Removal of Sumifix Yellow EXF Reactive Azo Dye By Electro-Fenton Method

Elif ÖZKUL1, Belgin KARABACAKOĞLU2

1 Pamukkale University, Department of Chemical Engineering, Denizli, 20160, Türkiye
2 Osmangazi University, Department of Chemical Engineering, Eskişehir, 26040, Türkiye

Abstract: Reactive dyes can be found in large quantities in textile industry wastewater due to their widespread use for dyeing cotton fabrics and their durable nature. In the treatment of wastewater containing dyestuffs in this class, advanced treatment methods have become necessary due to the inadequacy of conventional treatment methods and their disadvantages. For this reason, electro-Fenton, an electrochemical advanced oxidation method, is a strong alternative as a treatment technology that provides complete disintegration of dye molecules. In this study, the electro-Fenton method was used to treat model wastewater containing the reactive azo dye Sumifix Yellow EXF. The electro-Fenton process is based on the in situ generation of hydroxyl radicals (⦁OH), a strong oxidant, using Fe^{2+} and H_{2}O_{2} released at the electrodes or added from outside. In the electrochemical cell used, carbon fiber was used as the cathode and iron was used as the anode. While Fe^{2+} ion was produced at the anode, H_{2}O_{2} was added to the cell externally. In the experiments carried out at room temperature, a 250 mL glass beaker was used as a reactor. In the study, the optimization of the parameters was achieved by using the classical experimental design method. According to this method, one parameter is changed and other parameters are kept constant. In order to achieve the highest dyestuff removal, experiments were conducted by varying the voltage (5–10 V), H_{2}O_{2} concentration (9–74 mM), Na_{2}SO_{4} concentration (6–25 mM), and pH (3–5), and the impact of these factors on dye removal and energy consumption was evaluated. It was found that for the best dye removal, voltage is 7.5 V, the H_{2}O_{2} concentration is 74 mM, the Na_{2}SO_{4} concentration is 25 mM and the optimum pH value is 4. At these values, 98.14% removal at 30 minutes was achieved with an energy consumption of 7.98 Wh/L. The electro-Fenton method was found to be a highly effective approach for wastewater treatment and environmental remediation, showing remarkable dye removal efficiency with reasonable energy consumption under optimized conditions.

Keywords: Electro-Fenton; advanced oxidation; dye removal; Sumifix Yellow EXF; reactive azo dye.


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*Corresponding author. E-mail: eozkul@pau.edu.tr.

1. INTRODUCTION

Dyes are recognized as a wide variety of organic pollutants transmitted from different industries such as textile, leather, paper, food, beverage, pharmaceutical, and cosmetics to wastewater treatment systems or natural water sources. There are an estimated 10,000 different textile dyes. During the dyeing process, 10-25% of these dyes and 2-20% are mixed with water as aqueous wastes with different components, and large volumes of wastewater containing high amounts of dyes are discharged from industries to water bodies without being treated or sufficiently treated. As a result, one of the sectors that causes serious water pollution is the textile sector. The discharge of many dyes and degradation products from this industry into the aquatic environment can be toxic, carcinogenic, and/or mutagenic for life (1,2). Therefore, the treatment of dye compounds and degradation by-products that negatively affect life has become more important.
Reactive dyes are a type of dye that is widely used in the textile industry because they contain reactive groups that allow textile fibers to be bonded to each other through the formation of covalent bonds. Thanks to this feature, which improves the interaction of dye with textile fibers, low energy consumption is possible (3,4). Many reactive dyes are available in the azo dye category. Reactive azo dyes are anionic dyes with one or more azo (-N=N-) functional groups (5,6). These dyes are not biodegradable due to their aromatic nature and high stability (7). These paints, which have toxic, mutagenic and carcinogenic effects and are very difficult to remove from water, require good treatment.

Many different methods, including physical, chemical, and biological are used in the treatment of textile wastewater (8). Chemical coagulation, biological oxidation, and adsorption are the traditional methods for treating dyed wastewater. Biological methods are low-cost and easy to implement. However, dyed wastewater cannot be removed to a large extent with the activated sludge method, which is a classical biological treatment method. Therefore, in the presence of toxic and persistent organics in wastewater, biological treatment is not sufficient. In chemical coagulation and adsorption methods, there is only the transfer of pollutants from one phase to another; large amounts of sludge and waste are formed and further treatment becomes necessary to remove them. Therefore, the focus has been on the development of new purification technologies that provide complete degradation of dye molecules. Among these treatment technologies, electro-Fenton is an electrochemical advanced oxidation method. This method uses a highly oxidative hydroxyl radical (•OH) produced by the reaction of Fe$^{2+}$ and H$_2$O$_2$ reagents produced in situ or added externally under an electrical field for the removal of persistent organics. •OH radicals are very effective oxidants and can easily decompose organic materials. Electro-Fenton reactions generally take place by means of the chain reactions given below (9,10).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{H}_2\text{O} \quad (1)$$

$$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2 \cdot \quad (2)$$

$$\text{Fe}^{3+} + \text{HO}_2 \cdot \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \quad (3)$$

$$\text{Fe}^{2+} + \text{HO}_2 \cdot \rightarrow \text{Fe}^{3+} + \text{HO}_2 \cdot \quad (4)$$

$$\cdot\text{OH} + \text{RH} \rightarrow \text{R}^+ + \text{H}_2\text{O} \quad (5)$$

H$_2$O$_2$ added to the electrochemical cell reacts with the Fe$^{2+}$ ion, which acts as a catalyst, to form •OH radicals (Equation 1). The Fe$^{2+}$ ion is produced at the anode in the electrochemical cell. In addition, the reduction of the Fe$^{3+}$ ion provides regeneration of the Fe$^{2+}$ ion (Equations 2 and 3). Finally, pollutants (RH) are converted into non-toxic compounds such as CO$_2$ and H$_2$O with •OH radicals (Equation 5). In addition, H$_2$O$_2$ can be produced at the cathode in an acidic and oxygen-containing environment inside the cell (Equation 6) (11).

$$\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad (6)$$

The electro-Fenton method is effective for the treatment of synthetic and real wastewater contaminated with different organic substances such as pharmaceuticals, personal care products, endocrine disrupting compounds, pesticides, textile wastes, polycyclic aromatic hydrocarbons, surfactants, and landfill leachate (12).

In this study, the electro-Fenton method, which is an advanced oxidation method, was used to remove Sumifix Yellow EXF Reactive Azo dye from an aqueous solution. The effects of some important parameters (voltage, H$_2$O$_2$ concentration, Na$_2$SO$_4$ concentration, pH) on dye removal and energy consumption were investigated, and optimum working conditions were determined. 98.14% color removal and 7.98 Wh/L energy consumption were achieved under optimum operating conditions. The aim of this study is to investigate the usability of the electro-Fenton method for the reactive azo dyestuff used in this study, to determine the optimum working conditions for each parameter examined, and to be a source for further studies.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Hydrogen peroxide (H$_2$O$_2$ (35%), Merck) and sulfuric acid (H$_2$SO$_4$, Merck) were used in the studies. All chemicals used were of analytical grade and were used without further purification. Stock standard solutions were diluted to form working solutions. All experiments were performed at room temperature. A pH meter (OHAUS pH meter) and a spectrophotometer (Thermo Electron Corporation) were used in the study. Sumifix Yellow EXF was used as a reactive azo dyestuff. This dyestuff was purchased from a local company (Türkiye). Dye solutions were prepared by diluting the stock solution prepared by dissolving 1 g of dye in 1 L of distilled water. The solution with a dye concentration of 100 mg/L was used in all experiments.

Some physical and chemical properties and chemical structure of the commercial textile dye Sumifix Yellow EXF are given in Table 1.
Table 1: Some properties and chemical structure of Sumifix Yellow EXF

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Commercial name:</th>
<th>Sumifix Yellow EXF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol wt (g/mol):</td>
<td>1026.25</td>
</tr>
<tr>
<td></td>
<td>Molecular formula:</td>
<td>C28H20ClINa4O16S5</td>
</tr>
<tr>
<td></td>
<td>Color Index name:</td>
<td>Reactive yellow 145 (RY145)</td>
</tr>
<tr>
<td></td>
<td>Class:</td>
<td>Single azo</td>
</tr>
</tbody>
</table>

2.2. Electrochemical System

The apparatus used in the study consists of three main units: a DC power supply, a magnetic stirrer, and an electrochemical cell (Figure 1). The electrochemical cell is also called the electro-Fenton reactor. Experiments were carried out at room temperature in an undivided and cylindrical 250-mL glass beaker. The usable volume of the reactor was 200 mL. Electro-Fenton times of 0–30 minutes were used for all studies. An iron (anode) and a carbon fiber (cathode) with dimensions of 50 mm by 60 mm were used as electrodes. In the electro-Fenton reactor, electrodes parallel to each other and separated by 2 cm were connected to the direct current power supply (Stone). Current and voltage control were carried out with this power supply. As long as the active surface area did not change with the dissolution effect, the use of the anode continued. For each experiment, the EF reactor was filled with 200 mL of wastewater and stirred continuously at 500 rpm with a cylindrical magnetic rod. The anode was washed with concentrated HCl (37%), then with distilled water. Thus, the iron oxide compounds that had accumulated on the surface were removed. Since Fenton reactions occur in an acidic environment, the initial pH of the dye solution was adjusted to the desired level before the Fenton reagent H2O2 was added to all experiments. To create a 100 mg/L stock solution, a dye solution at a concentration of 1 g/L was prepared. 0.1 M H2SO4 was used for pH adjustment in all experiments. The pH-adjusted solution was placed in the experimental setup. Na2SO4 was used to provide conductivity in the solution. Before each experiment, the amount of iron dissolved in the anode was measured by weighing the Fe electrode. Electrolysis was carried out by giving the desired voltage to the system. Then, the time was started, and 35% H2O2 was added after 1 minute. The production of •OH radicals was achieved by adding H2O2.

Figure 1: Experimental Setup (1:EF reactor; 2:Magnetic stirrer; 3:DC power supply).

2.3. Analytical System

The dyestuff concentration (ppm) of the samples was determined by a UV-VIS spectrophotometer (Thermo Electron Corporation) at a wavelength of 423 nm. The color removal efficiency of the removal process was analyzed by evaluating the difference in absorbance values of the dye solution before and after removal. The Sumifix Yellow EXF removal efficiency was calculated according to the following equation:
Removal efficiency \( \% = \left( \frac{C_0 - C}{C_0} \right) \times 100 \) \hspace{1cm} (7)

Where \( C_0 \) and \( C \) are the dye concentration in mg/L at \( t=0 \) and \( t \), respectively.

The energy consumption in the Electro-Fenton process is calculated using the following equation:

Energy consumption \( \text{Wh} / L = \frac{V \times I \times t}{L} \) \hspace{1cm} (8)

3. RESULTS AND DISCUSSION

3.1. The Effect of Voltage

Increasing the voltage and hence the current density to the optimum value in electro-Fenton processes will increase the transition of \( Fe^{2+} \) from the anode electrode to the solution. In addition, \( \bullet OH \) radicals will be produced by causing more \( H_2O_2 \) formation at the cathode (Equation 1). As a result, the voltage value increases to an optimum value, the amount of \( \bullet OH \) radical, the removal efficiency will also increase. In addition, higher voltage values provide faster \( Fe^{2+} \) regeneration at the cathode electrode (Equation 9) (13).

Cathode Reaction:

\( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \)

(9)

Along with these, since the rate of parasitic reactions increases, the efficiency decreases when the voltage value is increased above the optimum value, resulting in the removal of the same or less pollutants compared to low voltage values (14). The optimum voltage value was selected as 7.5 V in view of high removal and low energy consumption (Figure 2).

3.2. The Effect of Electrolyte (Na2SO4)

Concentration

Supporting electrolytes should be used in electro-Fenton processes to treat wastewater with low conductivity. Electrolytes help increase the conductivity of solutions and accelerate electron transfer. The commonly used supporting electrolyte type in electro-Fenton processes is Na2SO4 (15). In addition to Na2SO4, NaCl, KCl,
Figure 2: The effect of applied voltage on the percentage of dye removal and energy consumption (Na₂SO₄: 25 mM; H₂O₂: 37 mM; pH: 3)
3.3. The Effect of pH

The pH of the solution has a significant influence on the electro-Fenton process as it regulates the Fe$^{2+}$ concentration and the formation of ⋅OH radicals (20). In general, Fenton reactions take place in an acidic environment. In the color removal studies performed with the electro-Fenton process, it has been confirmed that the best color removal efficiencies are obtained when the pH range of the environment is 2-5 (21,22).

Many studies have reported pH 3 as the pH at which Fenton reactions occur well (11,21,23,24). At higher pH levels, iron species begin to precipitate as their hydroxides. Iron species form stable complexes with H$_2$O$_2$ even at low pH levels. As a result, the removal efficiency decreases in both cases. An acidic environment is necessary for the production of H$_2$O$_2$ (Equation 6). However, an acidic environment limits the production of H$_2$O$_2$ (Equations 13 and 14) (25).

H$_2$O$_2$ + 2H$^+$ + 2e$^-$ → 2H$_2$O

2H$^+$ + 2e$^-$ → H$_2$ (14)

In addition, oxonium ions are formed at pH< 3 (Equation 15) (11).

H$_2$O$_2$ + H$^+$ → H$_3$O$_2^+$ (15)

The efficiency of the electro-Fenton process decreases due to the instability of H$_2$O$_2$, especially at pH> 5. H$_2$O$_2$ rapidly decomposes into water and oxygen (Equation 16) (26,27).

2H$_2$O$_2$ → 2H$_2$O + O$_2$ (16)
In this study, pH values of 3, 4 and 5 were studied to find the best removal efficiency. The best removal efficiency is at 97.31% at the end of 30 minutes at pH 4. The lowest energy consumption occurred at pH 5, as seen in Figure 4.

![Figure 4: The effect of solution pH on the percentage of dye removal and energy consumption (Na2SO4 : 25 mM; H2O2 : 37 mM; E: 7.5 V).](image)

3.4. The Effect of Initial H2O2 Concentration
In this study, 0.125 mL, 0.25 mL, 0.5 mL, and 1 mL H2O2 amounts were added to a 200 mL solution, and the removal efficiency resulted in 88.25%, 97.36%, 97.31%, and 98.14%, respectively, after 30 minutes. The concentrations of H2O2 in solution are 9 mM, 19 mM, 37 mM, and 74 mM, respectively. The highest removal efficiency is 98.14% at a 74 mM H2O2 concentration (Figure 5).
The initial concentration of H₂O₂ is an important parameter in electro-Fenton processes. Because it is the main source of H₂O₂ •OH radicals. Removal of pollutants increases with increasing H₂O₂ concentration. As the H₂O₂ concentration increases to an optimum value, the concentration of the •OH radical also increases (Equation 1) (28,29). However, at concentrations higher than the optimum value of H₂O₂, the decrease in removal efficiency is due to the scavenging effect of H₂O₂ on •OH radicals (Equations 17 and 18) and recombination of the OH radical (Equation 19) (20).

\[
\begin{align*}
\dot{\text{OH}} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2O \\
\text{HO}_2^- + \dot{\text{OH}} & \rightarrow \text{H}_2\text{O} + \text{O}_2 \\
2\dot{\text{OH}} & \rightarrow \text{H}_2\text{O}_2
\end{align*}
\]

4. CONCLUSION

In this study, color removal and energy consumption studies were carried out by the electro-Fenton method on aqueous solutions of Sumifix Yellow Reactive Azo dyes. In this method, the effects of voltage (5, 7.5, and 10 V), electrolyte (Na₂SO₄) concentration (6, 12, and 25 mM), pH (3, 4, and 5), and initial H₂O₂ concentration (9, 18, 37, and 74 mM) were investigated. As a result of studies of optimization, at 7.5 volts, 25 mM Na₂SO₄, pH 4, and 74 mM H₂O₂ for 30 minutes, the highest color removal efficiency value of 98.14% was obtained. The energy consumption at these parameter values is 7.98 Wh/L. According to Faraday’s law, as the voltage applied to the cell increases, the amount of iron dissolved at the anode increases, and accordingly, the rate of disintegration of the dyestuff increases with the increase in Fe²⁺ concentration. However, the degradation rate decreased above a certain concentration (Figure 2). As a result, determining the optimum voltage value becomes necessary both for the removal of pollutants and for reducing energy consumption. As the concentration of...
Na2SO4 used as the supporting electrolyte increases, the solution conductivity increases, and the current intensity increases according to Ohm’s law. All other variables being constant, energy consumption increased with the increase in current intensity (Figure 3). Since the removal is higher at pH 4 and the energy consumption is less than pH 3, subsequent experiments were carried out at pH 4. The best removal occurred at 74 mM H2O2 when the H2O2 concentration was changed while keeping all other parameters constant. In the study, dye removal was investigated between 5-30 minutes and it was observed that the dye removal efficiency increased with the effective realisation of the reactions due to increased Fe2+ formation and hydroxyl radical production as the time progressed for all parameters examined. In addition, energy consumption increased significantly with increasing time of treatment. This study successfully shows that Sumifix Yellow EXF azo dyestuff from an aqueous solution can be removed at a value close to 100% with low energy consumption in as little as 30 minutes.

5. CONFLICT OF INTEREST

The authors state that there is no conflict of interest.

6. ACKNOWLEDGMENTS

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