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Electro-chemical oxidation of Acid Blue 9 using DSA anode and rotating cathode in electro-chemical reactor

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Abstract: This study deals with the treatment of textile wastewaters containing acid blue 9 dye by electrochemical oxidation using Ti/RuO₂-IrO₂ anode and rotating stainless steel cathode in the presence of NaCl electrolyte in a batch reactor .The main objective of the present work is to reduce the COD and color of the dye effluent containing acid blue9 dye. The influence of various experimental parameters such as initial pH, initial dye concentration, cathode rotation speed, current density, electrolyte concentration, reaction temperature were calculated and presented. From the results, electrochemical oxidation process maximum COD removal of about 94% and complete color removal was achieved at an optimum current density of about 10 mA/cm². After post treatment, the treated effluent can be reused. **Keywords:** Electrochemical oxidation, Rotating cathode, AcidBlue9, Wastewater treatment.

1. Introduction

The major cause of industrial pollution is increasing industrialization and urbanization. One of the largest industrial producers of wastewater is the textile industries [1]. Approximately, for 1kg of textile product about 125-150 liters of water is used. Commercially over 10,000 dyes were available worldwide with total annual production of $7x10^5$ metric tons. Out of this without treatment 5-10% lost as effluent to the aquatic environment. The wastewater from textile industries contains residues from preparation, dyeing, finishing, slashing and other operations, which is chemically intensive one. When discharged recklessly into environment without treatment they will be seriously harmful to human being because of their high toxicity with high concentration accumulation [2-4].

In effluents from textile manufacturing process, average concentration of dye was 300 mg/l, where color is noticeable at a concentration higher than 1 mg/l [5]. The textile azo dyes with synthetic intermediates as contaminant and its degradation products, have attracted the attention with regard to the environmental impact, because of their widespread use and their potential to form toxic aromatic products with carcinogenicity and mutagenicity properties during primary and secondary treatment [6,7] Hence, removal of these dyes from the effluents is necessary.

Physio-chemical methods, biological methods and electrochemical methods are the various methods exist for the treatment of effluents. The conventional methods are inefficient as they result in large volume of sludge or in the release of toxic substance, which require further treatment [8]. A number of biological process, such as sequenced anaerobic/aerobic digestion, have been proposed in the treatment of textile wastewater [9,10].but they are limited because many of the dyes are xenobiotic and non-biodegradable. Due to the variation of wastewater characteristics, such as temperature, pH and heavy COD load the combined physical, biological and chemical method treatment systems become inefficient [11-16].On the other hand, electrochemical oxidation is becoming an alternative wastewater treatment method for toxic wastewaters, which are not easily biodegradable and requiring costly physical or physicochemical pretreatments [17]. The electrochemical process effectiveness depends upon the nature of the anode selected, stable anodes that are prepared by the deposition of a thin layer of metal oxides on a base metal. Many researchers have investigated electrochemical

oxidation for azo dye degradation through operating parameters optimization using various anodes including RuO₂ [18], SnO₂ [19], PbO₂ [20] and diamond electrode [21]. Usually Ti coated with SnO₂-Sb, are found to enhance a greater amount of degradation [22].

Shen et al. investigated the effect of operational parameters of electrolyte concentration, temperature, stirring and voltage in the degradation effect of electrochemical treatment of dye wastewater using nanophase TiO_2 catalyst and Co Bi PbO₂/Ti anodes with Na₂SO₄ electrolyte at 8V applied potential and 25°C temperature. except testing their influence [23]. Carneiro et al. stated that the electrochemical oxidation of Reactive Blue 4 using glassy carbon electrode, reticulated vitreous carbon electrode, dimensionally stable anodes of Ti/SnO₂/SbO_x/RuO₂ [24]. Ihos et al concluded that the electrochemical treatment of textile wastewater containing azo dyes on dimensionally stable anodes of two compositions Ti/Ruo_3Ti_0 , 70_2 and Ti/Ir_0 , Ti_0 , 70_2 with a current density of 25-75 A/m² and electrolysis time ranging from 05 to 60 minutes [25]. Daneshvar et al. used electro coagulation for the removal of color from C.I. BasicRed46 (BR46) and C.I. BasicBlue3 (BB3) containing solutions with NaCl electrolyte [26]. Awad and Galwa studied the electrocatalytic degradation of AcidBlue and BasicBrown dyes from simulated wastewater on lead dioxide anode in presence of H₂SO4, NaOH and NaCl electrolytes within a current density range of 0–45 mA/cm² [27]. Sakalis et al. studied the electrolytic degradation of ReactiveOrange91, ReactiveRed184, ReactiveBlue182 and ReactiveBlack5 azodyes using both synthetic and real wastewater samples using carbon fleece as cathode and the anode was made of titanium substrate coated with platinum film with NaCl or Na₂SO₄ electrolytes [28]. Fernandes et al studied the electrochemical oxidation of C.I. AcidOrange7 on boron doped diamond anode and copper foil cathode using KCl and Na₂SO₄ electrolytes at 25°C, with a current density of 1.25–10 mA/cm² [29]. Cer'on-Rivera et al. studied the electrochemical treatment of BasicYellow28 (SLY) and ReactiveBlack5 (CBWB) methine and sulfoazo textile dyes using diamond- aluminium- copper- and iron-zinc alloy electrodes [30].

AcidBlue9 was selected for this work because it is used in the dyeing of various materials and can be found in the wastewater of the textile, tanning and food industry. The dye AcidBlue9 has a molecular weight of 792.84 and chemical formula $C_{37}H_{34}N_2O_9S_{32}Na_{32}$, and is identified with the number 42000 in the color index catalog. It was used in the degradation tests without any treatment, and its structure and information is shown in Figure 1 and Table1.respectively.

In this work, the electrochemical treatment of AcidBlue 9 was carried using Ti/RuO_2 -IrO₂ anode and rotating stainless steel cathode in the presence of NaCl electrolyte in a batch reactor. The effect of initial pH, initial dye concentration, cathode rotation speed, current density, electrolyte concentration, reaction temperature, in the efficiency of the process was studied and the optimum condition for maximum reduction of COD was established.



 Table 1: Information of the dye used

Name of dye	AcidBlue9
Color index number	42000
Empirical formula	C37H34N2Na2O9S3
Molecular weight	792.84
Dye content	90%
λ_{max}	625 nm

Figure 1: Structure of AcidBlue9

2. Materials and Methods

The chemicals used for the experiments and the analysis techniques were AR grade unless otherwise mentioned.

S. no.	Parameters	Values
1	COD	1350 mg/l
2	Conductivity	16.42 m mho/cm
3	pН	12–13
4	Color	Blue

Table2: Chemical characteristics of synthetic textile dye effluent containing AcidBlue9 dye.

2.1. Preparation of dye effluent

Synthetic dye effluent was prepared by dissolving 1 g/L of AcidBlue 9, with 5 g/l of sodium chloride that acts as an exhausting agent and 3 g/l of sodium carbonate as a fixing agent. The prepared effluent is blue in color. The synthetic effluent characteristics give the nature of effluent, which is of very harmful to human kinds and aquatic organisms when fed into the aquatic environment. Chemical characteristics of synthetic effluent were shown in Table 2.

2.2 Experimental setup

The electrochemical reactor used in the present study was made of Pyrex glass of 1000ml capacity with a provision to fit a cathode and an anode (surface area of the electrode 38.46 cm^2). The Disc shaped Titanium based mixed oxide anode Ti/RuO₂-IrO₂ and rotating stainless steel (305 grade) as cathode were arranged horizontally and parallel to each other with 1cm inter-electrode gap. The current was supplied by multi-output 2A and 30 V, DC power source with ammeter and voltmeter.

2.3. Experimental procedure

Batch experiments were adopted in the present study in order to facilitate identification of the optimum operating conditions of the treatment process. At the beginning of each test run, 500ml of synthetic dye effluent was loaded in the electrochemical reactor; specific current at pre-determined interval of time was applied using a regulated power supply. Experimental factors namely current densities, speed of cathode, temperature were varied with development of experiment. At the pre-determined time interval, 5ml of sample was collected and reduction of COD and color removal were determined to know the extent of degradation of effluent.

2.4Analysis

2.4.1. Color Removal

Dye concentration was analyzed spectrophotometrically by measuring the absorbance of remaining dye at maximum wavelength 625 nm on UV-Vis Spectrophotometer (Elico, SL 164, Hyderabad, India).

2.4.2. COD

COD was measured by the standard method (closed reflux) [31]. COD or color removal efficiency (η) was calculated by the following formula:

$$\eta = \frac{C_0 - C_t}{C_0} X100 \tag{1}$$

Where c_o is the COD or absorbance of initial dye concentration, and c_t is the COD or the remaining dye concentration at given time t.

3. Results and discussions

3.1 Effect of current density

The current density was varied, 2.5 mA/cm², 5 mA/cm², 7.5 mA/cm², 10 mA/cm², and 12.5 mA/cm² to enumerate the effect of current density on effective removal of COD and color. The efficiencies of COD and color removal at different current densities were shown in Fig. 2 and Fig.3 respectively. The COD reduction was about 80% in case of current density 5 mA/cm² compared to 2.5 mA/cm² in which only 30% of COD reduction was attained. Thus, by the doubling of current density the COD reduction percentage was high this was due to release of metal ions increases with current density, which increases the COD reduction. At higher current densities 7.5mA/cm² and 10mA/cm² the reduction of COD was 91.56% and 94 %. Further increase in the current density to12.5mA/Cm² result in COD removal of 95.5%, which is low insignificant compared to 10mA/cm², as increase in current density decrease the current efficiency. The optimum reduction of COD was about 94% at the current density of 10 mA/cm² [32, 33, 34]. The complete color removal was achieved at 30,

20,12,8 and 6 minutes for current density of 2.5mA/cm², 5mA/cm², 7.5mA/cm²,10mA/cm², and 12.5 mA/cm² respectively..Color removal rate increases with the increase in current density. The rapid de-colorization indicates that initial azo group dyes are fully degraded, giving smaller and colorless organic or inorganic products, which can further be treated for complete mineralization. From the literature, chromophore groups of dyes are easily destroyed by direct and indirect oxidation. Later the subsequent intermediates and other organics undergo further anodic oxidation at a much lower rate [13]. In electrochemical degradation of textile dye solutions, the rate of color removal was higher than the COD removal due to the faster azo bond degradation [13, 28, 29, 30].

The rate of COD removal is lower than that of color removal, indicating the azo bond degradation is the first step of the electrochemical degradation mechanism with the comparison of COD removal and color removal. The optimum current density for complete color removal was 10mA/cm².



Fig. 2 Effect of current density on COD reduction [Initial pH=6: Cathode rotation speed=750RPM: Initial dye concentration=200mg/l: Electrolyte concentration=4g/l: Temperature=25⁰C]



Fig. 3 Effect of current density on Color removal [Initial pH=6: Cathode rotation speed=750RPM: Initial dye concentration=200mg/l: Electrolyte concentration=4g/l: Temperature=25^oC]

3.2 Effect of temperature

The effect of temperature was studied by varying the temperature 20°C, 25°C, 30°C, 35°C and 40°C. Fig [4] and Fig [5] shows the efficiency of percentage removal of COD and color with temperature, respectively. Increase in temperature increase the rate of color and COD significantly until 25°C further increase in temperature decrease the rate of removal this was due to chemical decomposition of sodium hypochlorite to sodium chlorate .Therefore, when temperature rises, production of NaClO falls and the degradation also decreases. The optimum condition for the process was 25°C where complete color removal was achieved at 12 minutes and COD removal percentage of 96.3% was obtained.



Fig. 4 Effect of Temperature on COD removal [Initial pH=6: Cathode rotation speed=750RPM: Initial dye concentration=200mg/l: Electrolyte concentration=4g/l: current density =10mA/cm²]

Fig. 5 Effect of Temperature on Color removal [Initial pH=6: Cathode rotation speed=750RPM: Initial dye concentration=200mg/l: Electrolyte concentration=4g/l: current density =10mA/cm²]

-20 60

-25 00

-30 of

35.00

40 of

40

3.3 Effect of cathode rotation speed

The effect of RPM (rotation per minute) of cathode was studied by varying the RPM, 250, 500, 750, 1000 and 1250. The effect of percentage removal of COD and color with RPM was shown in fig [6] and fig [7] respectively. The reduction rate increases with increasing cathode rotation speed this may be due to adequate high mass transfer. Increase in rpm decrease the time for color removal until 750 rpm where complete color removal was achieved at 12 minutes and COD removal percentage of 98.12% was obtained. Further increase in cathode rotation speed beyond optimum favors the cathodic reduction of generated hypochlorite thereby decrease the removal of color and COD.



Fig. 6 Effect of Cathode rotation speed on COD removal [Initial pH=6: Temperature =25^oC: Initial dye concentration=200mg/l: Electrolyte concentration=4g/l: current density =10mA/cm²]



Fig. 7 Effect of Cathode rotation speed on Color removal [Initial pH=6: Temperature =25^oC: Initial dye concentration=200mg/l: Electrolyte concentration=4g/l: current density =10mA/cm²]

3.4 Effect of initial concentration



Fig. 8 Effect of Initial dye concentration on COD removal [Initial pH=6: Temperature =25⁰C: Cathode rotation speed =750RPM: Electrolyte concentration=4g/l: current density =10mA/cm²]

The effect of initial concentration of dye was studied by varying the concentration 100, 200, 300, 400 and 500mg/l. The efficiency of percentage removal of COD and color with initial concentration was shown in fig [8] and fig [9] respectively .The percentage COD reduction and color removal rate was reduced with increase in the dye concentration. As the initial concentration increase, the degradation efficiency decrease. This shows that the generation of the powerful oxidizing agent Cl⁻ ions on electrode surface was not increased in constant current density. The optimum condition selected was 200mg/l .This value is included in the range of real dye concentration found in real textile effluents, where complete color removal was achieved at 8 minutes and COD removal percentage of 87.10% was obtained.



Fig 9 Effect of Initial dye concentration on Color removal [Initial pH=6: Temperature =25⁰C: Cathode rotation speed =750RPM: Electrolyte concentration=4g/l: current density =10mA/cm²]

3.5 Effect of pH

The effect of pH of dye was studied by varying the pH, 4, 5, 6, 8,10pH. The pH of the dye solutions was adjusted to desired values with 0.1mol/L HCl or 0.1 mol /L NaOH. The efficiency of percentage removal of COD and color with pH was shown in fig.10 and fig 11.Varying the initial pH between 2 and 10 does not have significant influence on the color removal. Many investigators explained the fact that the generation of chlorine/hypochlorite is not depending on the initial pH conditions. The generation of chlorine is more or less same under the fixed current density, irrespective of the initial pH values. At 6 pH complete color removal was achieved at 11 minutes and COD removal was 91 %.



Fig. 10 Effect of pH on COD removal [Initial Initial dye concentration =200mg/l: Temperature =25^oC: Cathode rotation speed =750RPM: Electrolyte concentration=4g/l: current density =10mA/cm²]



Fig. 11 Effect of pH on Color removal [Initial Initial dye concentration =200mg/l: Temperature =25^oC: Cathode rotation speed =750RPM: Electrolyte concentration=4g/l: current density =10mA/cm²]



3.6 Effect of Electrolyte concentration

Fig. 12 Effect of Electrolyte concentration on COD [Initial Initial dye concentration =200mg/l: Temperature =25^oC: Cathode rotation speed =750RPM: pH =6: current density =10mA/cm²]



Fig. 13 Effect of Electrolyte concentration on Color removal [Initial Initial dye concentration =200mg/l: Temperature =25⁰C: Cathode rotation speed =750RPM: pH =6: current density =10mA/cm²]

The effect of electrolyte concentration was studied by varying the concentration 1, 2, 3, 4 and 5g/l. The efficiency of percentage removal of COD and color with electrolyte concentration was shown in fig [12] and fig [13] respectively. An increase of the electrolyte concentration up to 4 g/l leads to increase in the color and COD removal. The NaCl solution liberates Cl_2 gas, which is consider as the active species for the degradation of organic compound. Further increase of the NaCl concentration has slightly effect on the color and COD removal. The optimum condition was 4g/l where complete color removal was achieved at 8 minutes and COD removal percentage of 95.7% was obtained.

4. Conclusion

Electrochemical oxidation of Acidblue9 can be achieved efficiently in medium containing NaCl using Ti/RuO₂-IrO₂ anode and rotating cathode in an electrochemical reactor. The percentage COD and color removal depends on current intensity, initial concentration of the dye, pH, temperature and cathode rotation speed. The increase in current density increases the COD and color removal, which decreases the current efficiency of the process. Temperature has no significance in the removal of COD and color, increase in temperature shows very low increase in removal where the energy requirement for heating the effluent will go high, increasing the process cost. Maximum removal was obtained at 6 pH. Increase in mass transport increases the percentage removal of COD and color, which was achieved by increasing the cathode rotation speed. The best conditions for the maximum COD and color removal were found to be 10mA/cm², 200mg/l, 6pH, 25°C, 4g/l NaCl and 750rpm. According to these results, the electrochemical method could be a strong alternative to conventional physicochemical methods for the treatment of industrial textile wastewater with further research.

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