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Electrochemical Degradation of Acridine Orange Dye at Ru-Doped Platinum Anode in Aqueous Solution

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Abstract

Degradation of acridine orange (AO) in aqueous solution by anodic oxidation with a Ru-doped Pt electrode (RuDPt) can be applied to the remediation of waste waters containing acridine orange. This environmentally friendly method decontaminates completely aqueous solutions of this dye. The COD value decreases to ~98% of the initial COD. Acridine orange (AO) is more rapidly removed in RuDPt electrode than in platinum electrode alone. The reaction was carried out in presence of dilute NaCl. The degradation rate increases with increasing current and follows I order kinetics up to 60% of the reaction. The rate increases with [NaCl] and decreases with [AO]. The dye is converted into CO_2, H_2O, NH_4^+ and simpler inorganic salts.

Keywords: Acridine orange; anodic oxidation; ruthenium-doped platinum electrode; mineralization.

Introduction

Acridine orange (AO) is a heterocyclic dye containing nitrogen atoms which is widely used in the fields of printing and dyeing, leather, printing ink, and lithography[1]. It has also been used extensively in biological stains. Toxicological investigation indicates that aminoacridine has mutagenic potential [2]. The release of this colored wastewater in the ecosystem is dramatic source of water pollution, eutrophication, and perturbation in aquatic life [3]. Conventional wastewater treatment methods such as precipitation, adsorption, air stripping, flocculation, reverse osmosis, and ultrafiltration can be used for color removal from dye-contaminated effluents [4]. However, these methods are non-destructive, since they only transfer the contamination from one phase to another, causing secondary pollution and requiring further treatment [5]. In recent years "advanced oxidation processes" (AOPs) have emerged as an alternative to conventional methods. AOPs are based on the generation of very reactive species such as hydroxyl radicals, which oxidize a broad range of organic pollutants quickly and non-selectively [6]. Anodic oxidation and electro-Fenton are the most usual techniques, since they have high degradation efficiency due to electrochemical reaction of OH radical as oxidant [7, 8]. However a limited number of papers have been published for the destruction of dyes by electrochemical methods [9, 10]. Here we have developed the electrochemical method for the degradation of acridine orange dye with Ru[III] doped Pt electrode(RudPt) [11, 12]. The kinetics of degradation of acridine orange was studied.

Experimental

A solution of acridine orange (AO) (LOBA CHEMIE) was prepared [0.0001M] and NaCl [0.5N] were prepared. The experimental set up is shown in the figure (1). Ruthenium was deposited on platinum electrode from $RuCl_3$ (Arora matthey) solution. All chemicals used were of accepted grades of purity. It consists of reaction chamber and a voltage power supply. The electrode system consists of a Pt sheet (0.25 sq cm) as cathode and a Pt wire electrode as anode in case of degradation of dye by anodic oxidation with Pt electrodes. The kinetic runs were carried out with platinum electrode alone as anode. In another case, Ru (III) thin film deposited on a conductive Pt sheet electrode has taken as anode and Pt wire electrode as cathode. The experiment was run from 15 to 360 minutes with continuous stirring. The kinetic runs were carried out for different concentration of acridine orange and NaCl as an electrolyte with different applied current.

To account for the mineralization of the dye solution COD was measured at regular intervals of time [13]. The pH of the solution before and after electrolysis was measured. A positive voltage was applied by using battery eliminator (NEULITE INDIA) and current output of 20mA-70mA using rheostat (INSIF INDIA). The experiments were performed with volume of electrolyte solution 20ml (1.0-5.0ml of NaCl). The decolourisation and disappearance of acridine orange was followed by using spectrophotometer (ELICO SL 171).

Figure 1: Experimental set up for the electrochemical degradation of AO

Results and Discussion

Reaction with platinum as anode electrode

Effect of acridine orange on the rate

The reaction performed in the presence of AO (0.0001M), NaCl (2ml of 0.5N) with constant current (40mA). The change in concentration of the acridine orange was recorded by change in color using spectrophotometer. A plot of log T_t (percentage transmittance of light) versus time was linear up to 60% of the reaction indicating disappearance of AO follows first order kinetics. The rate constant values are given in table (1). The reaction rate decreased with increase in [AO]. The decrease of rate at higher concentration is due to the formation of a thin film of dye on the surface of the electrode, decreases the rate of flow of current across the electrode-solution interface, which decreases the concentration of OH radicals. The pH value before and after the electrolysis shows slight increase towards the alkaline pH. The COD for acridine orange solution before and after electrolysis were measured. (Table-1, Fig-2). The values of rate constants were calculated for 50% of degradation during the reaction.

Table 1: Effect of [AO] on the rate of degradation and COD values.

10^4[AO]	10^4 k sec^{-1}	Effect of pH		COD values in mg/l	
		Before degradation	After degradation	Before degradation	After degradation
0.50	16.12	5.68	7.01	350	16
0.75	17.66	6.39	7.04	496	16
1.0	08.83	6.70	7.20	704	40
1.25	05.76	7.21	7.78	936	8
1.50	03.00	7.30	8.46	1352	16

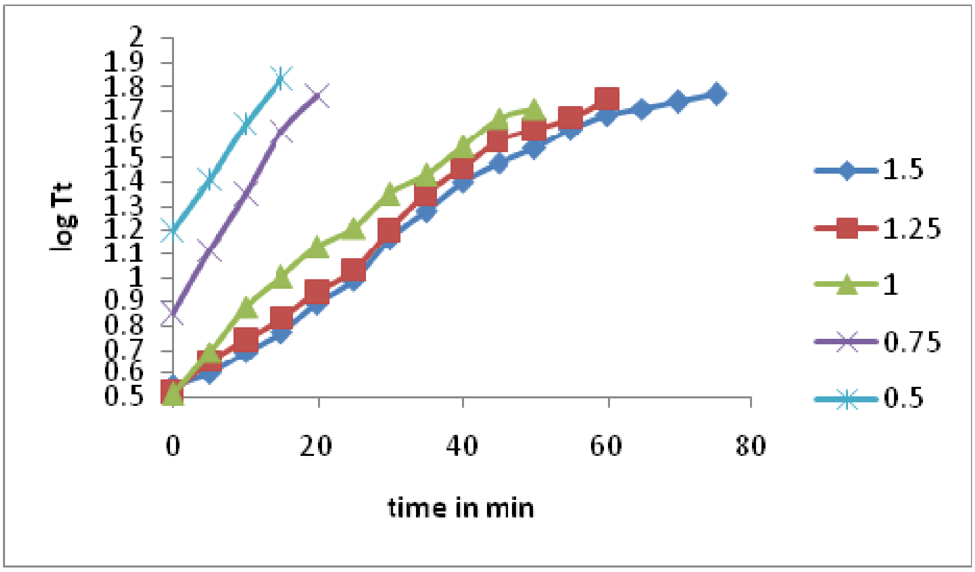

Figure 2. Effect of concentration of AO on the rate of degradation

Effect of current on the rate

At fixed [AO] and [NaCl] the rate of reaction increased with increase in applied current. The current is varied from 20mA-60mA. (Table-2, Fig-3). The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of degradation.

Table 2: Effect of current on the rate of degradation and COD values.

Current in mA	10^4 k sec^{-1}	COD values in mg/l	
		Before degradation	After degradation
20	3.0	704	40
30	4.61	704	16
40	8.83	704	16
50	30.32	704	16
60	51.05	704	24

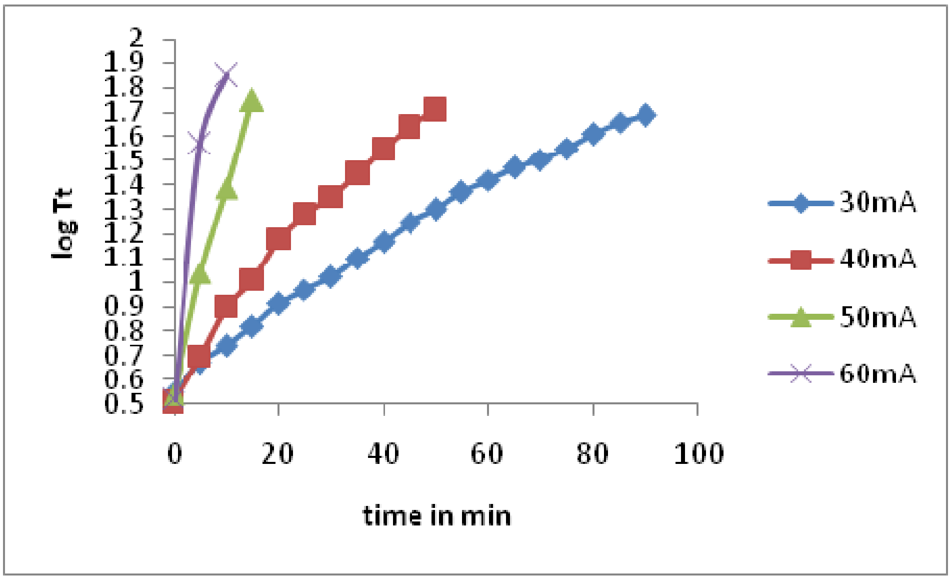

Figure 3: Effect of current on the rate of degradation.

Effect of NaCl on the rate

The reaction was studied with varying [NaCl] (1.0-2.5ml of 0.5N) and keeping the other experimental conditions the same. The rate increased with increase in [NaCl] due to the formation of HOCl oxidizing species during the reaction. The pH before and after electrolysis was measured for each run and it was observed that for a given run the pH increases towards the alkaline pH may be due to the formation of NaOH during the electrolysis (Table-3).

Table 3: Effect of concentration of NaCl on the rate of degradation and COD values.

Volume of NaCl(0.5N) in ml	10^4 k sec^{-1}	Effect of pH		COD values in mg/l	
		Before degradation	After degradation	Before degradation	After degradation
1.0	3.45	6.59	7.0	704	48
1.5	4.60	6.66	7.10	704	16
2.0	8.83	6.70	7.20	704	16
2.5	14.96	6.75	7.40	704	16

Effect of temperature

It is clear that increase in the reaction temperature increases the dye degradation. It is observed that the rate of removal of colour is not very significant at low temperature. However the reaction is more significantly influenced at higher temperature (Table 4,5). Since the diffusion rate is increased with temperature an increase of temperature could bring about an increase in the degradation rate.

Table 4: Effect of Temperature on the rate of degradation and COD values.

Temperature in K	10^4 k sec^{-1}	COD values in mg/l	
		Before degradation	After degradation
288	5.32	704	24
298	8.83	704	16
313	16.21	704	8
323	25.28	704	8

Table 5: Thermodynamic parameters for the degradation of AO.

Temperature in K	ΔH	ΔS	ΔG
288	30.59 kJ/mol	-201.11 J/K	88.51 kJ/mol
298	30.51 kJ/mol	-201.02 J/K	90.41 kJ/mol
313	30.38 kJ/mol	-220.83 J/K	99.50 kJ/mol
323	30.30 kJ/mol	-220.66 J/K	101.57 kJ/mol

Reaction with Ruthenium doped platinum (RuDPt) as anode electrode

Effect of acridine orange on the rate

The reaction has been carried out in the presence of AO (0.0001M), NaCl (4.0ml of 0.5N) by keeping current constant (50mA). The change in concentration of the acridine orange was recorded by change in color using spectrophotometer. A plot of log T_t (percentage transmittance of light) versus time was linear up to 50% of the reaction indicating disappearance of AO follows first order kinetics. The reaction rate decreased with increase in [AO] and the values of rate constants were higher compared to Pt electrode as anode alone. The pH value before and after the electrolysis indicates slight increase towards alkaline pH. The COD for acridine orange solution before and after electrolysis were measured. (Table-6, Fig-4).

Table 6: Effect of [AO] on the rate of degradation and COD values for RuDPt electrode.

10^4 [AO]	10^4 k sec^{-1}	Effect of pH		COD values in mg/l	
		Before degradation	After degradation	Before degradation	After degradation
0.75	43.37	6.39	7.01	496	8
1.0	44.91	6.70	7.20	704	8
1.25	16.50	7.21	7.78	936	16
1.50	15.70	7.30	8.46	1352	16

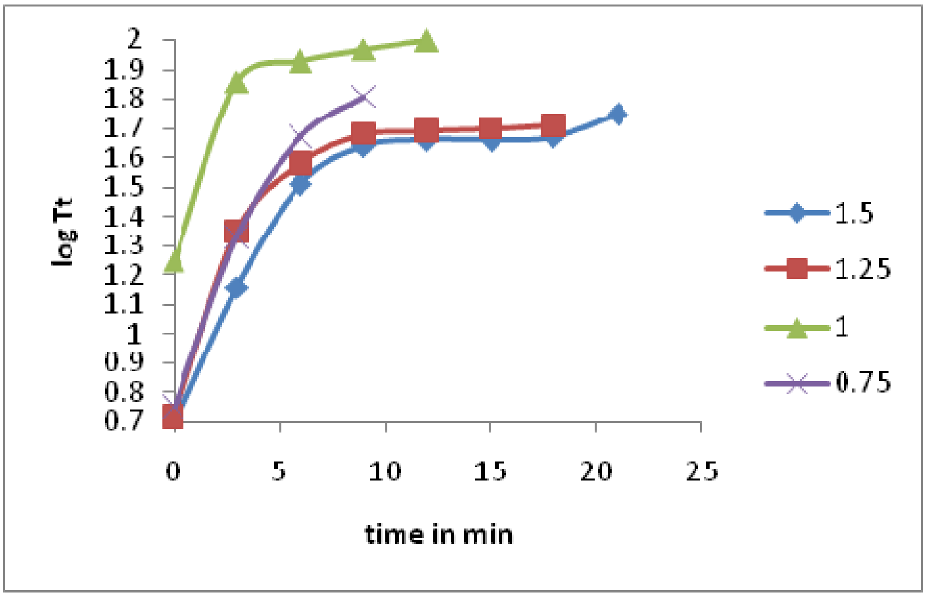

Figure 4: Effect of concentration of AO on the rate of degradation

Effect of current on the rate

At fixed [AO] and [NaCl] the rate of reaction increased with increased in applied current. The current is varied from 30mA-70mA. (Table-7, Fig-5). The rate of degradation is higher compared to Pt electrode as anode.

Table 7: Effect of current on the rate of degradation and COD values.

Current in mA	10^4 k sec^{-1}	COD values in mg/l	
		Before degradation	After degradation
30	43.37	704	8
40	44.10	704	8
50	44.91	704	16
60	67.17	704	16
70	71.39	704	8

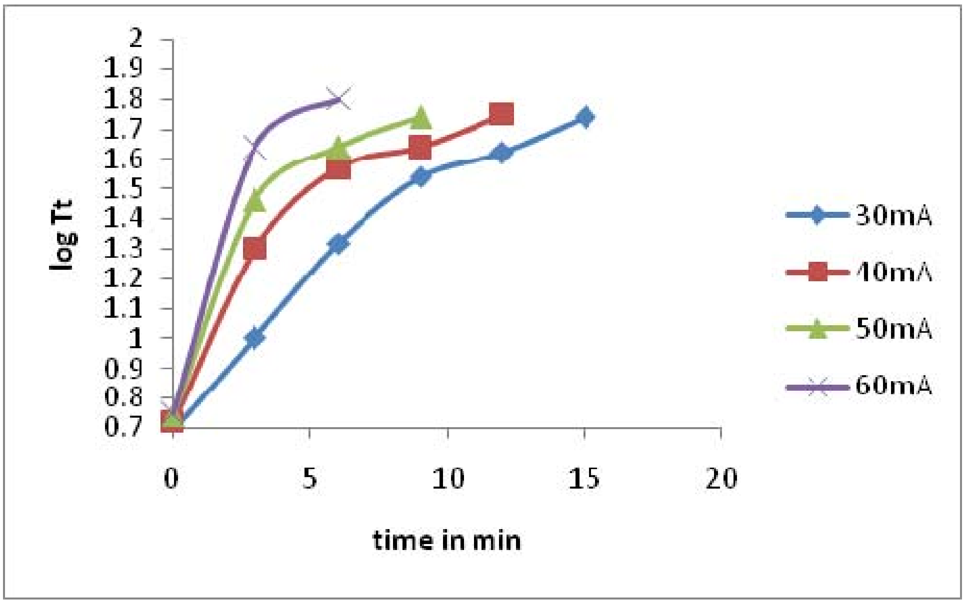

Figure 5: Effect of current on the rate of degradation

Effect of NaCl on the rate

The reaction was studied with varying [NaCl] (1.0-5.0ml) and keeping the other experimental conditions the same. The rate increased with increase in [NaCl] due to the formation of HOCl oxidizing species during the reaction and observed a higher rate of anodic oxidation than Pt anode. The pH before and after electrolysis was measured for each run. It was observed that for a given run the pH slightly increases towards the alkaline pH may be due to formation of NaOH during the electrolysis, which indicates that NaCl acts as supporting electrolyte during the reaction. (Table-8)

Table 8: Effect of concentration of NaCl on the rate of degradation and COD values.

Volume of NaCl in ml	10^4 k sec^{-1}	Effect of pH		COD values in mg/l	
		Before degradation	After degradation	Before degradation	After degradation
1.0	17.65	6.59	7.00	704	16
3.0	26.55	6.66	7.10	704	16
4.0	44.91	6.70	7.20	704	8
5.0	59.87	6.75	7.40	704	16

Effect of temperature

It is clear that increase in the reaction temperature increases the dye degradation. And observed that the rate of removal of colour is not very significant at low temperature. However the reaction is more significantly influenced at higher temperature (Table 9,10). Since the diffusion rate is increased with temperature an increase of temperature could bring about an increase in the degradation rate.

Table 9: Effect of Temperature on the rate of degradation and COD values.

Temperature in K	10^4 k sec^{-1}	COD values in mg/l	
		Before degradation	After degradation
288	28.12	704	16
298	44.91	704	8
313	70.08	704	16
323	96.52	704	8

Table 10: Thermodynamic parameters for the degradation of AO for RuDPt electrode.

Temperature in K	ΔH	ΔS	ΔG
288	24.08 kJ/mol	-229.01J/K	90.04 kJ/mol
298	24.00 kJ/mol	-228.49 J/K	92.09 kJ/mol
313	23.87 kJ/mol	-229.46 J/K	95.69 kJ/mol
323	23.79 kJ/mol	-229.68 J/K	97.98 kJ/mol

Production of OH radical

The degradation of Acridine orange solutions were carried out by anodic oxidation. In the electrochemical technique $^{\cdot}OH$ formed by direct electrolysis absorbed as intermediate at the surface of high O_2-overvoltage anode from oxidation of water.

$$H_2O \rightarrow {}^{\cdot}OH_{ads} + H^+ + e^- \quad (1)$$

Other than by direct electrolysis acridine orange can also be removed electrochemically by indirect electrolysis, in which the main oxidizing species formed is HOCl which is anodically produced from chloride ion formed during the electrolysis. The increase in chloride ion concentration accelerated the electrochemical mineralization and the current efficiency.

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

The strong oxidizing agent $^{\cdot}OH$ and other oxidizing species HOCl which reacts with most organics converting into CO_2 ,H_2O and inorganic ions until their total mineralization is reached. It has been found that Pt electrode possesses greater O_2-overvoltage (+0.77V), thus generating higher amount of oxidant $^{\cdot}OH$. A clear solution is obtained after degradation indicates the absence of formation of insoluble metal oxides. This suggests that oxidizing intermediates which are formed resulting in destruction of the dye.

$$MO_x + {}^-OH \rightarrow MO_x\,({}^{\cdot}OH) + e^- \tag{4}$$

$$MO_x\,({}^{\cdot}OH) + D \rightarrow x\,CO_2 + x\,e^- + 2H^+ \tag{5}$$

$$D + M[ClOH^{\cdot}] \rightarrow H^+ + Cl^- + x\,CO_2 \tag{6}$$

Here, M= anodic site, D= Dye molecule

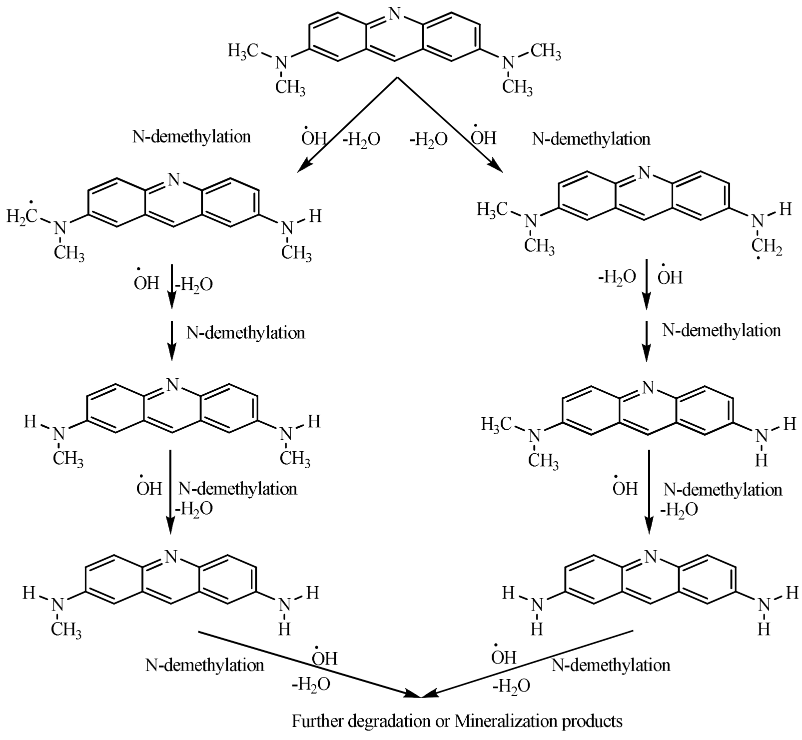

Figure 6: Proposed degradation pathway of acridine orange

Effect on COD of duration of treatment

The effect of rate of dye degradation on COD was determined. During the experiment the initial COD 704mg/l which gave rise to 40mg/l of COD, a 95% reduction in COD was achieved. The COD level obtained after degradation was within the permitted limit of 250mg/l. A graph showing COD reduction versus treatment time is shown in figure (7).

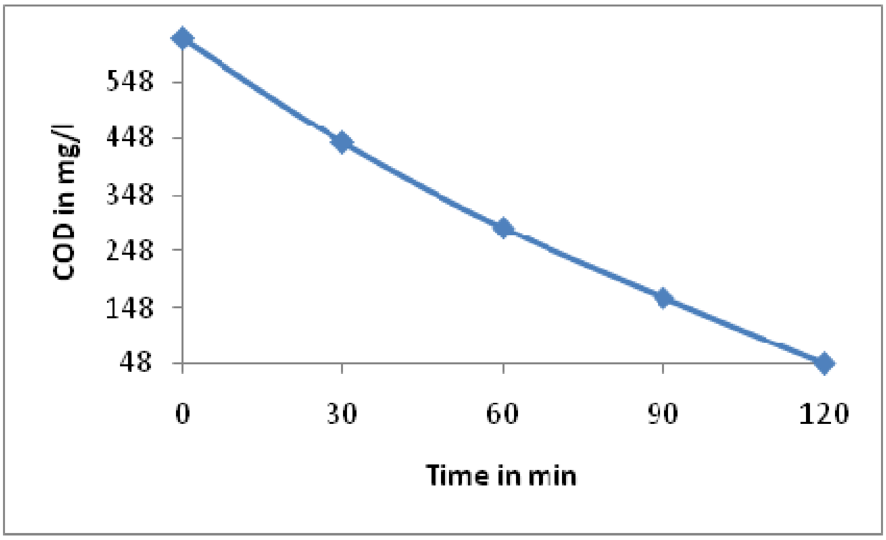

Figure 7: The rate of decrease of COD at different intervals of time.

The effect of current density, [dye] and [NaCl] on COD was measured. In all these cases the COD level decreased more than 90 %.

The instantaneous current efficiency (ICE) for the anodic oxidation of Acridine orange dye was calculated from the values of the COD using the equation,

$$\text{ICE } (\%) = \frac{(CODi - \text{COD}f)}{8It} \times FV \tag{7}$$

Here; COD_i and COD_f are the chemical oxygen demands before and after degradation respectively, 'I' the current , 'F' the Faraday constant, 'V' the volume of the electrolyte, 't' the treatment time and '8' is the oxygen equivalent mass (g eq^{-1}). The ICE data in tables (11, 12) indicates, the efficiency of the process linearly related to ICE and indicates higher efficiency of the process for RuDPt anode compared to Pt anode.

Table 11: ICE values at different experimental conditions for Pt electrode.

	Variables	*ICE*
Concentration of dye in 10^{-4}	0.50	36.93
	0.75	37.46
	1.0	28.52
	1.25	30.48
	1.50	39.62
Volume of NaCl in ml	1.0	16.17
	1.5	19.39
	2.0	28.52
	2.5	33.40
Current in mA	20	24.47
	30	25.36
	40	28.52
	50	56.18
	60	60.15
Temperature in K	288	18.80
	298	28.52
	313	41.97
	323	51.30

Table 12: ICE values at different experimental conditions for RuDPt electrode.

	Variables	*ICE*
Concentration of dye in 10^{-4}	0.75	235.46
	1.00	111.94
	1.25	118.37
	1.50	151.67
Volume of HCl in ml	1.0	44.68
	3.0	70.70
	4.0	111.94
	5.0	153.69
Current in mA	30	129.16
	40	131.13
	50	111.94
	60	158.08
	70	239.87
Temperature in K	288	66.39
	298	111.94
	313	132.78
	323	167.91

Kinetics of degradation

The degradation of dye depends with [dye], [NaCl], current and the concentration of surface active sites [S]. Since [S] remains constant, the rate of degradation in the present case is given by,

$$\frac{-dc}{dt} = \frac{k[NaCl]I}{[dye]} \tag{8}$$

The rate constant for the disappearance of Acridine orange for the degradation process was determined by plotting $\log T_t$ versus time (t). Here ‘Tt’ is percentage transmission of the light obtained from spectrophotometer, at /\max 490nm and it is inversely proportional to the concentration of the dye. A straight line was obtained for 60% of the degradation reaction and afterwards deviation in linearity was observed.

UV-Visible spectra

Figure 8 (A and B) represents UV-Visible spectra during the electrochemical degradation of Acridine orange dye. Broad visible colour absorption spectra at 490nm and 470 nm were completely removed at the end of the degradation process.

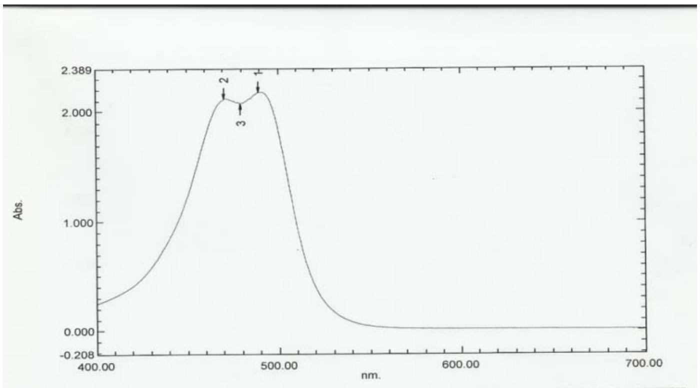

Figure 8 (A): UV-Visible spectra of AO before degradation.

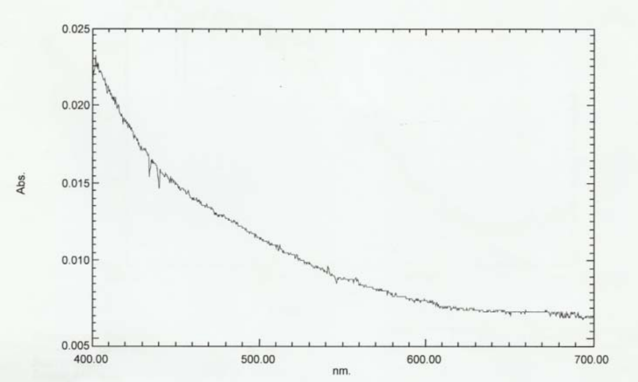

Figure 8 (B): UV-Visible spectra of AO after degradation.

Conclusion

Electrochemical oxidation is capable of destroying the chromophore groups of dyes found in industrial effluents at short treatment times and low energy consumption. This method can be applied to the remediation of waste waters containing this dye. The rates of Acridine orange elimination and COD removal were higher on the RuDPt electrode than that on the Pt electrode.

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