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DECOLORIZATION OF REACTIVE BLUE 19 FROM AQUEOUS SOLUTION BY ELECTROCHEMICAL OXIDATION USING GRAPHITE ELECTRODES

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Abstract

The electrochemical oxidation technique was studied to decolourize the dye Reactive Blue 19. Synthetic effluent was prepared to decolorize the color by electro oxidation using graphite electrode as both anode and cathode. Effect of dye concentration (100 - 400 ppm), effect of electrolyte concentration NaCl (0.025 - 0.1M), effect of pH (3, 5, 7, 9), effect of stirring speed (150-300 rpm) and effect current density (5-25V) on decolorization. It was observed that maximum decolourization was observed under optimistic conditions such as, NaCl concentration of 0.075M, initial pH 7.0, applied current density of 20Ma/cm², stirrer speed of 200rpm and electrolysis time of 60 min. The UV-Visible spectrum confirms the removal of color from aqueous solution.

Keywords; Reactive Blue 19; Electrochemical oxidation; Decolourization; Graphite electrode.

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INTRODUCTION

Large amount of water can be required for processing in textile industry thereby discharging huge amount of water [1]. Conventional treatment methods like coagulation / flocculation and biological treatments are not much efficient to decolourize the textile dye [2-7]. The major environmental concerned caused due to dye waste water because of its variable nature, huge quantity, low biodegradability, chemical composition and its toxicity to aquatic life [8]. Wastewater has undergone finishing, and dyeing in textile industries are major source of environmental pollution because of their high concentration of organic compounds will adversely affect the aqueous ecosystem [9]. In the textile industry, 60% of the dyes are azo dyes; the azo group of the dye is connected to an aromatic compound forcing a chromophoric group responsible to impart a characteristic color of the dye. Reactive dyes are widely used because of their high impart color and easy application in the dyeing process [10]. Electrochemical treatment is one of the methods carried out in the removal of organic and inorganic impurities from both water and wastewater [11,12]. In

oxidation process, strong oxidants such as ozone, chlorine, hypo chloride and hydroxyl free radicals are generated electrochemically to destroy the pollutants[13-15].The important advantages of electrochemical oxidation prevents the production of unwanted products, chemicals are not required and much cost effective.[16,17]. The frame was assigned to detect the decolourization efficiencies in aqueous Reactive Blue 19 using graphite electrode under various operating parameters in an electrochemical reactor.

MATERIAL AND METHODS:-

2.1. Materials

The dye Reactive Blue 19 was obtained from Merck (Mumbai, India). The working solution of required concentration was prepared by diluting the stock solution and adding appropriate concentration of supporting electrolyte. The pH of the synthetic effluent was adjusted to desired level using dilute NaOH and H₂SO₄ solutions. The other chemicals used were of analytical grade and purchased from M/S Merck Mumbai, India. Double distilled water was used in all experiments. Graphite electrode, supplied by M/S, Carbone Lorraine (Chennai, India) was used as both anode and cathode. The electrical resistivity of graphite sheets was 0.001Ω cm. The graphite sheet assays 99.8% C, < 150 mg/L of Fe and <30 mg/L of Cl. An active total anodic surface area of graphite sheets was 102 cm².The entire experiments was carried out in Double-distilled water [18].

2.2. Procedures and experiments

The experiments were carried out in an undivided cell of 650ml capacity.The thickness of the graphite electrodes were 0.2 cm used as a electrode. Internally looped structure of four graphite electrodes (two each of anode and cathode) were fixed. The gaps between the plates were maintained at 6mm to minimize the ohmic losses. Infact, O₂ overpotential is high on anode graphite while Cl₂ overpotential is low, this would increase current efficiency of Cl₂ evolution [19]. Electric power was supplied by a regulated Dc power supply, obtained from M/S Mighty Electronics Equipment Corporation Pvt Ltd, Coimbatore, India.The entire electrode assembly was placed on non-conductive wedges fixed to the bottom of the electrochemical cell [20].

2.3. Methods

For each and every experiment, 500 ml of the Reactive Blue 19 dye solution was taken into the electrochemical cell and the electrodes were connected to the respective anode and cathode leads the DC power supply and energized for a required duration at a fixed current. All the experiments were conducted at room temperature. During the experiment, the electrochemical cell containing a solution was placed on a magnetic stirrer for continuous mixing at 250 rpm in order to ensure the mass transfer efficiency. At different time intervals during the reaction, samples were collected and tested for percentage removal of color.

2.4 Analytical procedure

The UV-Vis spectra of Reactive Blue and its removal during electro oxidation were recorded using UV-Vis spectrophotometer (UV-1700 Pharma Spec, Shimadzu, Japan). The characteristics peak of dye was observed at 592nm.

Calculations

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

Where;

C_0 : Initial concentration of dye before electro coagulation (mg/L);

C_e : Present concentration of dye after electro coagulation (mg/L)

Energy consumption per ml of wastewater treated has calculated as follows.

$$E = \frac{U \times I \times t \times 1000}{V}$$

Where:

E: Energy Consumption (kWh/ml)

U: Cell voltage (v)

I: Current (A)

t: Time (h)

V: Volume of wastewater (ml)

3. Results and discussion

3.1. Effect of supporting electrolyte concentration

The electrical conductivity is major factor to conduct the current in the solution. Electron transport will be factor because of higher ionic strength and also leads to better degradation rate [21]. Different electrolyte concentrations were applied for various ionic strengths were obtained by preparing various concentrations of NaCl solution in this technique. Fig (1) represents the effect of various NaCl concentrations under fixed current density, pH and dye concentration. It is clear to investigate that increasing, the percentage removal due to increasing chloride concentration. When more current is consumed in Cl_2 and hypochlorite generation at the expense of O_2 evolution. The reason is that increasing NaCl concentration decreases the discharge potential of Cl_2 based on the Nernst equation [22].

The generation of active chlorine, has been found to increase the concentration of NaCl [23]. In one of our earlier studies, similar results have been reported in the electrochemical oxidation of bisphenol A from aqueous solution using graphite electrodes [24]. An optimum concentration of 0.075M was optimized in other experiments to minimize the negative influences of Chloride shown in Figure (2).

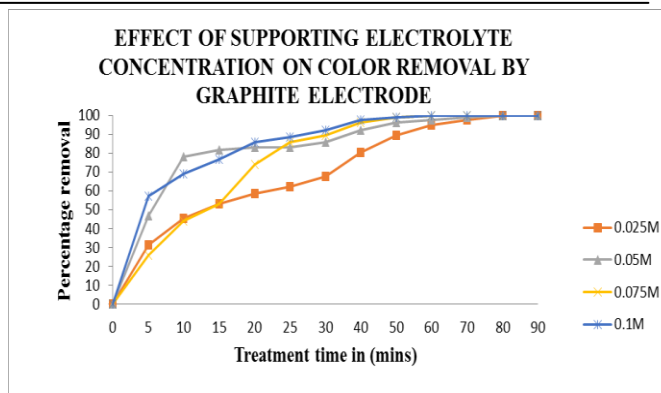


FIG 1. Effect of supporting electrolyte concentration on color removal (a) Supporting electrolyte concentration- 0.025M, 0.05M, 0.075M, 1.0M, (b) pH – Natural 8.3, (c) Reactive Blue concentration- 100 ppm, (d) Stirring speed- 250rpm, (e) Current density- 3.7mA/cm².

3.2. Effect of Initial pH

Natural pH places an important factor that influences the decolorization reaction. In order to evaluate the pH influence, the experiments were carried out at four different initial pH values (3, 5, 7 and 9) pH of the solution was adjusted using sulphuric acid (0.1N H_2SO_4) or sodium hydroxide (0.1N NaOH). The treatment processes, were conducted such as electrolysis time of 90mins, stirred speed of 250rpm, 0.075M of NaCl and current density was maintained at 3.75 mA / cm². Figure (3) shows the influence of initial pH on the percentage color removal by electrochemical oxidation in 90 mins of reaction.

It is clear that varying initial pH strongly affected the electrochemical degradation efficiency on the decolorization when reached 97% at pH 7 in 60mins, while lower color removal was observed at higher pH. The decolorization is mainly due to the oxidation and hydrolysis of Chlorine produces hypochlorous acid (HOCl) or the hypochlorite ion (OCl^-) depending on the pH of the solution. At neutral pH, in order to increase the contact time to achieve higher percentage removal. In this process, a low pH will cause corrode on the electrode and inhibit the adverse activity of electrodes, so there will be a reduction in decolorization process [21]. Therefore, when the pH is maintained between 6-8 the color removal is high [25]. The initial pH 8.3 was preferred, for the electrochemical oxidation of aqueous Reactive Blue 19 solution for all experiments.

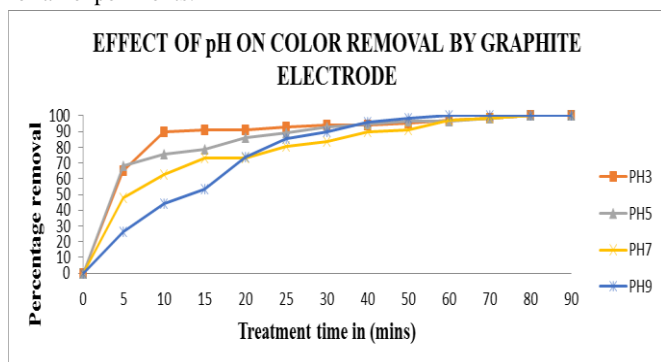


FIG 2. Effect of pH on color removal (a) pH -3, 5, 7, 9, (b) Reactive Blue concentration 100 ppm, (c) Stirring speed-250rpm, (d) Current density- 3.7mA/cm² (e) Supporting electrolyte concentration-0.075M.

3.3. Effect of Initial Reactive Blue dye concentration

The initial concentration of Reactive Blue 19 is one of the essential factors in degradation reaction in the experiments [26]. After 19

mins of electro oxidation process decolourization efficiency 100,100,99.17,98.26 % at the initial concentration of 100,200,300,400 mg/L at current density of 3.75 mA/cm² the Initial pH 8.3, and the supporting electrolyte concentration 0.075M of NaCl with the stirring speed of 250rpm. The results are shown in Figure (3). It can be reported that the percentage of color removal decreases when the Initial concentration is high, this may be explained by the fact the generated oxidizing species are identical in all the operational parameters. So, they have to react with Reactive Blue 19 molecules and their percentage of degradation intermediates [27].

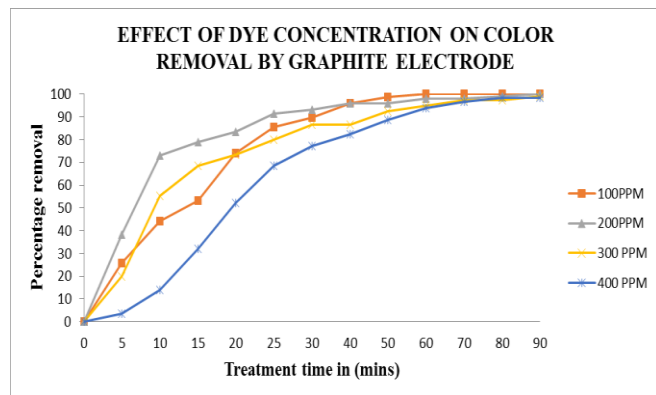


FIG 3. Effect of dye concentration on color removal, (a) Reactive Blue concentration- 50ppm,100ppm,150ppm,200ppm,300ppm,400ppm, (b) Current density- 3.7mA/cm² (c) Stirring speed- 250rpm, (d) pH - Natural 8.5, (e) Supporting electrolyte concentration-0.075M.

3.4. Effect of Applied current density

Another experimental study carried out to determine the effects of potential difference on color removal. The current density places a major role in the activation of electro oxidation processes. In this study 5,10,15,20,25 V potentials were applied corresponding to 0.9,1.87,2.81,3.75 and 4.68 mA/cm² at the initial pH of 8.3 and supporting electrolyte concentration of 0.075M and the Initial dye concentration was 100mg/L, at the stirring speed of 250rpm. Treatment efficiency was increased with increasing current density. This is attributed to the increase of Cl₂, HOCl and OCl⁻ Concentration in the solution, which eventually increases the degradation [28]. The results are shown in the Figure (4). Where the removal efficiency increased from 92.21 to 100% for the energy consumption of 5 to 25V. The highest removal efficiency was reached at 3.75 mA/cm². Therefore, it is considered as an optimal current density for this study.

3.5. UV -Visible absorbance changes in the degradation of Reactive Blue-19

The UV- visible absorbance of the initial and final electrolysis is presented in Figure (5). The UV region at 594nm was due to Reactive Blue-19. It represented that the peak disappears gradually during the electro oxidation process with increasing treatment time and high removal was achieved at 90mins of electrolysis at 3.7mA/cm² of applied current density. Figure (5) shows that a maximum absorbance peak at a 594nm. It can be concluded that when the electrochemical treatment was applied, it confirms the removal of Reactive Blue-19 completely from aqueous solution.

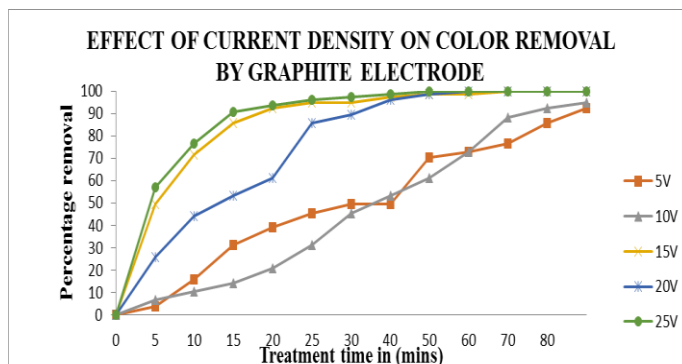


FIG 4. Effect of Applied current density on color removal- (a) Different current density- 0.9 mA/cm², 1.87 mA/cm², 2.81 mA/cm², 3.75 mA/cm², 4.68 mA/cm², (b) pH - Natural 8.5, (c) Reactive Blue concentration- 100ppm, (d) Stirring speed- 250rpm, (e) Current density- 3.7mA/cm².

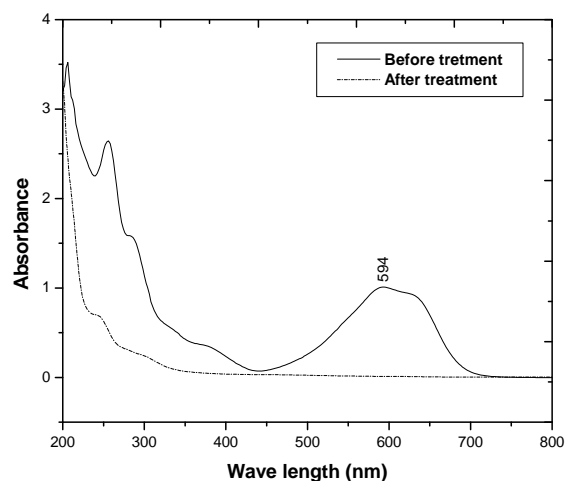


FIG 5. UV-visible spectrum of reactive blue before and AFTER electro oxidation process using graphite electrode (a) Reactive Blue concentration- 100 mg/L (b) Current density- 3.7mA/cm², (c) Stirring speed- 250 rpm, (d) pH - Natural 8.3, (e) Supporting electrolyte concentration-0.075M.

4. Conclusion

The results show that the electro oxidation process using graphite electrode is very effective treatment for Reactive Blue 19 and it is also cost effective. The color degradation of concentrated Reactive Blue 19 is completely removed through the electro oxidation process among different parameters. The maximum color removal was achieved in the presence of 0.075M NaCl to increase the efficiency of electro oxidation process. It can be concluded that maximum 98.70% color removal was reached under the optimized conditions of initial pH 8.3, current density of 3.75 mA /cm² and treatment time of 50 mins. Energy consumption was decreased when increasing the supporting electrolyte concentration from 0.025M to 0.1M NaCl, while it increases with increasing current density from 0.9 mA /cm² to 4.68 mA /cm². The results revealed that the complete color removal was achieved in 90mins under optimistic parameters. The UV- vis spectrum confirms the removal of Reactive Blue 19 from aqueous solution. The literature reveals that, all the essential operating parameters influencing the Electro oxidation process includes pH, current density, and type of electrode etc.

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