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Reactive Black 5 Removal with Electro-Oxidation Method using Ti/IrO_2/RuO_2 Anode and Stainless Steel Cathode

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In this study, the treatment of synthetic wastewater by electro-oxidation method was investigated. The experiments were performed in batch mode. As the anode material, Ti/IrO_2/RuO_2 sieve type anode material was used and stainless steel cathode plates were used as cathode material. The effects of experimental parameters such as initial dye concentration, pH, supporting electrolyte type, supporting electrolyte concentration and current density on the removal efficiency were investigated. NaCl, KCl, Na_2SO_4 and $NaNO_3$ as support electrolyte type were used. The obtained results showed that color removal optimal conditions are the following: initial pH of about 5, current density of 1.0 mA/cm^2 and supporting electrolyte of 5 mM NaCl. In the most favorable conditions, the dye removal is determined as 99.67%. It can be concluded that electro-oxidation process by Ti/IrO_2/RuO_2 electrode is very efficient and clean process for reactive dye removal from colored wastewater.

Keywords: Dye removal; Electro-oxidation; Steel cathode; Ti/IrO_2/RuO_2 anode

1. INTRODUCTION

Due to increased industrialization, changing product compounds have caused more toxic wastes to spread around. Therefore, toxic compounds contained in dye wastewater should to be removed before it can be discharged [1].

Different conventional methods in order to deal with textile wastewater were used such as electro-oxidation [2], fenton [3], electro-fenton [4], electrocoagulation [5], ozone [6], adsorption [7] and reverse osmosis [8].

Many studying put forth that the electro-oxidation (EO) technique could be an effective meyhod for treatment of textile wastewaters leading to high removal efficiency. Electro-oxidation is based on the direct or indirect oxidation of wastewaters containing organic matter using anodes resistant to electrochemical conditions (insoluble) [9]. In direct electro-oxidation, organic impurities are directly diffused to the anode surface, where oxidation occurs [10]. In indirect electro-oxidation, organic matter is oxidized by end-products using intermediates such as ozone, OCl, $HOCl^-$ and $S_2O_3^{-2}$ [11]. Graphite, boron doped diamond, platinum and coated titanium anodes are the most commonly used anode types in the electro-oxidation process.

In this study, the electro-oxidation of Reactive Black 5 (RB 5) using a $Ti/IrO_2/RuO_2$ anode was investigated. The effect of initial dye concentration, pH, supporting electrolyte type, supporting electrolyte concentration and current density as experimental parameters was examined in terms of dye removal efficiency.

2. MATERIAL AND METHODS

The Reactive Black 5 (RB 5) dye which was used in the work has an analytical purity and the molecular formula $C_{26}H_{21}N_5Na_4O_{19}S_6$.

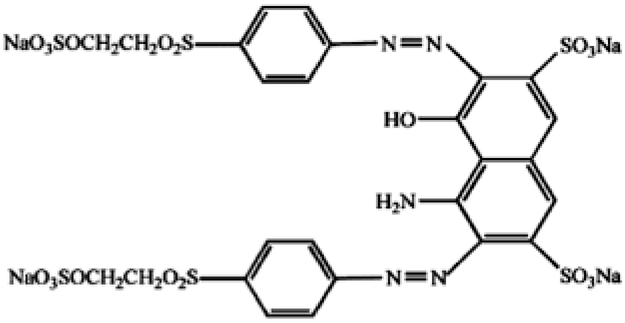

Figure 1. Molecular structure of Reactive Black 5 (RB5)

The molecular structure of the RB5 was given in Figure 1 and the molecular weight was calculated to be about 991.789 g/mol. Synthetic wastewater used in experiments were prepared synthetically using distilled water and diluting them to appropriate amounts at the beginning of the experiment. The concentration of RB5 in the sample solution was determined using a spectrophotometer with a wavelength of 597 nm.

The treatment of synthetic wastewater by electro-oxidation process and the energy consumption are calculated by the following equations;

$$\%\eta = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{1}$$

$\eta(\%)$: % removal efficiency, C_0 (mg/L): Initial dye concentration, C_t (mg/L): The concentration of the dye remaining in the solution at any time t.

$$Energy\ Consumption\left(kW - h/_{m^3}\right) = \frac{V \times I \times t}{v} \tag{2}$$

EC (kW-h/m^3): Energy consumption, I (Ampere): Current intensity, V (Volt): Potential difference, t (h): Time and v (m^3): Dyestuff volume.

$$J\left({}^{mA}\!/_{cm^2} \right) = \frac{I}{A} \tag{3}$$

J (mA/cm^2): Current density, I (Ampere): Current intensity, A (cm^2): Total wet surface area of anodes and cathodes.

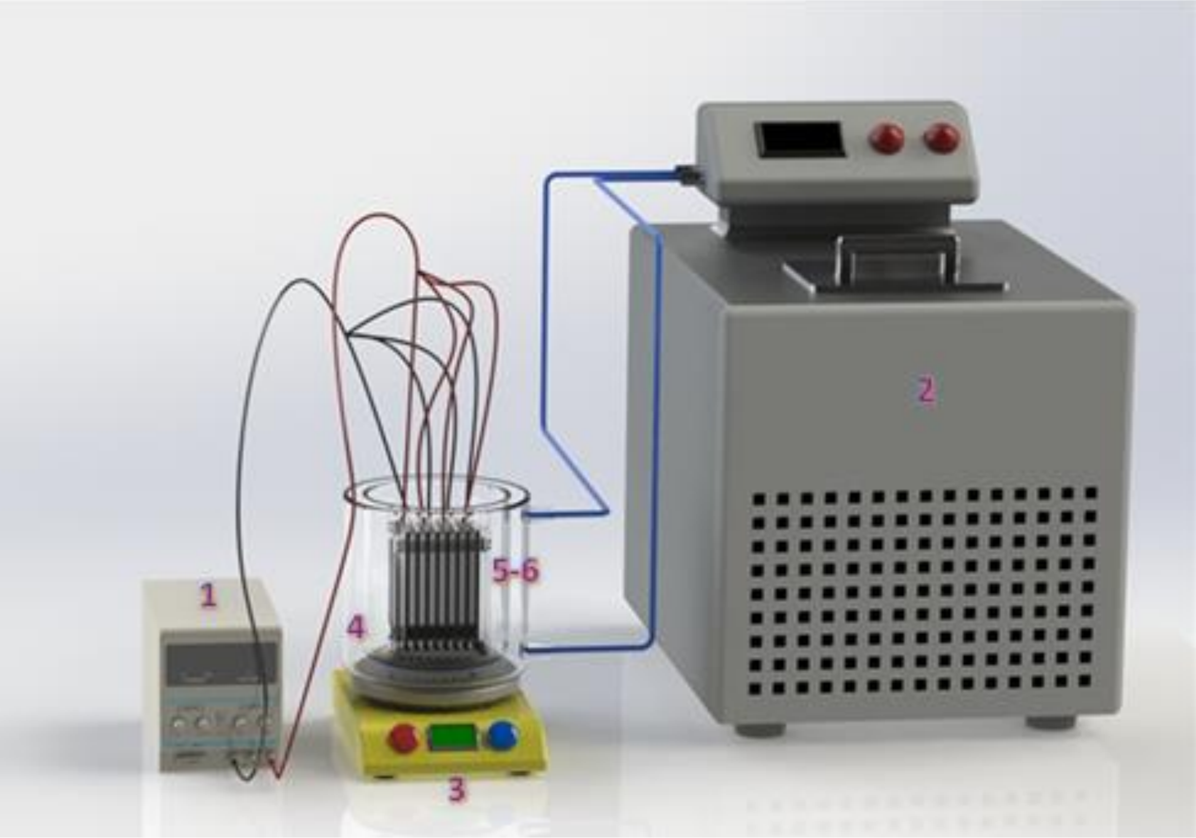

Figure 2. Experimental set up (1. DC Power, 2. Constant temperature water circulator, 3. Magnetic stirrer, 4. Glass reactor, 5. Steel plate cathode, 6. Ti/IrO_2/RuO_2 anode)

750 mL synthetic wastewater volume was used in the batch studies. In the study where 5 Ti/IrO_2/RuO_2 sieve type anodes and 5 stainless steel cathodes were used, the total areas of the electrodes were calculated as 2000 cm^2. The experimental setup in which the experiments are performed was shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1. Effect of Supporting Electrolyte Types

The effect of the supporting electrolyte types on the electro-oxidation of the RB5 dye using a Ti/IrO_2/RuO_2 anode was investigated for concentration of 5 mM of NaCl, KCl, Na_2SO_4 and $NaNO_3$ salts at a current density of 0.50 mA/cm^2, at initial dye concentration of 50 mg/L, temperature of 25

°C, at natural pH value (≈5.0), at stirring speed of 400 rpm for 30 minutes and the results which were obtained were shown in Figure 3. The dye removal efficiencies for NaCl, KCl, $NaNO_3$ and Na_2SO_4 the supporting electrolyte types were determined as 89.96%, 72.45%, 41.14% and 30.13%, respectively. It is observed that the removal efficiency of dye pollutants is influenced by support electrolyte significantly [12, 13]. The chlorine present in the wastewater is converted into oxidant species $HOCl^-$ and OCl^- by the effect of current density and wastewater pH value [14].

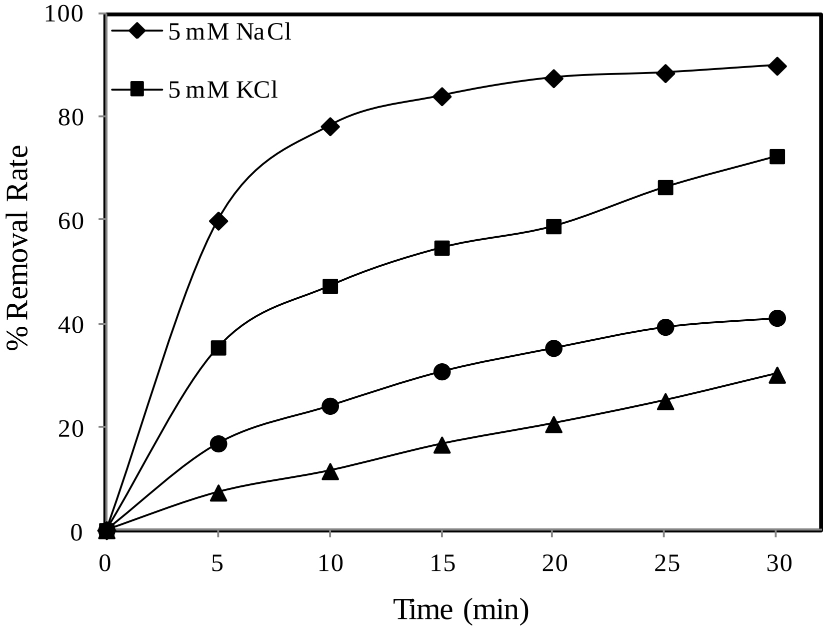

Figure 3. The effect of supporting electrolyte type on dye removal efficiency (C_0: 50 mg/L, J: 0.50 mA/cm^2, pH≈5.0, T: 25°C, SS: 400 rpm)

3.2. Effect of Supporting Electrolyte Concentration

In this section, the concentration of NaCl was 2.5, 5.0, 7.5 and 10.0 mM and the electrochemical degradation of RB5 dye was carried under the following operating conditions: current density of 1 mA/cm^2, pH of 5.0 and the initial dye concentration of 50 mg/L. Fig. 4 showed that shows the variation of dye removal % as a function of 30 minute electrolysis time. Supporting electrolyte concentration is one of the most important parameters affecting indirect electro-oxidation [15]. As the supporting electrolyte concentration increases, intermediates such as OCl^- and $HOCl^-$, which are more effective in the oxidative properties of chlorine, are increasing in wastewater, Thus, the efficiency of indirect electro-oxidation is increasing [16]. Removal efficiencies for 2.5, 5.0, 7.5 and 10 mM supporting electrolyte concentrations were 79.86%, 89.96%, 92.29% and 93.75%, respectively.

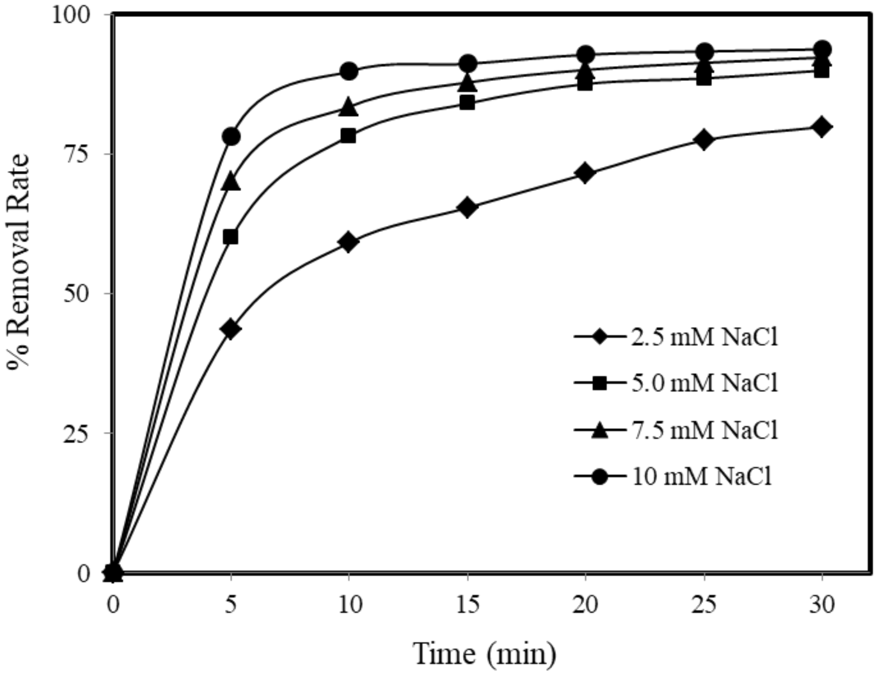

Figure 4. Effect of supporting electrolyte concentration on dye removal efficiency (C_0: 50 mg/L, J: 0.50 mA/cm^2, pH≈5.0, T: 25°C, SS: 400 rpm)

3.3. Effect of Initial Dye Concentration

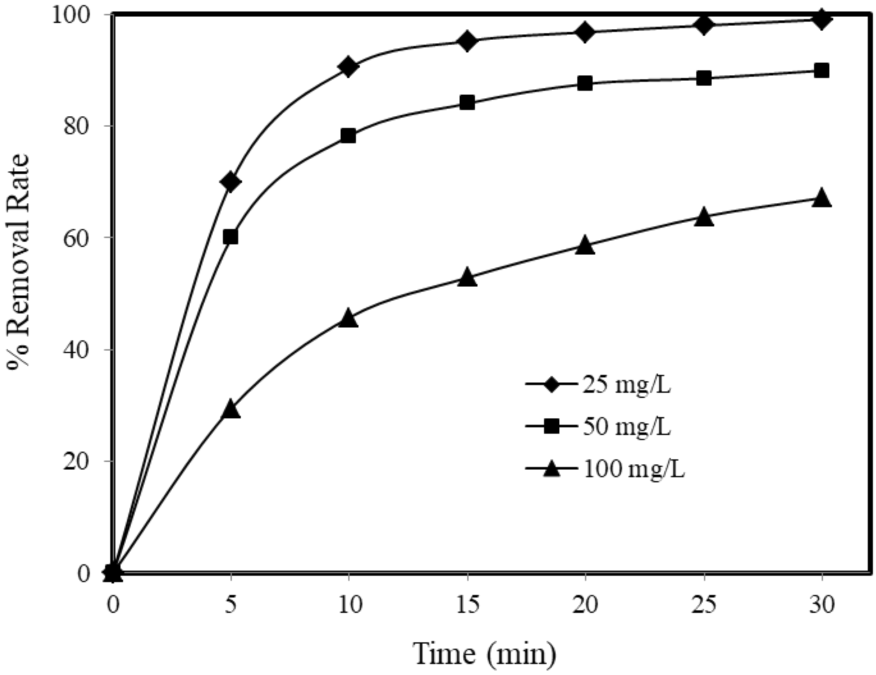

Figure 5. The effect of initial dye concentration on dye removal efficiency (J: 1.0 mA/cm^2, pH≈5.0, SEC: 5 mM NaCl, T: 25°C, SS: 400 rpm)

The effect of the initial dyes concentration on the electro-oxidation of the RB5 dye using a Ti/IrO_2/RuO_2 anode was investigated for concentration of 25, 50 and 100 mg/L at a current density of 0.50 mA/cm^2, at supporting electrolyte concentration of 5 mM NaCl, at natural pH value (≈5.0), temperature of 25°C, at stirring speed of 400 rpm for 30 minutes and the results which were obtained were shown in Figure 5. An increase in dye removal was found with an increase of initial dye concentration. Lower dye concentrations might cause total dye removal and therefore, slightly higher range of dye solution was selected in order to carry out these experiments. The removal efficiencies obtained for the initial dye concentrations of 25, 50 and 100 mg/L were 99.08%, 89.96% and 67.16%, respectively. The removal efficiency decreased as the initial dye concentration increased. But the amount of paint removed is significantly increased [17].

3.4. Effect of Initial pH

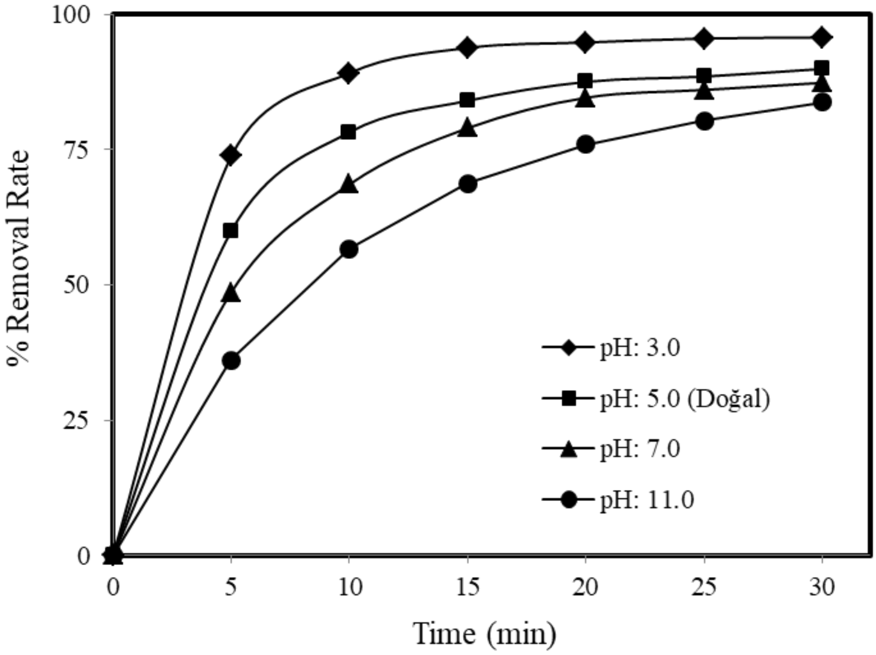

Figure 6. Effect of initial solution pH on dye removal efficiency (C_0: 50 mg/L, J: 0.50 mA/cm^2, pH≈5.0, SEC: 5mM NaCl, T: 25°C, SS: 400 rpm)

Solution pH is one of the important factors that affect the performance of electrochemical process. Therefore, studies were performed in four different initial pH values to investigate their effects. The experiments which were tested the effect of initial wastewater pH on the electro-oxidation of RB5 were carried out at 5 mM NaCl, 25 °C, a stirring rate of 400 rpm, an initial dye concentration of 50 mg/L, constant current density of 0.50 mA/cm^2, at the varying values of pH such as 3.0, 5.0, 7.0 and 11.0 for 30 minutes reaction time. The effect of initial wastewater pH on dye removal was given in Figure 6. Fig. 6 indicated that the highest electrochemical removal was obtained in the acidic range of pH.

Under acidic conditions, it is assumed that hypochlorous acid solution is dominate in the wastewater. For this reason, the color removal at low pH values is due to the high oxidation potential of hypochlorous acid. The reaction rate decreases at neutral pH. At neutral pH values, free chlorine can be converted to chlorine and perchlorate by cathodic reactions. This will lead to a decrease in the amounts of hypochlorous acid and hypochlorite, which are high in oxidant potential in water [18, 19]. A decrease in dye removal efficiency is observed at basic pH values.This decreasing value can be due to the presence of less potent hypochlorite ions which are the main oxidizing species in the bulk.

3.5. Effect of Current Density

Fig. 7 shows the decrease with time of the RB5 concentration from synthetic wastewaters containing 50 mg/L by applying different values of current density, 0.5, 0.75 and 1 mA/cm^2.

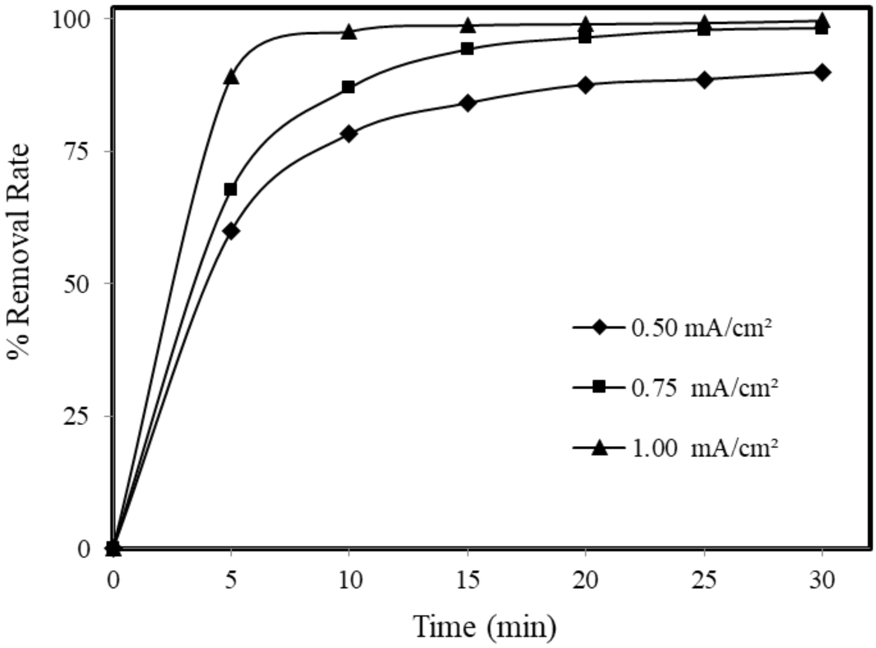

Figure 7. Effect of current density on dye removal efficiency (C_0: 50 mg/L, pH≈5.0, SEC: 5mM NaCl, T: 25°C, SS: 400 rpm).

Other experimental conditions were kept constant at natural wastewater pH value (≈5.0), 5 mM NaCl concentration and 50 mg/L initial dye concentration, 25°C temperature, and 400 rpm stirring speed for 30 min reaction time. Current density is an important variable in electrochemical process. It is significant that, as current intensity increases, the dye degradation efficiency increases. Color removal percent were 89.96%, 98.17%, and 99.67% at current densities 0.50, 0.75 and 1.00 mA/cm^2, respectively after 30 min of electrolysis. This behavior is expected [20] because of the increased rate of generation of oxidants, such as chlorine/hypochlorite and hydroxyl radicals at higher current densities [21-24].

4. CONCLUSION

In this study, the treatment of Reactive Black 5 (RB5) dye from synthetic wastewater by electro-oxidation method using $Ti/IrO_2/RuO_2$ anode was investigated and the following results were obtained:

1. In studies in which the effect of supporting electrolyte type was examined, it was concluded that the same concentration of support electrolyte addition under constant conditions increased the removal efficiency and that the most effective support electrolyte was NaCl at 89.96%
2. It was determined that in the studies in which the supporting electrolyte concentration was examined, the increasing concentration of the supporting electrolyte added increased the purification efficiency. It has been determined that the addition of more than 5 mM of the supporting electrolyte does not significantly affect the treatment efficiency. Therefore, the optimum supporting electrolyte was chosen as the dose of 5 mM.
3. It has been found that the removal efficiency decreases as percent with increasing dye concentration on the studies investigating the effect of initial concentration on the treatment of RB5. However, the amount of RB5, which is treated from waste water, has increased.
4. It was determined that the highest removal efficiency was reached in acidic conditions when the wastewater initial pH value was examined. Removal efficiencies were 95.77%, 89.96%, 87.39% and 83.75% for pH 3, 5, 7 and 11, respectively
5. It was noted that increasing current density increased the efficiency of dye treatment in studies investigating the effect of current density.

From these results, it can be concluded that electro-oxidation is an effective process in the treatment of wastewater containing dye and that $Ti/IrO_2/RuO_2$, an economical anode material, can be used effectively.

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