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Electrochemical decolorization of the dye Acid orange 10

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ABSTRACT

In the present study experiments were carried out to decolorize the dye Acid orange 10 using an electrochemical technique. A square packed-bed electrochemical reactor was constructed with a graphite rod as anode and stainless steel as cathode material. Effect of parameters including pH (1.7–7.5) and current intensity (0.1–0.6 A) was investigated. The complete removal of color was achieved within a short period of electrolysis for different concentrations of Acid orange 10. Studies were also made for the removal of chemical oxygen demand (COD) and total organic carbon (TOC).It was found that the electrochemical treatment reduced COD and TOC to 85% and 56% respectively, for 200 mg/L Acid orange and 1.5 g/L sodium chloride concentration. Maximum decolorization was achieved at a current intensity of 0.4 A at a pH of 1.7. Effect of current intensity on color removal was also investigated as a function of electrolysis time (30–210 min) and it showed that maximum removal efficiency (98%) was reached within 60 min at a maximum current intensity of 0.4 A. Studies were made to study the effect of pH on decolorization, COD and electrochemical activity.

Keywords: Current intensity; Electrochemical oxidation; Electrolysis time; Hydroxyl radicals; Acid orange 10; Decolorization

1. Introduction

The textile industry causes considerable water pollution by discharging effluents into various receiving bodies. These include public sewers, ponds, rivers and irrigation lands. The effluent of the textile manufacturing process contains a large variety of pollutants such as dyes, surfactants, detergents and suspended solids. Major pollution loads from the textile industry can be attributed to the liquid effluents from the various wet-processing operations like scouring, bleaching, mercerizing, dyeing, etc. The amount of composite effluent discharged from the textile mills varies from 1 to 10 ML/d, depending upon the quantity of cloth produced and various manufacturing processes employed.

Selection of treatment methods for these wastes will be governed by their character, the policy of the regulatory body covering the waters of receiving scheme and economics of the treatment. In order to meet the legislative requirements, textile wastewater is usually treated by chemical and physical methods. Another common way of treatment is by an active sludge biochemical plant. However, all these have there own setbacks. There might not be one single treatment process that fulfills all the generalized treatments for the various structured dyes [1]. The mixture of compounds dissatisfies the recovery of organics; the low calorific power of the waste frustrates the use of incinerators; the non-biodegradability disappoints biological treatment. Similarly, a conventional process generates large amounts of sludge and, in some cases, the removal efficiencies are not enough to achieve the discharge limits. Hence, further treatment is necessary [2].

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Under these circumstances, the use of an electrochemical oxidation process appears to be a promising alternative to solve the environmental problem generated by the discharge of textile effluent. Electrochemical oxidation is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorption step when electrodes are dipped into an electrolyte solution at a definite potential difference. Therefore, the electrolytes present in wastewater dissociate into ions and oxidation of electrons occurs at the anode. Efficiency of the method is a function of several parameters such as difference of potential, nature of electrodes and pH. Electrochemical methods offer many distinctive advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness [3]. Applications of this method for textile wastewater have been tested on a laboratory scale and good removal of organic substances at various operating conditions is obtained [4,5].

This paper concerns the study of the main parameters, current intensity and pH, which influence the performance of the electrochemical oxidation process in treating the dyes on laboratory scale. In this experiment, the influence of current density on chemical oxygen demand (COD) and color removal was studied along with the study on effect of pH on color reduction.

2. Materials and methods

2.1. Electrolytic reactor set-up

The reactor consisted of a cylindrical glass vessel. A strip-like structure of graphite (5 cm × 0.5 cm) was fabricated as the cathode and a TiO_2-coated titanium strip acted as the anode. The one working as anode had a plain surface to carry out oxidation. The reactor was filled with a specified volume of dye water. Uniform mass transport and electrolyte concentration were maintained by using a magnetic stirrer rotating at 300 rpm. A current of different amperes and a potential difference of 8 V were supplied. A DC source was used to supply the system with 30 V and 5 A.

2.2. Analytical method

The test solution was prepared by diluting 20 ml of a concentrated stock solution of the Acid orange 10 sample (150 μm to 100 ml) and adding it to the electrolytic cell jar. The electrolyte composition varied from 0–0.05 N sodium chloride in 0.01 increments. The salts were added to the cell as 0, 2, 4, 6, 8 or 10 ml of a 1.5 N sodium chloride stock plus 10, 8, 6, 4, 2 or 0 ml respectively of a 1.5 N sodium sulphate stock diluted to 100 ml with purified water.

The cell contents were diluted to 300 ml with purified water to provide a total electrolyte concentration equal to 0.05 N and a required dye concentration.

A new graphite electrode anode was used for each run, paired with a stainless steel cathode electrolyte that was thoroughly buffed with fine-gauge steel wool and sand paper and cleaned with purified water prior to each run.

2.3. Experimental method

Sample conductivity, pH, and temperature were measured before and after each run. Temperature and conductivity were measured using a thermometer and conductivity meter. The conductivity was calibrated to a potassium chloride calibration standard. Solution pH was measured with a pH meter equipped with an Ag/Agcl combination pH electrode.

Ultraviolet-visible (UV-VIS) absorbance spectra were measured using a UV/VIS Shimadzu spectrophotometer, model U 2000, with a 10 mm path length quartz cell. Absorbance readings in absorbance units (AU) were recorded at 1 nm intervals over a range of 190–1,100 nm with an integration time of 0.5 s.

Free and combined chlorine residuals were measured using 20 ml samples diluted to 100 ml using purified water; a titrametric method was used to analyze the data.

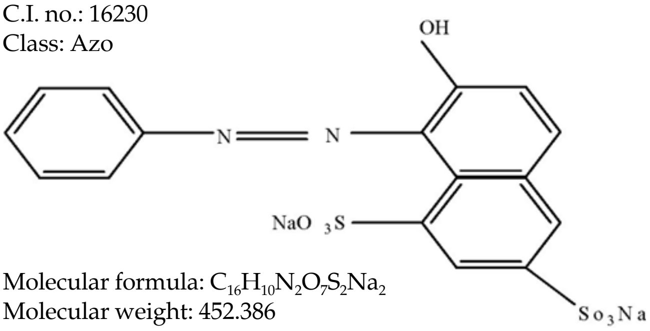
2.4. Chemicals and dye

A commercial dye, Acid orange 10, was used which was obtained from the Textile Department, Anna University. All chemicals were obtained from E Merck and were of analytical grade. The structure of the dye Acid orange 10 along with its CI name and number are given in Fig. 1.

2.5. Decolorization determination

The concentration of the dye in the samples was determined in a UV/VIS Shimadzu spectrophotometer, model U 2000, was measured at regular intervals, which took place for a period of maximum 6–8 h. Decolorizing

C.I. name: Acid orange 10
C.I. no.: 16230
Class: Azo



Molecular formula: $C_{16}H_{10}N_2O_7S_2Na_2$
Molecular weight: 452.386

Fig. 1. Structure of Acid orange 10 dye.

activity was calculated using standard curves and expressed in terms of percentage.

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\%$$

where A_0 and A_t are the absorbances of the dye wastewater initially and at time t respectively. Decolorization was determined by monitoring the decrease in absorbance at the absorbance maximum of 455 for the dye (λ_{max}) [6]. The experiments were carried out in triplicate and averaged for better results.

2.6. Determination of hydrogen peroxide

Hydrogen peroxide concentration was determined spectrophotometrically using the potassium titanium (IV) oxalate method (λ = 402 nm) [7]. The current efficiency for hydrogen peroxide generation is defined as follows [8]:

$$\text{Current efficiency} = \frac{f.C_{H2O2}V}{\int_0^t I.dt} \times 100\%$$

where F is Faraday's constant, C_{H2O2} is the concentration of hydrogen peroxide in mg/L, V is volume (L), I is current (A) and t the time (s).

3. Results and discussion

3.1. Effect of current intensity

The current intensity was varied from 0.1–0.65 A with 0–200 mg/L Acid orange 10 and 1.5 g/L sodium chloride. Results are presented in Fig. 2. The results show that the decolorization decreased after a level of 80 mg/l of the dye and intensity of current to 0.4 A gave a maximum decolorization. The results also clearly indicate that increasing the current intensity decreases the charge loading for the degradation of Acid orange 10. This might be due to the increased production of chlorine or hypochlorite at higher current intensities due to an over-potential requirement for generation of chlorine or hypochlorite [9]. At the same time, the performance of the reactor will be affected under different current intensities while altering the other operating conditions simultaneously because the generation of chlorine or hypochlorite depends on mass and charge. The removal of color was increased up to 0.4 A of current intensity; beyond that color removal did not show much increase.

An increase of current intensity also led to the reduction in COD. A maximum of 85% COD was reduced at 0.4 A. A study made by previous authors also reveals that increase in current intensity lead to the increase in COD reduction [10].

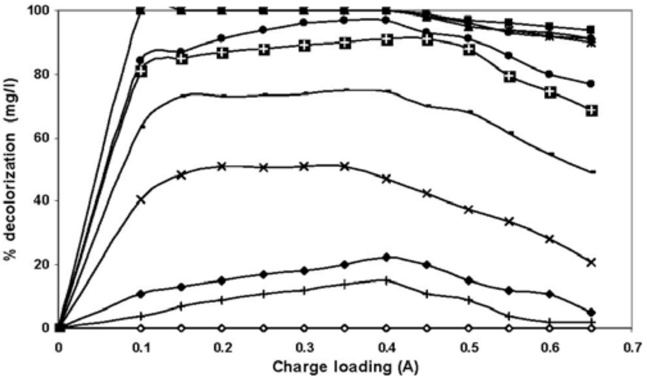


Fig. 2. Effect of current intensity on percentage decolorization. Acid orange 10 (in mg/L): ○, 0; ■, 20; Δ, 40; ●, 60; ✳, 80; ✱, 100; +, 120; –, 140; ×, 160; ◆, 180; ✢, 200.

3.2. Effect of sodium chloride on the decolorization of Acid orange 10

Fig. 3 presents color removal with different sodium chloride concentrations under a fixed current intensity of 0.4 A. It is apparent that increasing the chloride concentration increases the color removal due to increased mass transport of chloride ions to the anode surface and also increased diffusion in the diffusion layer of the anode. As a result, more chlorine or hypochlorite will be generated. Hence the rate of color removal also increased. However, a further increase in the salt dosage does not increase the color removal, which might be due to potential drop of the solution [11]. Further, experiments with more than 1.5 g/L sodium chloride concentration were not conducted because of the implementation of stringent limits for total dissolved solid concentration for the treated wastewater by various regulatory authorities.

3.3. Effect of initial pH on the decolorization of Acid orange 10

The variation of initial pH on the decolorization of Acid orange 10 during the electrochemical degradation is presented in Fig. 4. The color removal decreased with increase in the initial pH 7.5 of the solution. The charge loading required for the removal of 95% color increased from 0.2 to 0.4 A while increasing the initial pH from 7.5 to 9.0. The color removal drastically decreased if the pH was 9. This may be due to the decreased production of chlorine or hypochlorite at higher pH conditions.

3.4. Effect of reaction temperature on the decolorization of Acid orange 10

Fig. 5 presents the color removal at different operating temperatures. The rise or fall of temperature certainly has an impact on the decolorization. It is very much evident from the figure that increasing temperature decreases the color removal. The relatively lower decolorization might be due to a lesser conversion at higher temperatures [12]. The reason might also be that increasing reaction temperatures decreases the generation of chlorine or hypochlorite. At high temperatures, the mass transport controlled reduction of hypochlorite may also be the reason for a decreased decolorization.

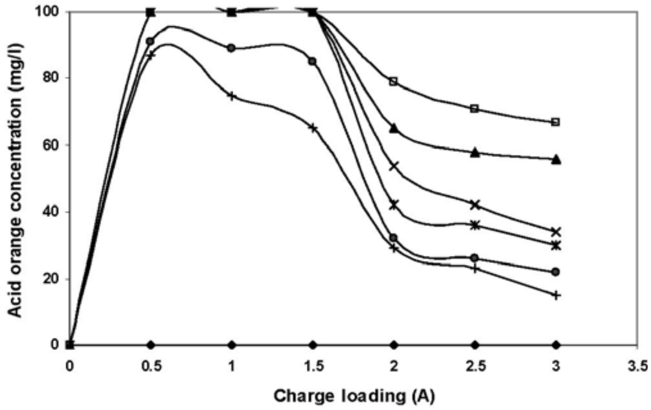


Fig. 3. Effect of salt concentration on electrochemical degradation. Current intensities (in A): ◆, 0.0; □, 0.1; ▲, 0.2; ×, 0.3; ✳, 0.4; ✱, 0.5; +, 0.6.

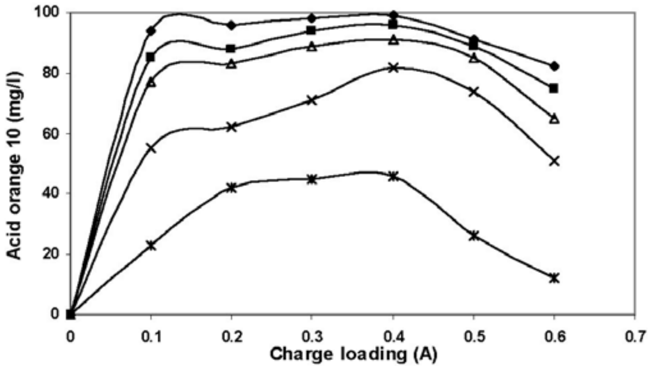


Fig. 4. Effect of pH on electrolytic degradation. pH: ◆, 7; ■, 7.5; Δ, 8; ×, 8.5; ✳, 9.

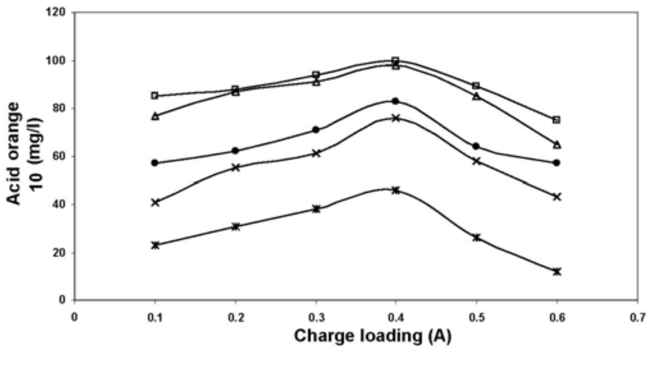


Fig. 5. Effect of temperature (in °C) on dye decolorization. ■, 25; □, 30; Δ, 35; ×, 40; ✳, 45.

3.5. *Effect of initial concentration of Acid orange 10*

The effect of initial dye concentration on the removal of dye color was studied in the range from 50 to 200 mg/L while the other conditions were fixed (Fig. 6). The net amount of color removal decreased with increase in the concentration. This may be explained by the fact that, under galvanostatic conditions, the production rate of chlorine or hypochlorite is constant; however, the active species involved in the degradation in the dye structure have a nonselective property, which results in an attack on intermediate compounds produced rather than on the chromophore of the initial dye molecule while increasing the initial dye concentration. The charges required for complete de-colorization of initial dye concentration of 50, 100, 150, 160, 170, 180, 190 and 200 mg/L were 0.2, 0.3, 0.35, 0.36, 0.37, 0.38 and 0.4 A respectively.

3.6. *Electrochemical activity*

Table 1 shows the H_2O_2 accumulation and current efficiency at 30°C under different conditions. It was observed that a supply of oxygen was a prerequisite for hydrogen peroxide generation. On continuation in stirring both the concentration of hydrogen peroxide and current efficiency increased. However, there was not much increase in the hydrogen peroxide after some time. Some researchers have indicated that an increase in oxygen flow rate enhances hydrogen peroxide production [13].

Experiments were also carried out in five different pH ranges (7.5, 5.2, 3.5, 2.9, 1.7 and 1.3) at a constant current intensity of 0.3 A. The rate of hydrogen peroxide production increased significantly from 35% to 75% when the pH was decreased from 7.5 to 1.5. Decrease in pH increases the hydroxyl radicals, which in turn favors the rate of oxidation [14,15].

3.7. *Effect of pH on COD and TOC reduction*

The pH value of solution affects the electrochemical reaction on the electrode surface. Studies were made on

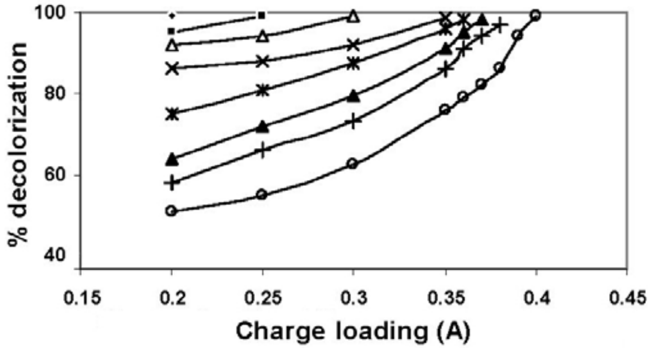


Fig. 6. Effect of initial concentration.

Table 1
Electrochemical activity and current efficiency

Stirrer speed (rpm)	CH_2O_2	Current efficiency
20	28.9	40.0
25	55.5	77.3
30	60.2	86.0
35	47.3	62.7
40	38.6	56.3
45	36.2	44.5
50	47.2	65.5
55	55.8	75.1
60	56.2	81.3
65	50.5	75.5
65	50.5	75.5

Table 2
Effect of pH on COD and TOC reduction

S. no.	pH	% of TOC reduced	% of COD reduced
1	7.5	18	22
2	5.2	28	34
3	3.5	32	43
4	2.9	44	48
5	1.7	52	62
6	1.3	56	85

the effect of pH on COD and TOC removal efficiency. The pH of the dye solution was adjusted using H_2SO_4 and NaOH (initial pH was 7.5) to study the effect. The initial COD and TOC present in the dye sample were around 2356 and 3417 mg/l respectively. Experiments were carried out in five different pH ranges (7.5, 5.2, 3.5, 2.9, 1.7 and 1.3) at a constant current intensity of 0.3 A. The results are tabulated in Table 2, and it can be ascertained that the rate of COD reduction increased significantly (from 22% to 85%) when the pH was decreased from 7.5 to 1.3. The rate of TOC reduction was not as drastic as that of the COD but reduced slowly from 18 to 56% for a pH of 7.5 to 1.3. This may be due to the lesser degree of reduction of aromatic rings present in the structure of the Acid orange 10. But it may be that a decrease in pH increases the hydroxyl radicals, which favors the rate of oxidation [16].

3.8. Kinetic studies

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of the electron transfer reaction with a dissociate chemisorption step.

- At cathode:

$$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \qquad (1)$$

Table 3
Values of rate constant for different current intensities

S. no.	Current intensity (A)	Rate constant K (min^{-1})	Coefficient of variance (%)
1	0.1	0.135	5.59
2	0.2	0.204	4.43
3	0.3	0.227	7.90
4	0.4	0.352	4.42
5	0.5	0.426	4.84
6	0.6	0.559	4.95

- At anode:

$$xC + H_2O \rightarrow C_xO\,(OH^{\bullet})_y + H^+ + e^- \qquad (2)$$

In the first step of anodic oxidation reaction, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction [17]. In the second step, the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide CO_{x+1}.

$$CO_x\,(OH^{\cdot}) \rightarrow CO_{x+1} + H^+ + e^- \qquad (3)$$

A simple kinetic model was applied to this electrochemical treatment technology where the data can be approximated to first order. The equation that is well described for the decolorization follows first-order kinetics and the rate equation is represented by

$$d\,[\text{decolorization}]/\mathrm{d}t = -K\,[\text{decolorization}]$$

where the rate constant K can be calculated for various values of current intensity. At each value of current intensity, decolorization was estimated at different time intervals and using the above equation, rate constant K was calculated at each time interval and averaged.

The coefficient of variance (CV) is a measure of dispersion of a probability distribution and it was calculated for all rate constants K at each value of current intensity; the results are shown in Table 3. Distributions with CV <1 (such as an Erlang distribution) are considered low-variance, while those with CV >1 (such as hyper-exponential distribution) are considered high-variance. In this study, the coefficient of variance did not reach more than 8% and this result reported that the decolorization estimation and K values calculated were correct and consistent.

The effect of current intensity on rate constant was also plotted in Fig. 7 and it can be noticed that the rate constant increased with increasing current intensity and the higher

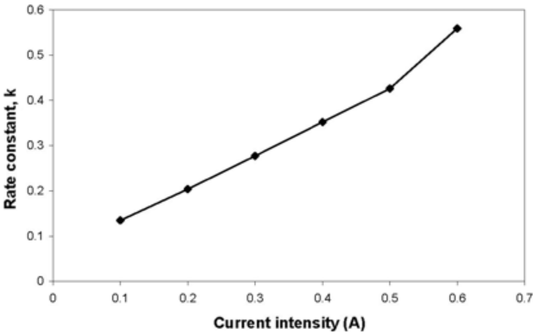


Fig. 7. Effect of current intensity on rate constant, *K*.

reaction rate constant (0.559 min^{-1}) was obtained at the maximum current intensity of 0.6A. The result indicated that the organic compounds were easily attacked by hydroxyl radicals at higher current intensities. Kinetics are enhanced by increasing the temperature, enhancing current density, alternating electrode potential, lowering the initial pH, and dissolving Fe_3^- ions in the analyte [18].

4. Conclusions

From the present study, it can be concluded that electrochemical oxidation can be feasible for the treatment of dye from the textile industry. Effects of current intensity on the treatment process were studied and the results displayed that the maximum degradation of organics was obtained at the current intensity of 0.4 A. At this condition, 85% of COD and 56% of TOC were removed. The rate constant, *K*, was also estimated at different time intervals for all values of current intensity and they were averaged along with the calculation of percentage of variance. It was observed from the result that the rate constant increased with increasing current intensity and higher value (0.559 min^{-1}) was obtained at the maximum current intensity of 0.4A. During the treatment process, the color removal efficiency reached maximum efficiency (98%) within 60 min at the maximum current intensity of 0.4 A. The effect of pH was analyzed and it showed that the COD removal was increased to the maximum of 85% at a pH of 1.3. These results demonstrate that current intensity and pH influence organics removal in electrochemical oxidation.

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