO₃ electrolyte concentration, 5-15 mA/cm² current density, and 20-60°C reaction temperature in 15 min electrolysis time. Reactive Violet 5 decolorization increased with increasing current density and electrolyte concentration, and decreasing the textile dye concentration. Although a slight increase obtained in color removal efficiency, the temperature did not show much significant effect on decolorization. Depending on electrochemical reaction conditions, Reactive Violet 5 textile dye decolorization were obtained between 42.8-100%.

Keywords: Decolorization, Electrochemical Wastewater Treatment, Pt/Ir Electrodes, Reactive Violet 5, Textile Dye.

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INTRODUCTION

Main processes in textile industry are singeing, desizing, sizing, bleaching, scouring, mercerization, dyeing, and finishing (1–3). Approximately 160 lb of water is required to produce 1 lb of textile product. Therefore, large amounts of wastewater are produced in textile manufacturing industry.

The application of color to the textile material is called dyeing and it may take place at any stage in the textile manufacturing process (2). In batch dyeing process, an amount of textile substrate is loaded into a dyeing machine and brings to the equilibrium with dyeing solution. In continuous dyeing processes, textile products are fed continuously into a dye solution at various speeds (2). Reactive and direct dyes are used for cotton, and disperse dyes are used for polyester in common. Dye molecules enter the fibers from the dye solution in a period of time depending on type of fabric and textile dye (2,4). The dye percentage in a bath that fixes to the textile fibers is called dye fixation. Direct and reactive dyes have a fixation rate of 90-95% and 60-90%, respectively (2,4). Dye fixation occurs more rapidly in continuous dying process than batch dyeing (2). Salt, auxiliary chemicals, and temperature controlled dye bath conditions enhance and optimize the fixation efficiency of the dyeing process (2). Typical cotton dyeing processes use sodium chloride and sodium carbonate as common salts (4).

The main source of dyeing wastewater is rinsing processes and spent dye bath which typically contains auxiliary chemicals, salt and residual dye (4). Textile wastewater is a hard-to-treat one due to its strong color, large amount of suspended solids, high chemical oxygen demand (COD), variable pH, salt content, and high temperature. Wastewater from textile processes that can cause damage if not treated before discharging to the environment (3). The major problems in the dyeing process are decolorization, removal of pollutants, salt elimination, and water-use reduction (4).

Electrochemical oxidation is a promising wastewater treatment method and replacing conventional processes in order to treat wastewater from industrial processes which are not easily biodegradable (4). Electrochemical technologies are novel treatment technologies for the elimination of broad-range of organic pollutants from water and wastewater including various types of textile dyes (5–8). Several advantages include easy operation and handling, automation, high efficiency, simple equipment, safety, operations under ambient temperature and pressure conditions. They can be applied to various types of effluents with chemical oxygen demand (COD) ranging from 0.1 g/L to about 100 g/L (5–8).
The strategies of electrochemical technologies include the treatment of effluents and wastes, and also the development of new processes or combined methods with less harmful effects (5–8). Electrolysis reactions involve electrical charges moving between the electrolyte and the electrodes. The process depends on the use of direct electric current for the chemical changes in non-spontaneous oxidation/reduction reactions.

In the literature, the electrochemical treatment have been tested for textile dye degradation with a large variety of electrodes including iron, aluminum, boron-doped diamond (BDD), carbon, graphite, doped and undoped PbO₂, mixed metal oxides of Ti, Ru, Ir, Sn and Sb, doped-SnO₂, Ti/Pt, Pt/Ir and Pt, carbonaceous electrodes, dimensionally stable anodes (DSA), and three-dimensional electrodes (5,6). The studies have utilized electrochemical systems for the treatment of synthetic and real textile dyeing wastewaters by three electrode cells with two or one compartments and divided or undivided two electrode cells or tank reactors equipped with monopolar and bipolar electrodes in batch and continuous modes (5,6). The influence of pH, pollutant concentration, current density, temperature, supporting electrolyte type and concentration, stirring rate and flowrate was investigated as main parameters for optimizing the degradation conditions (5–8).

In this study, the electrochemical decolorization of Reactive Violet 5 (RV5) textile dye was investigated using Pt/Ir electrodes. The effects of process variables such as electrolyte concentration, current density, initial dye concentration and reaction temperature on textile dye removal were analyzed.

**MATERIALS AND METHODS**

**Chemicals and Materials**

Reactive Violet 5 (RV5) textile dye (Sigma Aldrich) (Figure 1), Na₂CO₃ and NaCl (Merck) were purchased as extra pure grade. Textile dyeing wastewater was prepared synthetically using double distilled water, which was obtained using ultrapure water system (Millipore Simplicity® UV) and water still (GFL-2008) with the resistivity of 18.2 MΩ·cm@25°C, TOC < 5 ppb.
**Figure 1.** Molecular structure of Reactive Violet 5 textile dye (C\textsubscript{20}H\textsubscript{16}N\textsubscript{3}Na\textsubscript{3}O\textsubscript{15}S\textsubscript{4}).

**Experimental**

Electrochemical reactor (DURAN\textsuperscript{®} glass) used in this study has a heating and cooling jackets (Rettberg, Germany) as shown in Figure 2. Iron cathodes and Pt/Ir anodes were used as four pairs with 5 mm anode/cathode spacing. Total electrode surface area was 172 cm\textsuperscript{2}. Pt/Ir anodes (Dr. Wieland, Germany) were in spiral shape with 90% Pt and 10% Ir composition (w=150 mm, \( \phi_{\text{internal}} = 10 \) mm, \( \phi_{\text{wire}} = 1.10 \) mm). Iron electrodes were in cylindrical shape (\( \phi = 12.0 \) mm) and purchased from local sources. Pt/Ir and iron electrodes were used as received without further preparation and treatment. Batch electrochemical system was equipped with programmable DC power supply (Goodwill PST-3201), thermostat (Lauda RE 630 S), mechanical mixer (Heidolph RZR 2021), and peristaltic pump (Cole Parmer Masterflex\textsuperscript{®} RZ-77924-60). The reaction medium was mixed at 500 rpm. Influence of experimental parameters were operated as textile dye concentration, 300-1500 mg/L; electrolyte concentration, 4-20 g/L; current density, 5-15 mA/cm\textsuperscript{2}; and reaction temperature, 20-60°C in 15 min electrolysis time.
Samples in 10 mL volume were withdrawn from the reaction medium at 5 min time intervals for the analysis. Decolorization yield was analyzed using UNICO 4802 model UV/Vis double beam spectrophotometer at 520 nm wavelength.

RESULTS AND DISCUSSION

Textile dye concentration, current density, electrolyte (75% NaCl+25% Na$_2$CO$_3$) concentration and reaction temperature parameters were investigated on electrochemical decolorization efficiency of Reactive Violet 5 (RV5) textile dye using Pt/Ir anodes. In this study, 75% NaCl+25% Na$_2$CO$_3$ (w/w) mixture was used as a supporting electrolyte in order to increase the ionic conductivity of the reaction medium which are also main components in real textile industry wastewater (1).

Experimental results were analyzed using Design-Expert® 10 software. Reactive Violet 5 textile dye decolorization were obtained between 59.7-98.7% depending on electrochemical reaction conditions as shown in Table 1. In the study, complete decolorization was also achieved over 15 min electrolysis time.
Table 1. Influence of process parameters in electrochemical decolorization of textile dyeing wastewater containing Reactive Violet 5 (RV5) using Pt/Ir electrodes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reaction Conditions</th>
<th>Decolorization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textile dye concentration</td>
<td>300-1500 mg/L (Electrolyte=12 g/L, J=10 mA/cm², T=40°C, t=15 min)</td>
<td>59.7 - 98.7</td>
</tr>
<tr>
<td>Electrolyte concentration</td>
<td>4-20 g/L (RV5=900 mg/L, J=10 mA/cm², T=40°C, t=15 min)</td>
<td>73.3 - 95.0</td>
</tr>
<tr>
<td>Current density</td>
<td>5-15 mA/cm² (RV5=900 mg/L, Electrolyte=12 g/L, T=40°C, t=15 min)</td>
<td>65.0 - 96.7</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>20-60°C (RV5=900 mg/L, Electrolyte=12 g/L, J=10 mA/cm², t=15 min)</td>
<td>95.1 - 97.1</td>
</tr>
</tbody>
</table>

In electrochemical treatment processes, organic pollutants could be removed from wastewater by indirect and direct mechanisms (5–7,9,10). Indirect oxidation occurs in the liquid bulk phase by the mediated oxidants, and direct oxidation at the anode surface (5–7,9,10). Most electrochemical processes are based on indirect oxidation because direct oxidation of organic pollutants are very slow on inert anodes due to limiting reactions and reaction kinetics (8,11).

Hydroxyl radicals are produced by the anodic discharge of water in indirect electrochemical oxidation of organic pollutants at Pt/Ir anodes. Hydroxyl radicals adsorb on the anode surface [S], and oxidize the organic material (12,13). This reaction could also occur in acidic medium at high current densities (13). Oxidation process continues by the formation of hydroxyl radicals with anodic discharge of water molecules (12,13).

\[
\text{H}_2\text{O} + \text{S} \rightarrow \text{S}[\text{OH}^+] + \text{H}^+ + \text{e}^- \quad \text{(Eq. 1)}
\]

\[
\text{R} + \text{S}[\text{OH}^+] \rightarrow \text{S} + \text{RO} + \text{H}^+ + \text{e}^- \quad \text{(Eq. 2)}
\]

Chlorohydroxyl radicals are also produce with the presence of chloride ions, and adsorb on the active sites of the anode surface [S], and then oxidize the organic material (12,13).

\[
\text{H}_2\text{O} + \text{S} + \text{Cl}^- \rightarrow \text{S}[\text{ClOH}^+] + \text{H}^+ + 2\text{e}^- \quad \text{(Eq. 3)}
\]

\[
\text{R} + \text{S}[\text{ClOH}^+] \rightarrow \text{S} + \text{RO} + \text{H}^+ + 2\text{e}^- \quad \text{(Eq. 4)}
\]

Therefore, electrochemical oxidation of textile dyeing wastewater results in decolorization with the formation of chlorohydroxyl and hydroxyl radicals. The reactions can also yield \text{O}_2, \text{H}_2\text{O}_2, \text{and Cl}_2 (12,13).
Indirect oxidation also occurs with the formation of HOCl/OCl\(^{-}\) redox mediators by the presence of NaCl which provides the anodic evolution of Cl\(_2\) (12–16). The percentage distribution of HOCl/OCl\(^{-}\) depends on the solution pH (16). Chloride-chlorine-hypochlorite-chloride cycle occurs in neutral to moderate pH solutions which maintain the initial concentration of chlorides stable (13).

\[
\begin{align*}
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2\text{e}^- & \quad (\text{Eq. 8}) \\
\text{Cl}_2 + \text{H}_2\text{O} & \Leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- & \quad (\text{Eq. 9}) \\
\text{HOCl} & \Leftrightarrow \text{H}^+ + \text{OCl}^- & \quad (\text{Eq. 10}) \\
6\text{OCl}^- + 3\text{H}_2\text{O} & \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 6\text{H}^+ + \frac{3}{2}\text{O}_2 + 6\text{e}^- & \quad (\text{Eq. 11}) \\
\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{Cl}^- + 2\text{OH}^- & \quad (\text{Eq. 12})
\end{align*}
\]

The effect of textile dye concentration on decolorization efficiency, pH, and cell voltage can be shown in Figures 3-5. The decrease in Reactive Violet 5 concentration resulted in increased decolorization rates and removal efficiency. The rate of degradation could be related to the formation of OH radicals and HOCl/OCl\(^{-}\) redox reagents.

**Figure 3.** Effect of textile dye concentration on decolorization efficiency (Electrolyte=12 g/L, J=10 mA/cm\(^2\), T=40°C).
It can be seen from Figure 3 that decolorization of RV5 dye exponentially decreases with time and almost disappears after 60 minutes resulting in complete decolorization of the solution. This exponential decrease of textile dye decolorization can be described by Equation (13):

$$- \frac{dC_{\text{dye}}}{dt} = kC_{\text{dye}}$$  \hspace{1cm} \text{(Eq. 13)}

Several studies in the literature indicated that textile dye degradation reaction follows pseudo first order kinetics. Generally, first-order kinetics is appropriate for the entire concentration range and several studies were reasonably well fitted to this kinetic model (5,6,17–25). In our study, the rate constants were obtained for pseudo first order reaction as $12.7 \times 10^{-3}$ s$^{-1}$, $3.1 \times 10^{-3}$ s$^{-1}$ and $1.2 \times 10^{-3}$ s$^{-1}$ for 300 mg/L, 900 mg/L, and 1500 mg/L RV5 dye, respectively. Reaction rate constants decreased and reaction rate increased as the initial concentration of the textile dye increased. It is generally noted that the degradation rate increases with the increase in dye concentration (17). The rate of degradation relates to the probability of OH radicals formation on the electrode surface and production of oxidizing redox reagents. As the initial concentrations of the dye increase the probability of reaction between dye molecules and oxidizing species also increases leading to an enhancement in the decolorization rate (17,23–25). In this study, reaction rate constants were obtained in a good agreement with the data previously reported in the literature for the electrochemical treatment of various types of textile dyes (5).

The pH of the reaction medium was changed between 10 and 11.5 as shown in Figure 4, which was observed in most of the runs and was most likely due to hydrolysis, ionization and HOCl/OCl$^{-}$ consumption reactions, and production of hydroxyl ions and oxygen evolution reaction as well (4,26). The effect of alkaline medium was also investigated in the literature for electrochemical and photocatalytic oxidation processes (5,17,21). Konstantinou and Albanis (23) reported the difficulty of the interpretation of pH effects on the efficiency of dye degradation process due to its multiple roles. The authors stated that in alkaline solution OH radicals are easier to be generated by oxidizing more hydroxide ions. Saquib and Muneer (17) indicated that the efficiency of degradation rate for the decomposition of textile dye was better at pH 3.5 and 11, whereas it was lower at pH values 5.8 and 9. In contrast, the degradation rate for the mineralization of the dye was found to decrease with the increase in pH from 3.5 to 9 and further increase in pH leads to increase in the efficiency of the degradation rate for TiO$_2$-mediated photocatalytic degradation of a triphenylmethane dye. Gonçalves et al. (21) obtained complete decolorization in photochemical treatment of azo dye solutions with TiO$_2$ catalyst after an irradiation period of 20 hours at an optimum pH 13. The authors indicated that the decolorization efficiency was lower both at pH 11 (70%) and pH 14 (55%) (21). Neppolian et al. (24) indicated that acidic pH has not
shown much influence on the percentage degradation of dye whereas the presence of hydroxyl ions in alkaline medium (pH > 10) enhances the degradation efficiency for TiO$_2$ assisted degradation of Reactive Blue 4 textile dye.

![Figure 4. Effect of textile dye concentration on pH change (Electrolyte=12 g/L, J=10 mA/cm$^2$, T=40°C).](image)

In this study, the cell voltage was changed between 2-3% with changing initial RV5 concentration as shown in Figure 5. It can be assumed that there were no mass transfer limitations depending on pollutant concentration and increasing dye concentration did not show significant effect on cell voltage. The runs were conducted at constant current and therefore cell voltage was variable to maintain the constant current density. As a general trend cell voltage raised about 20-25% from its initial value during the electrochemical reaction. This behavior could be attributed to the consumption of electrolyte that decreased the ionic conductivity. Ionic conductivity of the reaction medium is a very important parameter in electrochemical cells. If the concentration of electrolytes changes in the solution, then the charge difference changes. Increasing electrolyte strength decreases the solution resistance. A decrease in electrolyte concentration decreases ionic conductivity of the reaction medium that results in increase of electrical resistance and cell voltage as well (4,27–29).
Figures 6-8 shows the effect of process parameters on textile dye decolorization that was obtained by the quadratic model in Equation 14 using Design-Expert® 10. Equation 14 evaluated with regression coefficients of $R^2$ and $R^2_{adj}$ as 0.919 and 0.849, respectively, and signal/noise ratio value as 16.573 ($\geq 4$) indicating that the model is adequate and can be used for the mathematical analysis. In Equation 14, $x_1$, $x_2$, $x_3$, and $x_4$ are Reactive Violet 5 concentration (mg/L), 75% NaCl + 25% Na$_2$CO$_3$ electrolyte concentration (w/w) (g/L), current density (mA/cm$^2$), and reaction temperature (°C), respectively.

\[
\text{Decolorization (\%) = -0.088883x_1 + 3.11857x_2 + 3.59660x_3 - 1.85973x_4 + 1.94681 \times 10^{-3}x_1x_2 + 7.11715 \times 10^{-3}x_1x_3 + 1.39549 \times 10^{-4}x_1x_4 + 0.28736x_2x_3 + 0.052851x_2x_4 + 0.11345x_3x_4 - 2.43265 \times 10^{-5}x_1^2 - 0.12276x_2^2 - 0.38817x_3^2 + 7.76927 \times 10^{-5}x_4^2 + 123.34789}
\] (14)

In Figure 6, dye decolorization was obtained as 42.8-100.0% between 300-1500 mg/L Reactive Violet 5 concentration and 4-20 g/L 75% NaCl+25% Na$_2$CO$_3$ (w/w) electrolyte mixture. Increase in Reactive Violet 5 concentration decreased the decolorization efficiency as shown in Figure 6. Textile dye decolorization obtained with the degradation of azo group in the dye molecule by formation of HOCl/OCl$^-$ redox reagents and weakly adsorbed hydroxyl and chlorohydroxyl radicals at the anode surface. In Figure 6, higher than 95% decolorization was achieved below 915 mg/L initial textile dye concentration. It can be concluded that mass transfer limitations have
predominant effect at low pollutant concentrations (7). Increasing electrolyte concentration increased the decolorization efficiency as shown in Figures 6 and 7. In Figure 6, higher than 95% decolorization was achieved between 14.5-18.8 g/L electrolyte concentration. Increasing NaCl concentration increased the decolorization efficiency by generation of HOCl/OCl$^-\$ redox reagents (4).

![Figure 6](image)

**Figure 6.** Effect of textile dye concentration and electrolyte concentration on electrochemical decolorization of Reactive Violet 5 textile dye using Pt/Ir electrodes ($J=10\ mA/cm^2$, $T=40^\circ C$, $t=15$ min).

In Figure 7, dye decolorization was obtained as 56.2-100% between 5-15 mA/cm$^2$ current density and 4-20 g/L 75% NaCl+25% Na$_2$CO$_3$ (w/w) electrolyte mixture. Increasing current density increased the decolorization efficiency as shown in Figures 7 and 8. In Figure 7, higher than 95% decolorization was achieved between 14.5-18.8 g/L electrolyte concentration. Increasing NaCl concentration increased the decolorization efficiency by generation of HOCl/OCl$^-\$ redox reagents (4). Degradation efficiency increased with increasing current density that resulted in formation of OH radicals at Pt/Ir anode, and increased formation rate of HOCl/OCl$^-\$ oxidants in the bulk phase. It is very well known that current density is one of the effective parameters for controlling the mass transfer and reaction rate in electrochemical processes (4). Although increasing current density increases electrochemical oxidation efficiency, applied current may be consumed by secondary reactions at high cell potentials (10,30). Therefore, optimum current density was determined as 12.8 mA/cm$^2$ for the highest electrochemical decolorization efficiency.
Figure 7. Effect of electrolyte concentration and current density on electrochemical decolorization of Reactive Violet 5 textile dye using Pt/Ir electrodes (RV5=900 mg/L, T=40°C, t=15 min).

Dye decolorization was obtained as 62.3-100% between 5-15 mA/cm² current density and 20-60°C reaction temperature in Figure 8. In Figure 8, higher than 95% decolorization was achieved above 10.2 mA/cm² current density and 30°C reaction temperature. Therefore, optimum reaction temperature was determined in the mid of the experimental conditions as 40°C.
Figure 8. Effect of current density and reaction temperature on electrochemical decolorization of Reactive Violet 5 textile dye using Pt/Ir electrodes (RV5=900 mg/L, Electrolyte=12 g/L, t=15 min).

The optimum operating region was determined for the highest electrochemical decolorization efficiency of Reactive Violet 5 textile dye using Pt/Ir electrodes in Figure 9. The shaded region in Figure 9 shows the decolorization efficiency of higher than 95% for Reactive Violet 5 concentration and 75% NaCl+25% Na₂CO₃ electrolyte mixture at optimum operating values of 40°C reaction temperature and 12.8 mA/cm² current density. The optimum operating region was found to be applicable for the electrochemical treatment of industrial textile wastewater.
**CONCLUSIONS**

Electrochemical textile dye decolorization were investigated using Pt/Ir anodes in the presence of 75% NaCl+25% Na₂CO₃ supporting electrolyte mixture. Reactive Violet 5 decolorization increased with increasing current density and electrolyte concentration, and decreasing the textile dye concentration. Although a slight increase obtained in color removal efficiency, the temperature was not show much significant effect on decolorization. Reactive Violet 5 textile dye decolorization were obtained between 42.8-100% depending on electrochemical reaction conditions in 15 min reaction time without any further treatment. The optimum operating region at higher than 95% decolorization efficiency was determined for the Reactive Violet 5 textile dye. It can be concluded that Reactive Violet 5 textile dye decolorization obtained with the degradation of azo group in the dye molecule by the formation of redox reagents and weakly adsorbed hydroxyl and chlorohydroxyl radicals at the anode surface. Experimental findings showed that electrochemical oxidation could be an alternative for the decolorization of textile wastewater effluent.
ACKNOWLEDGEMENTS

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Öz: Reaktif Viyole 5 (RV5) içeren tekstil boyama atık sularının elektrokimyasal olarak renginin giderilmesi, Pt/Ir elektrotlarda %75 NaCl + %25 Na₂CO₃ (w/w) destek elektrolit karışımında kesikli bir elektrokimyasal reaktörde incelenmiştir. Deneysel parametreler 300-1500 mg/L tekstil boyarmadde derişiminde, 4-20 g %75 NaCl + %25 Na₂CO₃ elektrolit derişiminde, 5-15 mA/cm² akım yoğunluğunda ve 20-60 °C tepkime sıcaklığında ve 15 dakika elektroliz zamanı içinde yürütülmüştür. Reaktif Viyole 5'in renginin giderilmesi artan akım yoğunluğu ve elektrolit derişimi ile artarken tekstil boyarmadde derişiminin azalması ile de artmaktadır. Renk giderme etkinliğinde hafif bir artışa rağmen, sıcaklığın renk giderme üzerinde belirgin bir etkisinin olmadığı saptanmıştır. Elektrokimyasal tepkime koşullarına dayanarak, Reaktif Viyole 5 tekstil boyarmadde renk gidermesi %42,8-100 arasında değişmiştir.

Anahtar kelimeler: Renk giderme, Elektrokimyasal Atık Su Teribi, Pt/Ir Elektrotlar, Reaktif Viyole 5, Tekstil Boyarmaddesi.