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Mineralization of an Azo Dye Reactive Red 195 by Advanced Electrochemical Electro-Fenton Process

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***Abstract*—In this paper, the electro-Fenton (EF) process was used for Degradation of a monoazo dye, Reactive Red 195 (RR195). Hydrogen peroxide was electro-generated by reduction of dissolved oxygen in acidic solution. EF process allows the production of active intermediates, which react with the organic compounds leading to their mineralization. In the electrochemical cell carbon paper (CP) was used as cathode and a Pt sheet was used as anode. The experiments were conducted at room temperature in an open, undivided and cylindrical glass cell of 500 mL capacity. H_2O_2 was continuously generated from the two-electron reduction of O_2 at cathode electrode while Fe^{3+} was added to the solution. The effect of operational parameters such as applied current, initial pH and reaction time was studied in an attempt to reach the higher dye removal efficiency. The degradation of RR195 was followed by total organic carbon (TOC) analysis. The results of TOC measurements indicated that electro-Fenton with carbon paper allowed 75% degradation after 240 min of electrolysis.**

***Index Terms*—Reactive red 195, electro-Fenton, carbon paper, dye removal.**

I. INTRODUCTION

Dyes present in wastewater are of a particular environmental concern since they give an undesirable color to the waters and in some cases they are harmful compounds and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the waste phase [1], [2]. Recently, increasing attention has been focused on complete degradation of organic compounds to harmless products such as CO_2 and H_2O. The treatment methods, based on the generation of hydroxyl radicals ($^\bullet OH$), known as advanced oxidation processes (AOPs), have been applied for degradation of toxic organic pollutants. AOPs consist of the production of hydroxyl radicals from different systems, such as the Fenton, photo-Fenton, electrochemical (anodic oxidation) and electro-Fenton processes [3], [4]. The development of a new process ensuring an *in-situ* production of the Fenton reagent (Fe^{2+}/H_2O_2) by electro-Fenton has been considered therefore. Electro-Fenton process uses as reagent the compressed air and a catalytic amount of ferric ions. In this technique, H_2O_2 is continuously supplied to the contaminated solution from the two-electron reduction of O_2 usually at carbon-felt and its components cathodes [5]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

The oxidizing power of the hydrogen peroxide is highly enhanced by the addition of Fe^{2+} generating the Fenton reaction [6]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \qquad (2)$$

The EF method utilizes a Pt anode in an undivided cell, while Fe^{3+} is added to the solution to permit degradation of pollutants by $^\bullet OH$ generated from reaction (2). Soluble Fe^{3+} can be reduced to Fe^{2+} through reaction (3) on cathode [5]:

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

The optimal pH for the electro-Fenton process is around 3.0 because at this pH the main species, $Fe(OH)^{2+}(H_2O)_5$, has the largest light absorption coefficient and quantum yield for $^\bullet OH$ production, along with Fe(II) regeneration in the range of 280–370 nm [4]. The electro-Fenton has successfully been used for the treatment of wastewaters including phosphonate herbicides [7] and decolorization of various structurally different dye in wastewaters [2], [3], [8]. In the electro-Fenton process property of cathode electrode is one of the affecting factors on the efficiency of process. The protection of hydroxyl radicals is increased with increasing the conductivity and specific surface of the cathode which causes the enhancement of removal of pollutants. In this work, EF process was performed using carbon paper as cathode electrode for removal of Reactive Red 195 as a monoazo dye from contaminant water. This electrode is very resistant in aqueous solutions and it has particular characterizes such as high conductivity and large specific surface. Reactive Red 195 is soluble in water and idoneous for acrylic fiber dyeing and is used in the wool, towel and blanket factories, so their effluents have a great deal of this dye.

II. MATERIALS AND METHODS

Carbon paper (TGP-H-060, thick: 190 μm, conductivity: 12.5 S/cm and porosity: 80%) was purchased from Toray, Japan. Fig. 1(a) shows the scanning electron microscopy (SEM) image of applied cathode electrode. The commercial dye (Reactive Red 195) used in this project was purchased from Ciba-Geigy, Switzerland. Dye solution was prepared by dissolving dye in distilled water. All chemicals used in this study were of the highest purity available from Merck. The Na_2SO_4 was used as support electrolyte. All the runs were performed at room temperature. In each run, 250 mL of the dye solution containing 0.05 M of Na_2SO_4 was decanted into the electrolytic cell. The batch experimental cell is shown in Fig. 2(b). Pt sheet of 25 cm^2 area was used as anode and

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carbon paper of 40 cm^2 area was used as cathode.

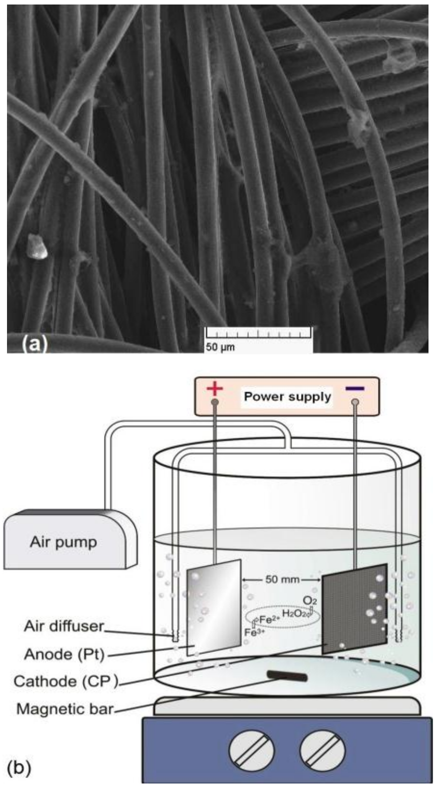

Fig. 1. SEM image of used carbon paper (a) and an apparatus electrochemical cell (b).

The dye concentration was determined from them absorbance characteristics in the UV–Vis range with the calibration method. A Hach UV–Vis spectrophotometer (DR 5000, USA) was used. For the measurement the maximum absorption (λ_{max}=542 nm) wavelength of dye was determined by measurement of it absorbance at various wavelengths. The calculation of dye removal efficiency after electro-Fenton treatment was performed using Eq. (4):

$$\mathrm{DR}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{4}$$

where C_0 and C are concentrations of dye before and after decolorization in mg/L, respectively. The total organic carbon (TOC) of dye solution was measured by Shimadzu TOC analyzer (ON-LINE TOC-VCSH, Japan). The TOC decay percentage was defined as:

$$\mathrm{TOC\ \ Decay\ \ }(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100 \tag{5}$$

where TOC_0 and TOC_t are total organic carbon at times $t = 0$ (initial) and t (reaction time) in mg/dm^3.

III. RESULTS AND DISCUSSION

A. Influence of Electrolysis Time and Applied Current on the Dye Removal

In all electrochemical processes, reaction time and current density are the most important parameters for controlling the reaction rate and the treatment efficiency within the electrochemical reactor. The dye removal efficiency depends directly on the generation of hydroxyl radicals on the dyestuff wastewater [4]. The influence of applied current on dye mineralization has been investigated in the range of 200-400 mA under 30- 240 min electrolysis time and initial pH of 3 and the results are reported in Fig. 2(a). This result shows a gradual increase in dye removal efficiency with raising current and time. This enhancement of the oxidation power can only be associated with a great production of H_2O_2 from reaction leading to the generation of high amount of hydroxyl radicals from Fenton's reaction. According to the results, dye removal percent at the time of 150 min were obtained more than 90% for both of 300 and 400 mA current and for saving the electrical energy consumption, current upper than this data was not appropriate.

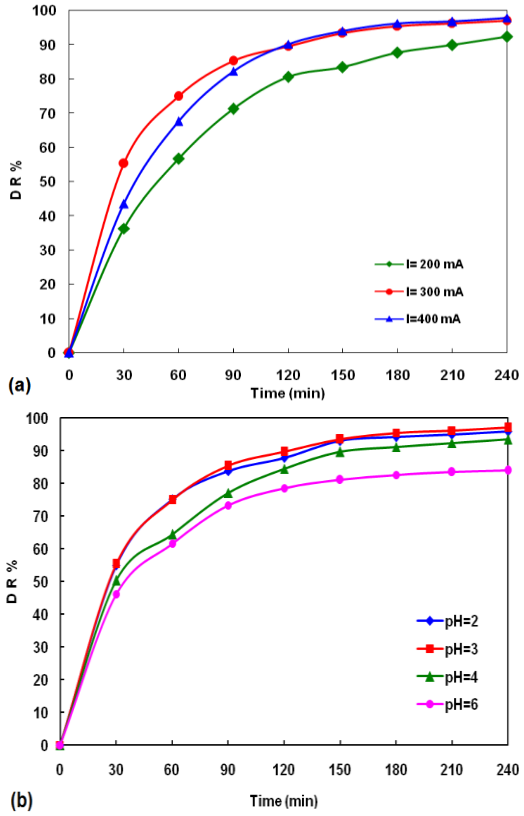

Fig. 2. Influence of applied current (a) and initial pH (b) on the dye removal ($[Dye]_0$ =100 mg/L, Fe^{+3} =0.15 mM, and $[NaSO_4]$=0.05M).

B. Influence of Initial pH on the Efficiency of Dye Removal

The initial pH of solutions was selected 3.0 as the optimum pH to carry out Fenton's reaction (Eq. (2)), according to several studies on electro-Fenton process [4]. It is maintained about 2.8-3 during the treatment (H^+ consumed by Eq. 1 being compensated by oxidation of water at the anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). To clarify the effect of pH, dye solution with initial pH of 2.0, 3.0, 4.0 and 6.0 were electrolyzed the results are illustrated in Fig. 2(b). For the 100 mg/L of dyestuff containing RR195, the natural pH was 4.35 and after 150 min electrolysis time for the initial pH 3.0, dye removal percent was around 93%.

C. Influence of Electrolyte Type on the Efficiency of Dye Removal

In electrochemical process, table salt is usually employed to increase the conductivity of the wastewater to be treated. For the studying influence of electrolyte type, three different salts Na_2SO_4, Na_2SO_3 and $MgSO_4$ with concentration of 0.05 M were employed (Fig. 3(a)). According to the results, electrolyte Na_2SO_4 electrolyte was chosen for the support electrolyte after 150 min time, dye removal percent was around 93%. However, other salts weren't suitable because $MgSO_4$ electrolyte was precipitating to the cathode electrode surface and with Na_2SO_3 electrolyte, the initial pH of dye solution was around 8.90.

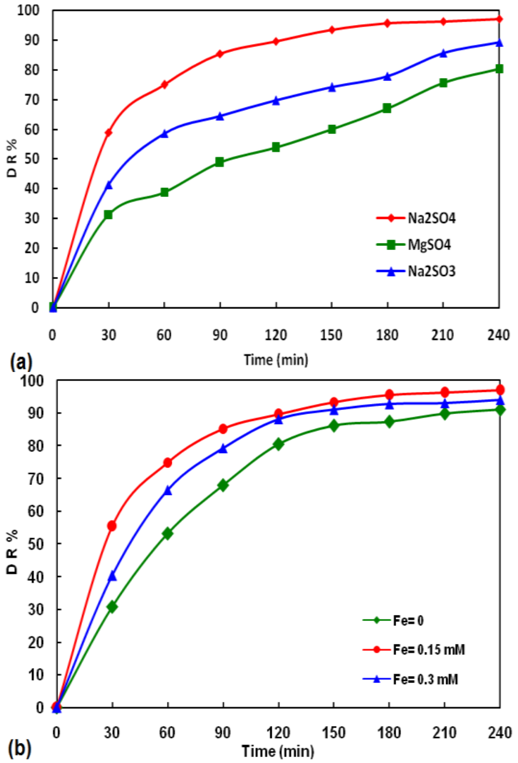

Fig. 3. Influence of electrolyte type (a) and of Fe^{+3} concentrations on the dye removal (I=300 mA, pH=3.0)

D. *Influence of Fe^{+3} Concentrations on the Efficiency of Dye Removal*

Ferrous ion concentration was shown to have a significant effect on dye removal in the EF process. Fig. 3(b) shows the effect of different ferrous ion concentrations ranging from 0 to 3.0 mM under EF conditions for the 30 to 240 min electrolysis time. The ferrous ion catalyzes the decomposition of H_2O_2 into the reactive species ($^{\bullet}$OH) that oxidize the RR195 molecules [8] After 150 min of treatment, the dye removals were 86%, 93%, and 91% for 0, 0.15 and 0.3 mM of Fe^{3+} concentrations, respectively. When the initial concentration of Fe^{2+} ions in the solution 0.15 mM, a remarkable enhancement in the dye decay was observed. However, when the Fe^{2+} concentration was in the range of 0.15 mM, the dye removal decreased to 93%, as presented in Fig. 3(b).

E. *TOC Reduction and Spectra of the Dye Solution*

Influence of electrolysis time on the TOC reduction and UV–Vis absorbance spectra changes at the optimized conditions (I=300 mA, pH=3.0, $[Dye]_0$ =100 mg/L, Fe^{+3} =0.15 mM and $[NaSO_4]$=0.05M) were shown in Fig. 4. As can be seen in Fig. 4(a), TOC decay percent at 240 min electrolysis time was more than 80%. According to the Fig. 4(b), EC process caused almost complete dye removal after 240 min.

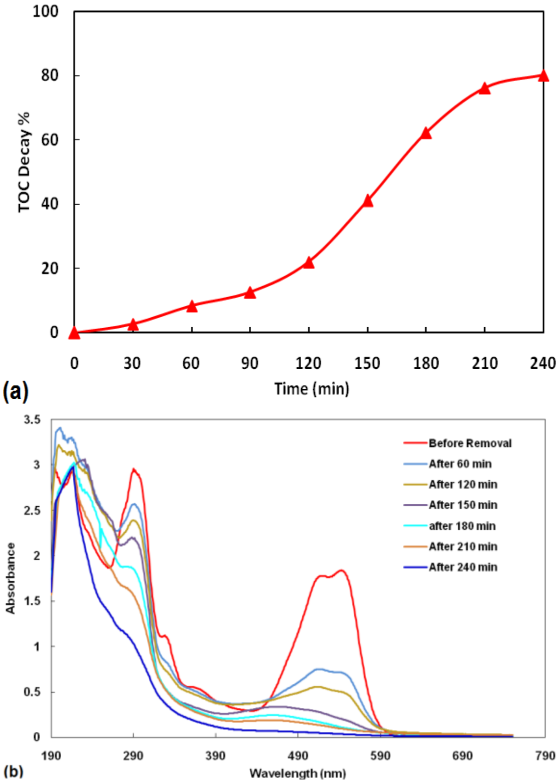

Fig. 4. Influence of time on the TOC reduction (a) and UV–Vis spectra changes for RR195 solution by EF (b). (I=300 mA, Fe^{+3} =0.15 mM, pH=3.0, $[Dye]_0$ =100 mg/L and $[NaSO_4]$=0.05M).

IV. CONCLUSIONS

This study demonstrated that the electro-Fenton process for mineralization of textile dyestuff, Reactive Bed 195 from contaminate water with Carbon Paper electrode as a cathode. The effect of operational parameters such as applied current, initial pH, support electrolyte type and initial Fe^{+3} concentration was studied. Our results showed that for mineralization of 250 mL of RR195 solution with initial concentration of 100 mg/L, applied current was 300 mA, electrolysis time was 150 min and initial pH was 3. The reduction of TOC was 90% and dye removal percent was 93%, at the upper conditions.

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