Understanding the Effect of Electro-Oxidation Process Variables on Reactive Navy Blue Rx Dye Decolorization

Abhipsa R Makawana, Vishva Odedra

Abstract: The study investigated the study of electro-oxidation treatment on Reactive Navy Blue RX dye simulated wastewater using graphite and stainless steel electrode material as anode-cathode assembly. The effect of initial pH, electrolyte dose, applied current, dye concentration, and time, has been investigated. Preliminary test to understand influence of initial pH and NaCl dose on EO process has also been investigated and further work was carried at optimized initial pH 5 and NaCl dose 500 mg/L. From the experiments it was observed that with increase in current density the color removal also increases while with increase in initial dye concentration, removal efficiencies decreases.

Keywords: Electro-oxidation, Navy Blue RX Dye, Graphite.

I. INTRODUCTION

Industries contributed to high financial boom of the arena in last certain decades but at the same time they have been creating intense environmental pollutions. Maximum of the industries along with fabric production, plastic, sugar, cement, paper, petroleum and food manufacturer are mounted as major industries for the development of society.

Color in wastewater happens because of the presence of synthetic dyes of untreated dye effluents. Synthetic dyes have complex aromatic molecular structures and they are classified as refractory molecules which are resistant molecules to the degradation, cleavage of azo linkages of their structures can produce toxic aromatic amines. Hence efficient treatment for the dye effluent is necessary before discharging it to the water bodies for maintaining the environmental quality and also for the account of human health [1]. Some dyes are having carcinogenic properties and also some are toxic in nature which are harmful to the humans and aquatic life. Synthetic dyes reduces the penetration of light through water and hence the photosynthetic activities of the aquatic plants are decreased which will have harmful impact on their growth [2]. According to Daneshvar [2] dyes can also cause severe health hazards to human beings especially to the reproductive system, liver, brain, and central nervous system. Hence decolorization of dye effluent has become necessary aspect of textile wastewater. If not taken the steps, the concentration of pollutants will be increased to such a high level that it would rather be obstacle for the re-establishment of microbes which will result in degradation of water quality permanently.

For the removal of organic pollutants Electrochemical Oxidation or electro-oxidation (EO) is proving itself an efficient procedure. At present this treatment is being used for the decolorization and demineralization of dye from the wastewater. The oxidation of pollutant, in the process occurs in the electrolytic cell [3] through direct anodic oxidation and chemical reactions [4,5].

Fig. 1. Structure of Reactive Navy Blue RX

For the understanding of the EO process the dye used in the present study is Reactive Navy Blue RX with chemical structure C₆₀H₃₀Cl₂N₁₄O₂₉S₈ is used (Fig.1)

The oxidation of organics occurs in presence of chloroline by following bulk reaction [6,7].

Bulk Reactions:

1. 2Cl → Cl₂ + 2e⁻ (1)
2. H₂O + Cl₂ → HOCl + H⁺ + Cl⁻ (2)
3. HOCl → OCl⁻ + H⁺ (3)

II. MATERIALS AND METHODS

A. Electro-oxidation Experiments

For the electrochemical study a batch reactor of 1000 mL volume was used for all experiments. DC Power Supply (TSTRONIX 92B, 0-32V, 0-2A) was used to apply constant voltage, which was having maximum output of 5A current and 30V voltage. Magnetic stirring was adopted for proper mixing of the reactor content during the experimental run. Graphite carbon was kept as anode and stainless steel as cathode during this study. Graphite was selected as the anode because it is having high efficiency and is relatively cheaper compared to other oxidizing substances.

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Dimensions of insoluble graphite and stainless steel electrodes used in this study were 85x70x10 mm and 85x70x5 mm respectively, with contact surface area of 52.5 cm² (7.5 cm submergence). (Fig. 2)

![Fig. 2. Schematic representation of the set-up](image)

**B. Experimental Procedure**

Electrooxidation was employed for decolorization of simulated dye wastewater sample of Navy Blue RX. All the run were conducted at ambient temperature (25-27°C). Each run used 800 mL sample in the reactor. Experimental runs with one-factor-at-a-time (OFAT) approach were conducted to understand the effect of various EO process parameters on color removal. The parameters included: (i) current density (in the range 5-15 mA/cm²) at pH 7.51, (ii) electrolysis time (0-90 min), (iii) initial pH (in the range 1-11), (iv) presence of electrolyte NaCl & Na₂SO₄ (0-1250 mg/L) and (v) dye concentration (100-200 mg/L). After particular electrolysis time the solution of about 10 mL was derived from the effluent outlet for further analysis. No centrifuging or filtration of sample was carried out before analysis. Before every experimental run, electrodes were cleaned by washing many times with (DW) distilled water to remove any pollution/sediments, dried and weighted. The treated dye wastewater samples were collected and observed under spectrophotometer.

### III. RESULTS AND DISCUSSION

As stated in materials and method the present study evaluated the influence of EO process parameters like dye concentration, current density, electrolyte dose, pH and operating time on color removal efficiency and effluent dye concentrations. The tests were conducted with three different initial dye concentrations and with three different current densities and then sample was collected and analyzed under spectrophotometer.

#### A. Effect of Initial pH

Effect of initial pH was investigated at various initial pH (1, 3, 5, 7, 9 and 11) at operating time of 60 min considering color removal (%) and final dye concentration as analyzing parameters (Fig. 3). At initial pH of 1, maximum color removal of 88% had been observed. Increase in pH showed reduction in color removal, similar trend has also been reported by Radha, et al., 2009 [9]. The two main forms of dye are quinone and azo structures, and the quinone exist at acidic pH. It is the fact that as the pH value decreases the removal efficiency increases and it is because quinone structure of the dye gets more easily electrochemically oxidized [7]. Also acidic pH increases the hydroxyl radical generation, which accelerates the oxidation rate [10].

![Fig. 3. Effect of electrolyte dose on (a) color removal (b) Effluent dye concentration at 5mA/cm² current](image)

Acidic pH showed better removal than neutral and alkaline but considering the initial pH of studied dye solution during dying process, 5 initial pH has been considered as the optimum one under OFAT study, and hence all further experimental runs were carried at 5 initial pH of synthetic dye solution.

#### B. Effect of Electrolyte Dose

The experiments was carried out with varying NaCl and Na₂SO₄ dose such as 0, 250, 500, 750, 1000 and 1250 mg/L and % color removal were found to be 61.96%, 76.36%, 80.72%, 79.52%, 75.56% and 81% for NaCl dose and 59.84%, 46%, 45.28%, 43.72%, 38.16% and 37.76% for Na₂SO₄ as shown in Fig. 4 below. It was observed that increase in Na₂SO₄ concentration, there was no increase in % color removal while with increase in the concentration of the NaCl there was increase in the % color removal [7,11]. Hence NaCl was selected as the preferable electrolyte. For NaCl experiments showed increase in the % removal of color till 500mg/L concentration of electrolyte dose and then decrease in the % removal was observed but at 1250 mg/L concentration maximum removal was obtained but considering the economical point of view 500mg/L NaCl dose was considered as the optimum concentration. The reason for the better removal by NaCl dose was it prefers more indirect oxidation by ClO₂ and HOCl and hence better removal is obtained [12].
Effect of Current Density and Time

Displayed three different current densities i.e., 5, 10, and 15 mA/cm$^2$ were experimented on three different initial dye concentration i.e., 100, 150, and 200 mg/L. It was observed that an increase in applied current density or time increased decolorization rate and reduction effluent dye concentration (Fig. 5). This could be explained by the verity that with an increase in the current density more the reaction rates at anode and cathode will occur which enhances the % color removal [9]. Every current density has specific time to achieve target decolorization hence optimization of the current density and time is must otherwise unnecessary wastage of electricity or electrode material may take place, which eventually leads to an increase in overall process cost. As from the fig. 5 below it can be observed that there is not much difference in the % color removal by 10 mA/cm$^2$ and 15 mA/cm$^2$. Hence more energy consumption will be resulted if 15 mA/cm$^2$ CD is used compared to 10 mA/cm$^2$.
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Fig. 5. Effect of time and current density on color removal (%) (a) 100mg/L (c) 150 mg/L (e) 200 mg/L and on effluent dye concentration (b) 100mg/L (d) 150 mg/L (f) 200 mg/L (pH:5, NaCl dose:500mg/L)

D. Effect of Initial Dye Concentration

All the experimental run were performed at different initial dye concentration from 100, 150 and 200mg/L with constant current density (5, 10 and 15mA/cm²), pH (optimum pH = 5) and electrolyte (NaCl dose = 500mg/L) (Fig. 6). It was observed
IV CONCLUSION

From the all the experimental work we can conclude that better removal was observed in acidic condition. As the Navy blue RX dyeing process is done at 5 pH in dyeing industries, the optimum pH taken was 5. Two electrolytes were studied and it was concluded that NaCl as a better electrolyte dose due to indirect oxidation because of OCl and HOCl species hence gives more percentage color removal. The lower potential of Na₂SO₄ hinders the oxidation of organics in wastewater as the presence of sulfate ions in the wastewater makes it more difficult, thus affects oxidation by the indirect oxidation process. After 60 min electrolysis time around 70, 96 and 100 % color removal has been observed at 100 mg/L dye concentration at 5, 10 and 15 mA/cm² CD respectively. It was around 46, 64 and 81 % for 150 mg/L dye concentration while 44, 67 and 78% for 200 mg/L dye concentration at 5, 10 and 15 mA/cm² CD respectively. Hence, all the 5 variables :ph, electrolyte type/dose, current density, time and dye concentration were concluded to be very significant and can be considered certainly during optimization study of the EO process.

Fig. 6 Effect initial dye concentration on % color removal (a) 5 mA/cm² (c) 10 mA/cm² (e) 15 mA/cm² and on effluent dye concentration (b) 5 mA/cm² (d) 10 mA/cm² (f) 15 mA/cm² (pH:5, NaCl dose:500mg/L)
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