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ELECTROCHEMICAL DEGRADATION OF DYE EFFLUENTS USING MIXED OXIDE COATED DSA ELECTRODE-A KINETIC STUDY

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ABSTRACT

This study deals with the treatment of dye wastewaters from textile industries by electrochemical oxidation using Ti/RuO_2-IrO_2 anode and rotating stainless steel cathode in a batch reactor. The main objective of the present work was to reduce the COD of the dye effluent. The influence of various experimental parameters such as initial pH, initial dye concentration, cathode rotation speed, current density, electrolyte concentration, reaction temperature, etc. were calculated and presented. Electrochemical oxidation process maximum COD removal of about 89.01% was achieved at an optimum current density of about 100 mA/cm^2.

Key words: Electrochemical oxidation, Rotating cathode, Wastewater treatment, Mixed oxide anode.

INTRODUCTION

The significant development in industrial sector leads to the pollution of ground and surface waters, which is mainly due to the disposal of refractory liquid and solid wastes. The problems associated with pollutants are likely to increase in the future due to increase in population and urbanization. Textile industries use large quantities of chemicals and dyes, which are wasted in the effluents, pollute the ground and surface water bodies[1,2]. The inefficiencies in the dyeing process result in dyestuff losses between 2-50%[3].

Various physio-chemical, biological and electrochemical 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[4]. A number of biological process, such as sequenced anaerobic/aerobic digestion, have been

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proposed in the treatment of textile wastewater[5,6]. 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[7-12]. 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[13]. The effectiveness of electrochemical process depends upon the nature of the anode selected and 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 optimization of operating parameters using various anodes including RuO_2,[14] SnO_2,[15] PbO_2 [16] and diamond electrode[17].

In this work, the electrochemical treatment of textile effluent was investigated using Ti/RuO_2-IrO_2 anode and rotating stainless steel cathode in a batch reactor. The effect of initial pH, initial dye concentration, cathode rotation speed, current density, electrolyte concentration, reaction temperature, on the efficiency of the process was studied and the optimum condition for maximum reduction of COD was established.

EXPERIMENTAL

Materials and methods

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

Table 1: Chemical characteristics of textile dye effluent

Parameters	Values
COD	3500 mg/L
Conductivity	16.42 m mho/cm
pH	9
Color	Purple blue
Chloride content	42943 mg/L
Total dissolved solids	48000 mg/L
Suspended solids	2100 mg/L

Experimental setup

The electrochemical reactor used in the present study was made of Pyrex glass of 1000 mL 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/RuO_2-IrO_2 as anode and rotating stainless steel as cathode were arranged horizontally and parallel to each other with 1 cm inter-electrode gap. A DC power supply was used as a source for electric power for the experiments, with ammeter and voltmeter. The experimental setup is shown in Fig. 1.

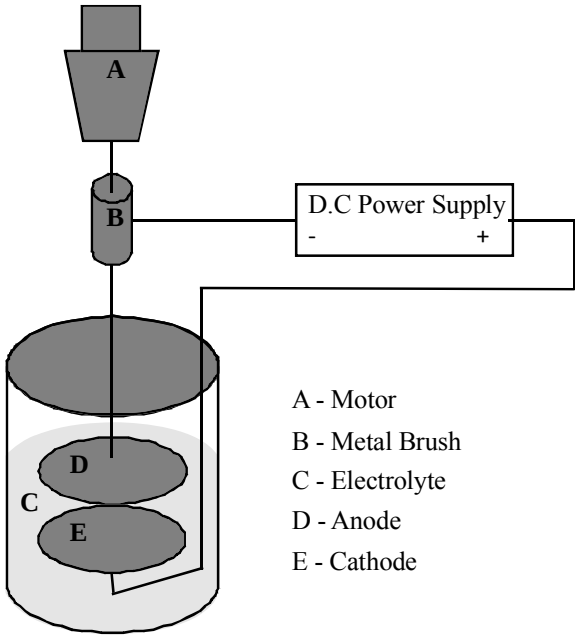

Fig. 1: Rotating disc electrochemical oxidation unit

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, 500 mL 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 initial pH, initial concentration, cathode rotation speed, current density, electrolyte concentration and reaction temperature was varied with development of experiment. At the pre-determined time interval, 5 mL of sample was collected and reduction of COD was determined to know the extent of degradation of effluent.

Analysis

COD: The COD was measured by the standard method (closed reflux/photometry)[18]. The COD or color removal efficiency (η) was calculated by the following formula:

$$\eta = \frac{C_o - C_t}{C_o} \times 100 \quad \ldots(1)$$

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.

RESULTS AND DISCUSSION

Effect of current density

The current density was varied 25 mA/cm^2, 50 mA/cm^2, 75 mA/cm^2, 100 mA/cm^2, and 125 mA/cm^2 to enumerate the effect of current density on effective removal of COD. It was observed that increase in current density increases the percentage COD removal. The optimum condition for COD removal is 100 mA/cm^2, where 89.01% was achieved. Further increase in current density to 125 mA/cm^2, results in 94%, which is insignificant and efficiency of the process also decreases as current density was increased.

Effect of temperature

The effect of temperature was studied by varying the temperature as 20^{o}C, 25^{o}C, 30^{o}C, 35^{o}C and 40^{o}C. Increase in temperature increases the rate of COD significantly until 25^{o}C, but further increase in temperature was found to 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^{o}C, where 89.01% of COD removal percentage was obtained.

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 reduction rate increases with increasing cathode rotation speed. This may be due to adequate high mass transfer. At 750 rpm, COD removal percentage of 92% was obtained. Further increase in cathode rotation speed beyond optimum favors the cathodic reduction of generated hypochlorite; thereby, decrease in the removal of COD was observed.

Effect of initial concentration

The effect of initial concentration of dye effluent was studied by varying the dilution 20, 40, 60, 80 and 100%. The percentage COD reduction was reduced with increase in the initial concentration. As the initial concentration was increased, the degradation efficiency decreased. 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 was obtained with 20% COD removal percentage of 90.54%.

Effect of pH

The effect of pH of dye was studied by varying the pH, 4, 6, 8,10. The pH of the dye solutions was adjusted to desired values with 0.1 mol/L HCl or 0.1 mol/L NaOH. Varying the initial pH between 2 and 10 does not have significant influence on the COD removal. Many investigators explained this fact that the generation of chlorine/hypochlorite is not dependent 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 pH 6, maximum COD removal was found to be 90.01%.

Table 2: Results of electrochemical degradation of textile dye effluent

Parameters	Values	Rate constant k (min^{-1}) × 10^{-3}	R^2	Mass transfer coefficient (cm/sec) × 10^{-4}	Current efficiency (%)
Current density (mA/cm^2)	25	0.0026	0.99	5.63	34.43
	50	0.0062	0.99	13.43	32.97
	75	0.0085	0.99	18.42	23.96
	100	0.0125	0.99	27.08	20.50
	125	0.0153	0.99	33.15	18.04
Electrolyte concentration (mg/L)	1	0.0032	0.99	6.93	10.08
	2	0.0054	0.99	11.70	14.32
	3	0.0071	0.99	15.38	16.58
	4	0.0126	0.99	27.30	20.75
	5	0.0140	0.99	30.33	21.23

Cont…

Parameters	Values	Rate constant k (min^{-1}) × 10^{-3}	R^2	Mass transfer coefficient (cm/sec) × 10^{-4}	Current efficiency (%)
Initial concentration (%)	20	0.0126	0.99	27.30	20.75
	40	0.0084	0.99	18.20	20.41
	60	0.0058	0.98	9.53	20.38
	80	0.0032	0.99	6.93	18.51
	100	0.0021	0.99	4.55	15.38
Cathode rotation speed (RPM)	250	0.0110	0.99	23.83	19.81
	500	0.0115	0.99	24.92	20.18
	750	0.0127	0.99	27.52	20.73
	1000	0.0125	0.99	27.08	20.48
	1250	0.0121	0.99	26.22	20.38
Temperature (^oC)	20	0.0152	0.98	32.93	21.19
	25	0.013	0.98	28.17	20.50
	30	0.0123	0.99	26.65	20.29
	35	0.0095	0.98	20.58	18.43
	40	0.0090	0.98	19.50	17.97
pH	2	0.0098	0.99	21.23	19.12
	4	0.0102	0.99	22.10	19.38
	6	0.0128	0.99	27.73	20.73
	8	0.0120	0.99	26.00	20.27
	10	0.011	0.99	23.83	19.81

Effect of electrolyte concentration

The effect of electrolyte concentration was studied by varying the concentration 1, 2, 3, 4 and 5 g/L. An increase in the electrolyte concentration up to 4 g/L leads to increase in the COD removal. The NaCl solution liberates Cl_2 gas, which is considered as an active species for the degradation of organic compound. Further increase of the NaCl concentration

has slight effect on COD removal. The optimum condition was 4 g/L, where COD removal percentage of 88.04% was obtained.

Kinetics

In an attempt to correlate the present data with a kinetic equation, a pseudo first-order reaction was assumed. The present data fit the equation:

$$\ln\left(\frac{C_o}{C_t}\right) = kt \qquad \ldots(2)$$

Where - C_o and C_t is the initial and final COD (mg/L), k is the rate constant (min^{-1}) and t is the time (min).

The values of rate constants are shown in Table 2. The increase in k with current density was due to the increase in amount of hypochlorite.

From the result, it is inferred that the operating variables current density, electrolyte concentration, initial concentration, cathode rotation speed influence the COD removal, where temperature and initial pH are insignificant in COD removal.

CONCLUSION

Electrochemical oxidation of textile effluent can be achieved efficiently in medium containing NaCl using Ti/RuO_2-IrO_2 anode and rotating cathode in an electrochemical reactor. The percentage COD removal depends on current intensity, initial concentration of the dye, pH, temperature and cathode rotation speed. The increase in current density increases the COD, which decreases the current efficiency of the process. Temperature has no significant role in the removal of COD. Increase in temperature shows very less increase in COD removal, where the energy requirement for heating the effluent will go high, increasing the process cost. Maximum removal was obtained at pH 6. 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 100 mA/cm^2, 20% initial concentration, pH 6, 25^oC, 4 g/L NaCl and 750 rpm. The degradation of effluent follows pseudo-first order kinetics. According to these results, the electrochemical method could be a strong alternative to conventional physicochemical methods for the treatment of industrial textile wastewater.

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