

Electrochemical Degradation of indigo carmine Dye at Pd/graphite Modified Electrode in Aqueous Solution

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Abstract: Degradation of indigo carmine dye(IC) in aqueous solution by Anodic oxidation with a Pd/graphite modified electrode (PdGME) can be applied to the remediation of waste water containing indigocarmine. It indicates that the graphite modified had excellent catalytic performance. The deposited Pd/graphite modified electrode was applied to electrochemical degradation of indigo carmine dye solution. This environmentally friendly method decontaminates completely aqueous solutions of this dye. These findings suggest that electrode based reactive sediment capping via sequential reduction/oxidation is a potentially robust and tunable technology for in situ contaminants degradation. The COD value decreases to -98% of the initial COD. Indigocarmine (IC) is more rapidly removed in Pd/graphite modified electrode than in Graphite electrode. The degradation rate increases with increasing current and electrochemical degradation of indigo carmine at palladium graphite follows 1 order kinetics up to 60% of the reaction. The ICE values of different experimental conditions are evaluated. These results indicated that the Pd/graphite modified electrode would be promising anode for electrochemical degradation of indigo carmine. The dye is converted into CO₂, H₂O, and simpler inorganic salts.

Keywords: Indigocarmine, anodic oxidation, palladium graphite modified electrode, Mineralization

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I. Introduction

The removal of indigo carmine from water and wastewater is a need of the highest order. Various technologies have been employed to remove IC from water and wastewater [1]. Wastewater from textile industries frequently contains significant amounts of non-biodegradable dyes [2]. Most of these dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental concern [3]. A variety of hazardous pollutants are discharged into the aquatic bodies from several industrial streams [4]. The dye from textile industries and other commercial dyestuffs have been a focus of environmental remediation in the last few years [5]. Conventional methods for the abatement of water pollution from dye and textile industries like adsorption, absorption, incineration and biodegradation were found to be ineffective and expensive. Moreover, they pose secondary disposal problems and associated increase in time and cost of operation [6, 10]. Large amounts of different dyes used in different industries. To avoid accumulation of dyes in the environment, powerful oxidation techniques are developed for the removal of dye in the industrial waste water [11, 12]. Studies have shown that indigo carmine reacts with chemical oxidants such as, Peroxo disulphite ion, chloramine-T and ozone [13, 14]. In the recent years, environmentally friendly electrochemical methods are developed to degrade organic pollutants in waste waters. 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 [15, 16]. However a limited number of papers have been published for the destruction of dyes by electrochemical methods [17, 18, 19]. Here we developed the electrochemical method for the degradation of indigo carmine dye with Pd/graphite modified electrode (PdGME) and the kinetics of degradation of indigo carmine was studied.

II. Experimental

A solution of indigo carmine(IC) (E-Merck) was prepared [0.0001M]. The 8cm length and 0.63cm diameter graphite electrode (ALFA AESAR) was using. The 2.5cm length graphite electrode is dipped into the above solution. Prior to experiment the surface pretreatment of graphite electrode was performed by hand polishing of the electrode surface with successive grades of emery papers down to 3000 grit up to a mirror finish. The polished electrode was then degreased with 1:1 HCL solution, acetone and washed with running doubly distilled water and utilized for further electro deposition. The experimental set up is shown in the figure (1). Palladium was deposited on Graphite electrode from PdCl₂ (Arora matthey) solution. All chemicals used were of accepted grades of purity. The experimental apparatus is shown in fig (1). It consists of reaction

chamber and a voltage power supply. The electrode system consists of a Graphite modified Electrode as anode and Pt electrode as cathode in case of degradation of dye by anodic oxidation with Graphite electrode. The distance of the anode and cathode was 2cm. The kinetic runs were carried out with Graphite electrode alone as anode. In another case, Pd (II) thin film deposited on a conductive Graphite electrode has taken as anode and Pt electrode as cathode. The experiment was run from 6 to 660minutes with continuous stirring. The kinetic runs were carried out for different concentration of indigo carmine with different applied current. To account for the mineralization of the dye solution COD was measured at regular intervals of time [20]. 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 2.1mA-6.1mA using rheostat (INSIF INDIA). The Decolonization and disappearance of indigo carmine was followed by using spectrophotometer (ELICO SL 171).

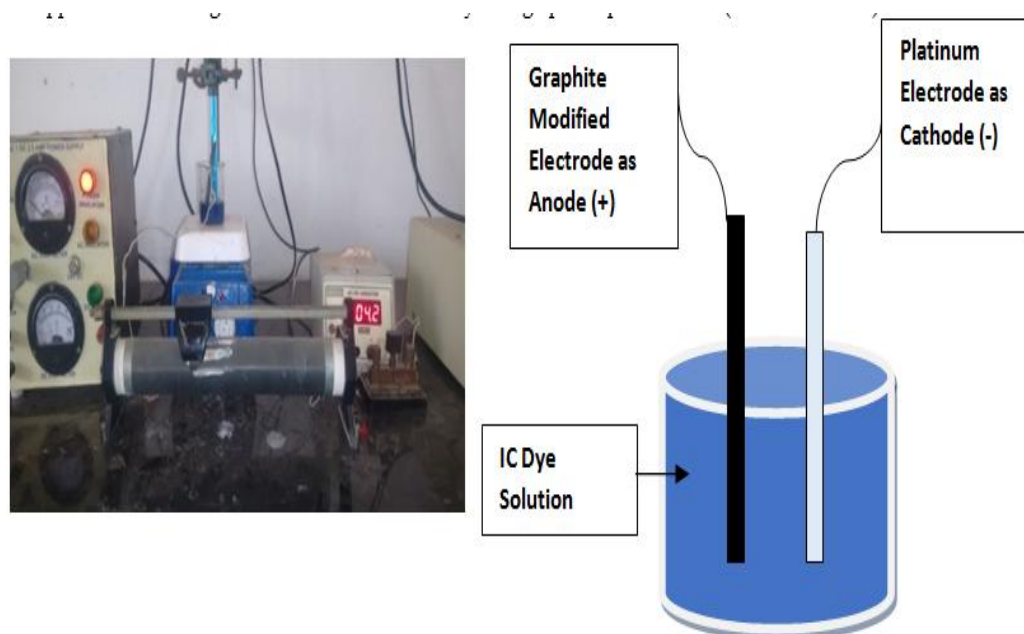


Fig. 1: Experimental set up for electrochemical degradation of IC Dye

III. Results And Discussion

3.1 Reaction with Graphite as anode electrode

3.1.1 Effect of Indigo carmine

The reaction performed in the presence of IC (E-Merck) was prepared [0.0001M] with constant current (4.1mA). The change in concentration of the indigo carmine was recorded by change in color using spectrophotometer. A plot of log%T (percentage transmittance of light) versus time was linear up to 60% of the reaction indicating disappearance of IC follows first order kinetics. The rate constant values are given in table (1), the reaction rate decreased with increase in [IC]. The decrease of rate at higher concentration is due to the formation of a thin film of dye on the surface of the graphite 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 remain constant. The COD for Indigocarmine solution before and after electrolysis were measured. (Table-1, Fig-2 and 3)

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

10 ⁴ [IC]	10 ⁴ k (Sec ⁻¹)	Effect of pH		COD values in mg/l	
		Before degradation	After degradation	Before degradation	After degradation
0.25	5.37	0.40	0.43	464	16
0.50	4.60	0.82	0.83	512	16
1.00	3.83	1.54	1.55	624	32
1.50	3.07	2.22	2.23	816	48
2.00	2.68	2.56	2.56	992	32

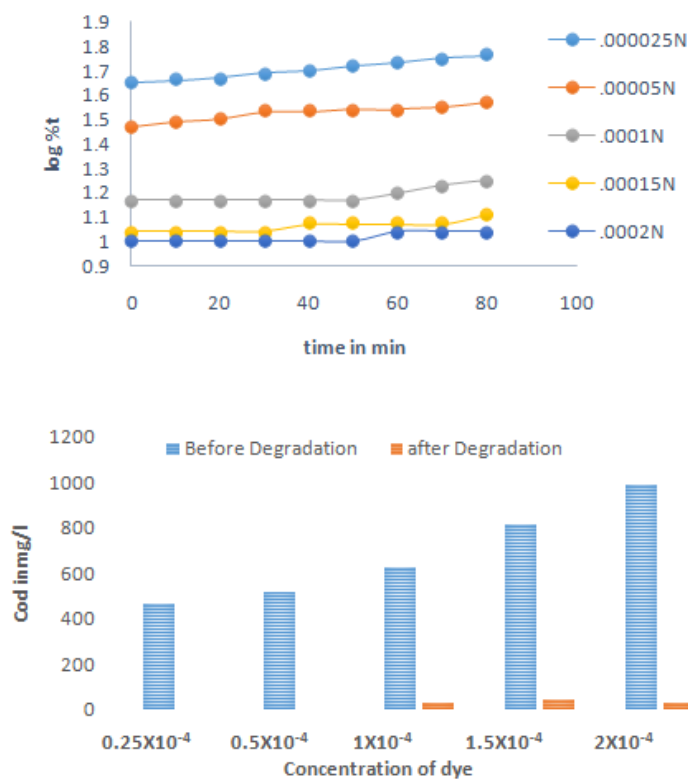


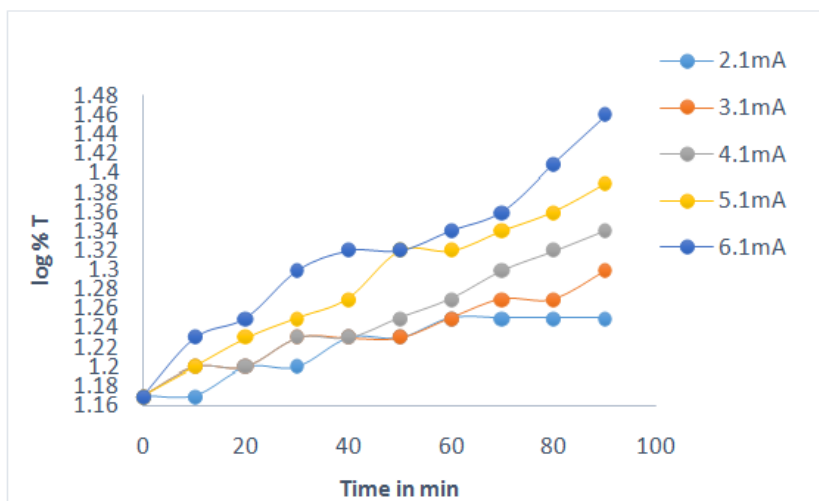
Figure 2 and 3: Effect of Concentration of IC on rate of degradation and COD Value

3.1.2 Effect of current on the rate

At fixed [IC] the rate of reaction increased with increase in applied current. The current is varied from 2.1mA-6.1mA. The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of degradation. The COD for different current of Indigocarmine solution before and after electrolysis were measured.(Table-2, Fig-4 and 5)

Table2: Effect of current on the rate of degradation and COD values.

Current in mA	$k^4 \text{ sec}^{-1}$	COD values in mg/l	
		Before degradation	After degradation
2.1o	0.38	624	48
3.1	0.49	624	16
4.1	0.69	624	32
5.1	0.92	624	32
6.1	10.74	624	16



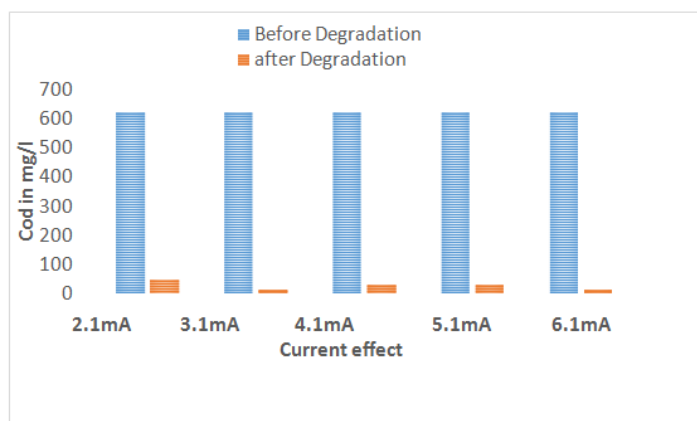


Figure 4 and 5: Effect of current of IC on the rate of degradation and COD Values

3.1.3 Effect of temperature.

The rate constant with respect to temperature increases first and then falls off with raising temperature. Indicates variation of chemisorption with temperature. The initial increase shows that, like the chemical reaction chemisorption also needs activation energy. However the later decrease indicates that at higher temperature desorption does occur in chemisorption process. Frequently during the high temperature desorption of some atoms of the adsorbent are in a chemically bound form. This indicates at lower temperature increases the adsorption capacity of the graphite. Hence the rate constant at higher temperature the desorption increases and the rate decreases. Thermodynamic parameters for the degradation of IC were calculated (Table-4)

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

Temperature in °C	10 ⁴ k sec ⁻¹	COD values in mg/l	
		Before degradation	After degradation
10	04.60	624	96
15	05.75	624	64
20	06.90	624	32
35	06.52	624	16
40	06.14	624	48
45	03.83	624	16

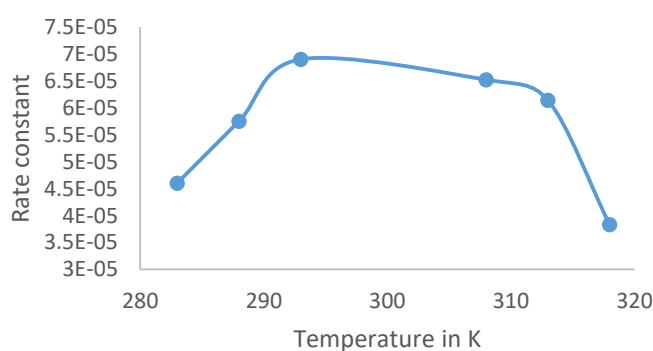


Figure 6: Effect of temperature of IC on the rate of degradation

Table 4: Thermodynamic parameters for the degradation of AO.

Temperature in K	ΔH	ΔS	ΔG
283	23.57	-244.26	92.69
288	23.52	-244.13	93.83
293	23.48	-244.30	95.06
308	19.84	-260.90	100.21
313	19.79	-262.71	102.04
318	19.75	-267.94	104.96

3.2 Reaction with palladium doped graphite (PdGME) as anode electrode

3.2.1 Effect of Indigo carmine

The reaction has been carried out in the presence of IC (0.0001M), by keeping current constant (4.1mA). The change in concentration of the Indigo carmine was recorded by change in color using spectrophotometer. A plot of logT (percentage transmittance of light) versus time was linear upto 60% Reaction indicating disappearance of IC follows first order kinetics. The reaction rate decreased with increase in [IC] and the values of rate constants were higher compared to graphite electrode as anode alone. The pH value before and after the electrolysis indicates slight increase towards alkaline pH. The COD for Indigocarmine solution before and after electrolysis were measured. (Table-5, Fig-7 and 8).

Table 5: Effect of [IC] on the rate of degradation and COD values for PdDGE electrode

10 ⁴ [IC]	10 ⁴ k Sec ⁻¹	Effect of pH		COD values in mg/l	
		Before degradation	After degradation	Before degradation	After degradation
0.25	23.42	0.40	0.42	464	16
0.50	19.18	0.82	0.83	512	32
1.00	27.25	1.54	1.55	624	32
1.50	13.81	2.22	2.24	816	48
2.00	11.51	2.56	2.57	992	48

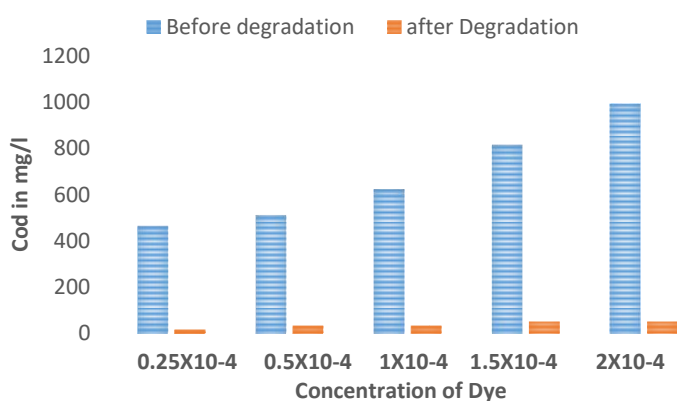
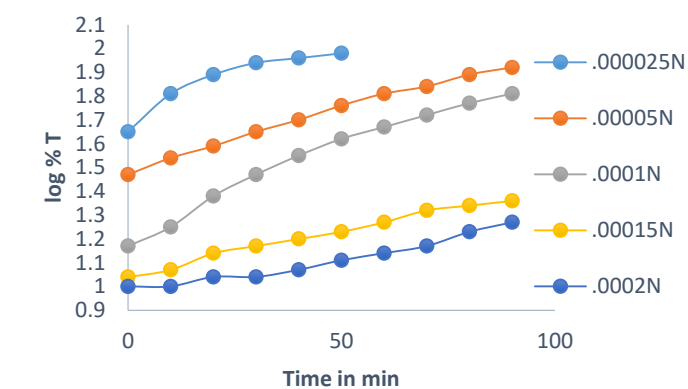


Fig. 7 and 8: Effect of concentration of IC dye on the rate of degradation and COD values

3.2.2 Effect of current on the rate

At fixed [IC] the rate of reaction increased with increased in applied current. The current is varied from 2.1 mA-6.1 mA. The rate of degradation is higher compared to graphite electrode as anode. The COD for different current of Indigocarmine solution before and after electrolysis were measured. (Table-6, Fig-9 and 10)

Table 6: Effect of current on the rate of degradation and COD values.

Current in mA	$10^4 k \text{ sec}^{-1}$	COD values in mg/l	
		Before degradation	After degradation
2.1	23.41	624	16
3.1	26.48	624	32
4.1	27.25	624	32
5.1	29.93	624	48
6.1	30.32	624	48

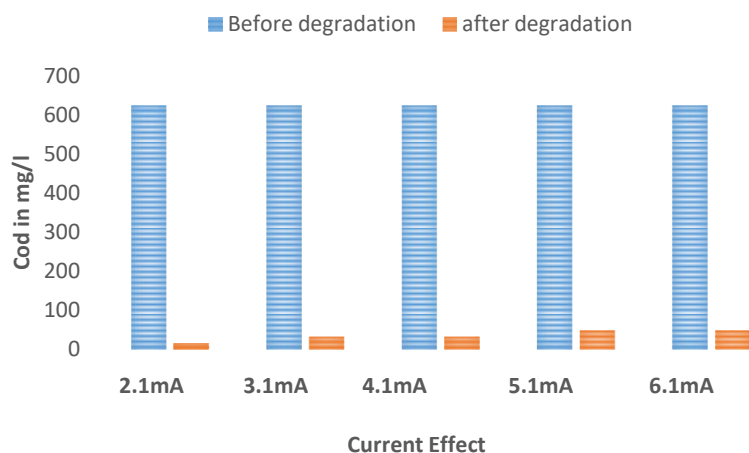
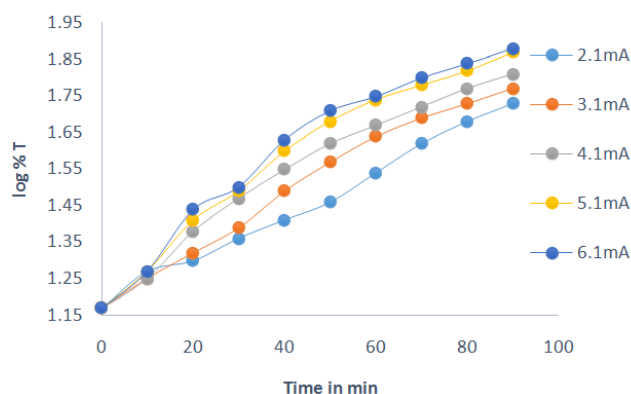


Figure 9 and 10: Effect of current of IC on the rate of degradation and COD Values

3.2.3 Effect of temperature

The rate constant with respect to temperature increases first and then falls off with raising temperature. Indicates variation of chemisorption with temperature. The initial increase shows that, like the chemical reaction chemisorption also needs activation energy. However the later decrease indicates that at higher temperature desorption does occur in chemisorption process. Frequently during the high temperature desorption of some atoms of the adsorbent are in a chemically bound form. This indicates at lower temperature increases the adsorption capacity of the graphite. Hence the rate constant at higher temperature the desorption increases and the rate decreases. The rate constants absorbed for Pd/graphite modified electrode are higher than the reaction taking place for graphite electrode. Similarly to previous observation here also the rate constant increases with temperature and falls of at higher temperature indicating the chemisorption at lower temperature and desorption at higher temperature. Thermodynamic parameters for the degradation of IC for Pd/graphite modified electrode were calculated (Table-8).

Table 7: 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
10	16.50	624	64
15	17.65	624	16
20	21.11	624	32
35	26.10	624	48
40	19.57	624	16
45	12.66	624	32

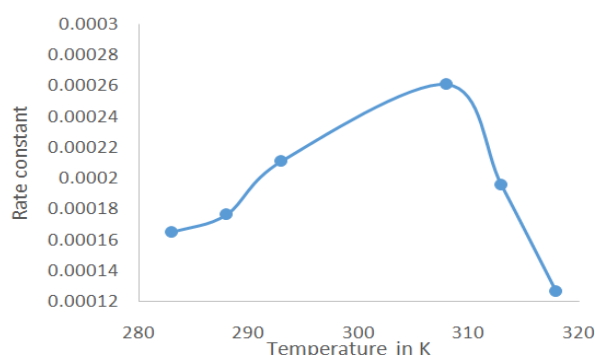


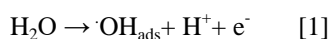
Fig 11: Effect of temperature of IC Dye with Pd modified graphite Electrode

Table 8 : Thermodynamic parameters for the degradation of IC for PdDGEelectrode

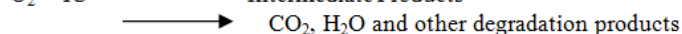
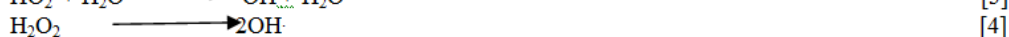
Temperature in K	ΔH	ΔS	ΔG
283	17.31	-255.80	89.76
288	17.31	-256.64	91.21
293	17.30	-256.10	92.34
308	14.66	-266.22	96.66
313	14.62	-269.61	98.96
318	14.58	-274.21	101.78

3.2.4 Production of OH radical

The degradation of Indigocarmine solutions were carried out by anodic oxidation. Further, the experiment is carried out in the presence of electrodes with Pt as cathode and graphite as anode. In the electrochemical technique .OH formed by direct electrolysis absorbed as intermediate at the surface of high O₂- overvoltage anode from oxidation of water.



The degradation of IC takes place due to sequential electrochemical reduction and oxidation. Graphite electrodes have high affinity for IC with implication that it will adversely affect electrode performance by competitive adsorption and interaction such as electron shuttling may increase the reactivity. The strong oxidizing agent .OH Radical, the sequential reduction/oxidation with graphite and Pt electrodes which reacts with IC converting into CO₂, H₂O and inorganic ions until their total mineralization is reached. It has been found that Pt electrode possesses greater O₂- over voltage (+0.77V), thus generating higher amount of oxidant 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. Considering the graphite electrode (GE) advantages such as commercial availability, low costs and easy of modification [21]. The present method can be used for remediation of waste water.



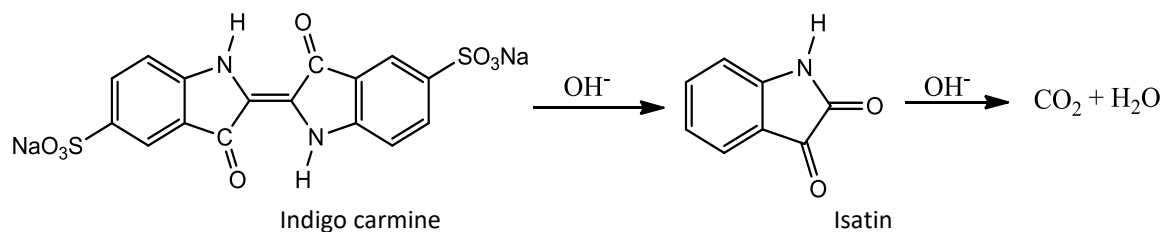


Fig. 12: Degradation pathway of Indigo carmine

3.2.5 Effect on COD of duration of treatment

The effect of rate of dye degradation on COD was determined. During the experiment the initial COD 624mg/l which gave rise to 48mg/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 (13).

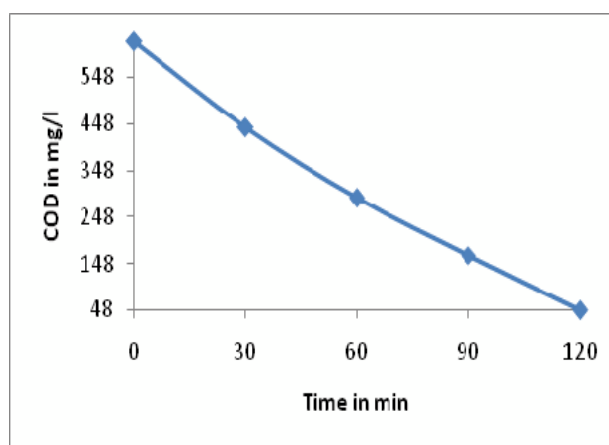


Fig.13: The rate of decrease of COD at different intervals of time.

The effect of current density, [dye] and COD was measured. In all these cases the COD level decreased more than 90 %.The instantaneous current efficiency (ICE) for the anodic oxidation of Indigocarmine dye was calculated from the values of the COD using the equation

$$ICE \quad (\%) = \frac{(COD_i - COD_f)}{8It} \times FV \quad [7]$$

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 (geq-1). The ICE data in table indicates, the efficiency of the process linearly related to ICE and indicates higher efficiency of the process for PdGME anode compared to GE anode

Table 9: ICE values at different experimental conditions for Graphite Electrode

Variables	ICE	
	Value	ICE
Concentration of Dye 10^{-4}	0.25	219.67
	0.50	208.46
	1.00	165.87
	1.50	161.39
Current in mA	2.10	228.17
	3.10	181.98
	4.10	165.87
	5.10	147.38
Temperature in K	283	91.53
	288	96.91
	293	124.40
	308	149.06
	313	135.5

Table10: ICE values at different experimental conditions for PdGME electrode

Concentration of Dye 10 ⁻⁴	Variables	ICE
		0.25
	0.50	470.73
	1.00	387.04
	1.50	347.61
Current in mA	2.10	582.06
	3.10	418.82
	4.10	387.04
	5.10	340.58
Temperature in K	283	299.5
	288	357.7
	293	387.04
	308	423.65
	313	397.50

3.2.5 Kinetics of Degradation

The degradation of dye taken place in the absence of electrolyte HCL or NaOH. The degradation of dye depends with [dye], current and the concentration of Surface active sites[S].Since[S]remains constant, the rate of degradation in the present case is given by

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

The rate constant for the disappearance of Indigo carmine for the degradation process was determined by plotting logT versus time (t). Here ‘T’ is percentage transmission of the light obtained from spectrophotometer, atλmax610nm 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.

3.2.6 Reuse of Palladium Graphite Modified Electrode

The possibility of reusing the Pd/graphite modified electrode was tested to see the cost effectiveness of the method adopted. After the degradation of the dye, the graphite modified electrode was thoroughly washed with double distilled water and then reused for the degradation by taking fresh dye solution. From the degradation study it was observed that the reuse of the graphite modified electrode to degrade the dye solution showed slightly lesser efficiency.

3.2.7 UV-Visible spectra

Figure 14 (A and B) represents UV-Visible spectra during the electrochemical degradation of Indigocarmine dye. A broad visible colour absorption spectra at 610nm was completely removed at the end of the degradation process. However, the absorption in the UV-region indicates less intense small peak which shows the presence of a minute concentration of organics (<48mg/l COD).

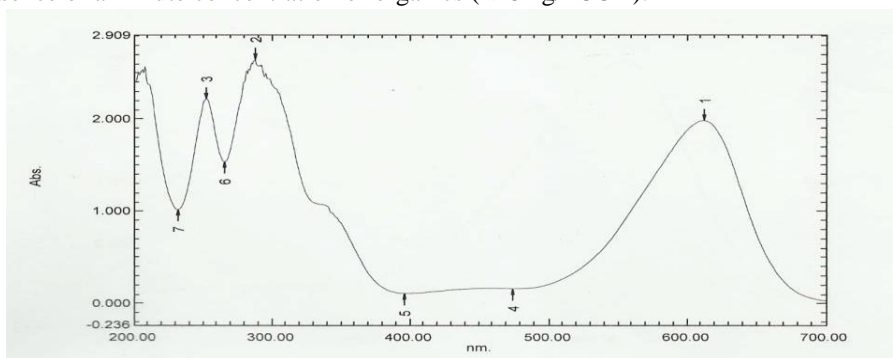


Fig. 14 (A): UV-Visible spectra of IC before degradation

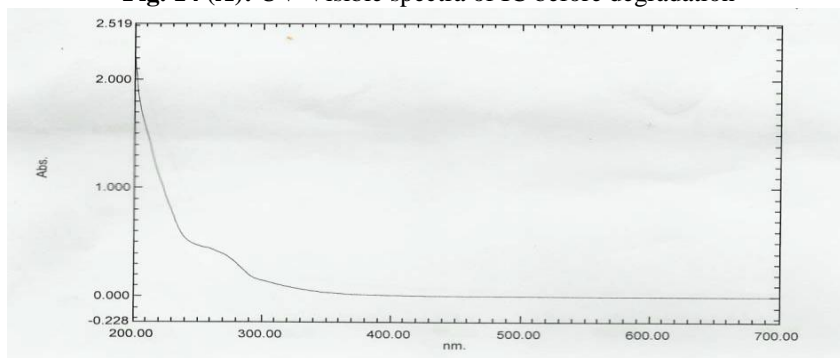


Fig. 14 (B): UV-Visible spectra of IC after degradation.

IV. Conclusion

Electrochemical oxidation in presence of graphite and palladium modified electrode is capable of destroying the chromophore groups of dye found in industrial effluents at short treatment times, low energy consumption and reuse of graphite electrode. This method can be applied to the remediation of wastewater containing dyes and organics. Hence the method is cost effective as graphite electrode is used. The rates of Indigo carmine elimination and COD removal were higher on the Pd/graphite modified electrode than that of the graphite electrode.

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