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Electrochemical Degradation of 9-(2-Carboxyphenyl)-6-(diethyl amino)-N, N-diethyl-3H-xanthen-3-iminium chloride Dye at Sn/graphite Modified Electrode in Aqueous Solution

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ABSTRACT

The main aim of this research is to develop a systematic method for the electrochemical degradation of Rhodamine-b dye from its aqueous solution by synthesized Sn/graphite modified electrode. It can be used to investigation of waste water containing Rhodamine-b. It indicates that the Sn/graphite modified electrode had very good catalytic activity. The deposited Sn/graphite modified electrode was applied to electrochemical degradation of Rhodamine-b dye solution. It gives the comparison between the kinetics of degradation by graphite and Sn/graphite modified electrode. On the basis of the effect of Rhodamine-b dye concentration, pH, current density and different temperature, degradation rate is to be studied. UV-Visible spectra before and after degradation of dye was measured. The anodic oxidation by Sn/graphite modified electrode showed the complete degradation of aqueous solution Rhodamine-b, which is confirmed by UV-Visible and COD measurements. This process is one of the advanced oxidation processes (AOPs).It generates hydroxyl free radicals ($^{\cdot}OH$) which attack the dye molecules, resulting in degradation of the dye molecules. The thin film formation of Sn or encapsulated in graphite rod is observed from SEM/EDAX. The ICE values of different experimental conditions are calculated. These results indicated that the Sn/GME would be promising anode for electrochemical degradation of Rhodamine-b. This dye is converted into CO_2, H_2O and simpler inorganic salts. This method can be applied for the remediation of waste water containing organics, cost effective and simple.

Graphical Abstract

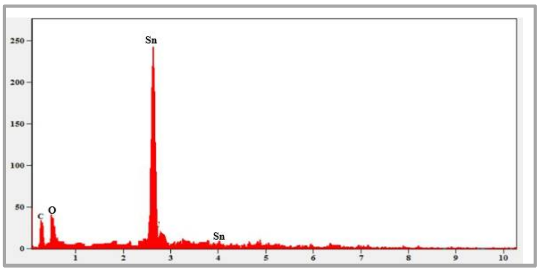


Figure 12(B). EDAX spectra of Sn/GME

Keywords: Rhodamine-b, Stannous graphite modified electrode (Sn/GME).

INTRODUCTION

Nowadays, to improve application performances, many dyes are synthesized with improved properties, such as thermal stability, photo-resistance and chemical resistance. Dyes are organic compounds that represent an important group of pollutants. They are used in various areas, such as the textile, plastics, rubber, leather, cosmetics and paper indus-tries, with highly toxic components and serious environmental impacts. It is believed that the dyeing industry is responsible for releasing 100 tons of dyes per year into the environment, contaminating rivers and springs of these dyestuffs,5–10% is lost in industrial effluents, and consequently, wastewater treatment is one of the biggest problems we face today once the dyes are exposed to water, they are difficult to remove, as they are of synthetic origin and have a very complex molecular structure, with stability designed to withstand degradation by light, chemical, biological and other factors. This makes them very difficult to degrade [**1-5**]. Textile industries use large volumes of water in their operations and thus release large amounts of waste water. Waste waters from textile industries are unique in their composition; they are usually released containing various dyes and heavy metals. In particular, the dyes tend to be reactive dyes since these have such qualities that make them a preferred option in textile industries. However, they have been reported to be the most problematic of all dyes used in these industries. Their high solubility makes their treatment by conventional methods difficult. The effects of dyes in the water body are not limited to toxicity, but also include reduction in dissolved oxygen and interruption of photosynthetic processes. Most of the reactive dyes, including rhodamine B, used in the textile and allied industries are known to be carcinogenic [**6-10**]. One of the most important dyes within the overall category of dyestuffs is Rhodamine B. Rhodamine B, an important representative of xanthene dyes, is a water-soluble synthetic dye extensively used as a colorant in textile industries and food stuffs, and is also a well-known water tracer fluorescent, which has the property of carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and chronic toxicity towards humans and animals.Therefore, it is very important to remove Rhodamine B and other dangerous dyes from industrial wastewater before being discharged into environment. There are various methods available for dye removals which include chemical coagulation-flocculation, adsorption, chemical oxidation, photocatalytic,degradation and membrane filtration. Amongst the numerous techniques of dye removal, the adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater. Therefore, many researchers have studied the feasibility of using various types of adsorbents for the removal of Rhodamine B from aqueous solutions [**11-14**]. Carbon based electrodes are widely used in electrochemical applications due to their good electrical conductivity and chemically inert behavior. Moreover, the inexpensive manufacturing costs compared to alternative electrode materials such as precious metal electrodes, in addition to adaptable morphology and capability of change in surface chemistry which can greatly influence its electrochemical behavior, make them a favorable choice [**15**]. Here we developed the electrochemical method for the degradation of Rhodamine-B dye with Sn/graphite modified electrode (Sn/GME) and the kinetics of degradation of Rhodamine-B was studied.

MATERIALS AND METHODS

A solution of Rhodamine-B (LOBACHEMIE) was prepared [0.0001M]. The 8.9 cm length and 0.55 cm diameter graphite electrode (ALFA AESAR) was using. The 1.6 cm length graphite electrode is dipped into to 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 electrode position. The experimental setup is shown in the figure 1. Stannous was deposited on graphite electrode from $SnCl_2$ (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 graphite modified electrode as anode and a Sn electrode as cathode in case of degradation of dye by anodic oxidation with graphite electrode in the figure 2. The distance of the anode and cathode was 2

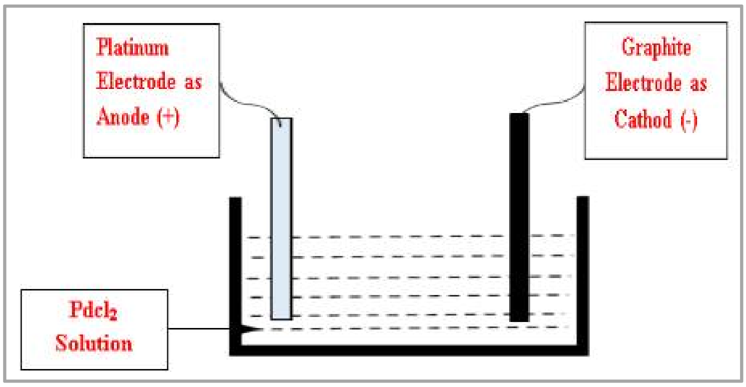


Figure 1. Synthesis of Sn/GME by electrochemical method.

cm. The kinetic runs were carried out with graphite electrode alone as anode. In another case, Sn (II) thin film deposited on a conductive graphite electrode has taken as anode and Sn electrode as cathode. The experiment was run from 10 to 360 minutes with continuous stirring. The kinetic runs were carried out for different concentration of Rhodamine-b and different applied current. To account for the mineralization of the dye solution COD was measured at regular intervals of time. 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 3.2 mA-6.2 mA using rheostat (INSIFINDIA). The decolourisation and disappearance of Rhodamine-b was followed by using spectrophotometer (ELICO SL171).

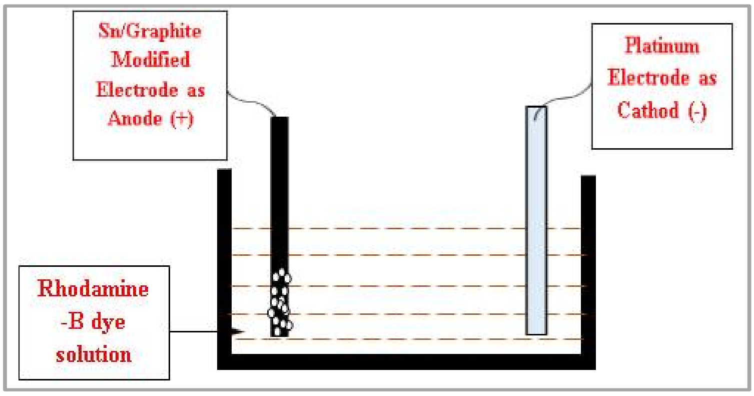


Figure 2. Experimental set up for electrochemical degradation of Rhodamine-b Dye.

RESULTS AND DISCUSSION

Reaction with graphite as anode electrode

Effect of Rhodamine-b on the rate: The reaction performed in the presence of Rhodamine-b (0.0001M), with constant current (5.2 mA). The change in concentration of the Rhodamine-b was recorded by change in colour using spectrophotometer. A plot of log%T (percentage transmittance of light) versus time was linear upto 65% of the reaction indicating disappearance of Rhodamine-b follows first order kinetics. The rate constant values are given in table 2. The reaction rate decreased with increase in Rhodamine-b. 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 shows slight increase towards the acidic pH after degradation. The COD for Rhodamine-b solution before and after electrolysis were measured (Table 2, Figure 3).

Table 2. Effect of Rhodamine-b on the rate of degradation and COD values

Conc of Rhodamine-b in 10^{-4}M	10^4 k in sec^{-1}	Effect of pH		COD Values in mg L^{-1}	
		Before degradation	After degradation	Before degradation	After degradation
0.5	0.614	6.67	6.71	446	16
1.0	0.307	6.96	7.13	816	16
1.5	0.268	7.09	7.19	992	32
2.0	0.230	7.15	7.23	1224	48

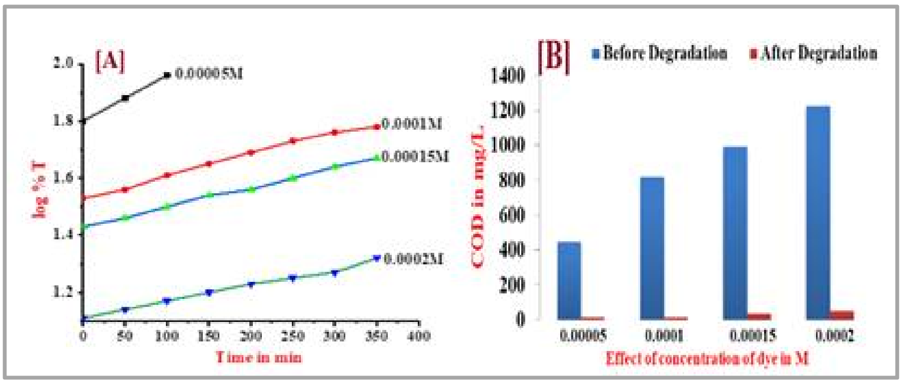


Figure 3. Effect of Concentration of Rhodamine-b on rate of degradation and COD Value.

Effect of current on the rate: To examine the effect of applied current the experiment is carried out for four different current varied from 3.2 mA-6.2 mA and keeping Rhodamine-b (RB) dye concentration as constant. The rate of the reaction is increased with increase in applied current. The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of degradation. The rate constant values are given in table 3. The COD for different current of Rhodamine-b dye solution before and after electrolysis were measured (Table 3, Figure 4).

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

Current in mA	10^4 k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
3.2	0.191	816	16
4.2	0.230	816	32
5.2	0.307	816	16
6.2	0.345	816	32

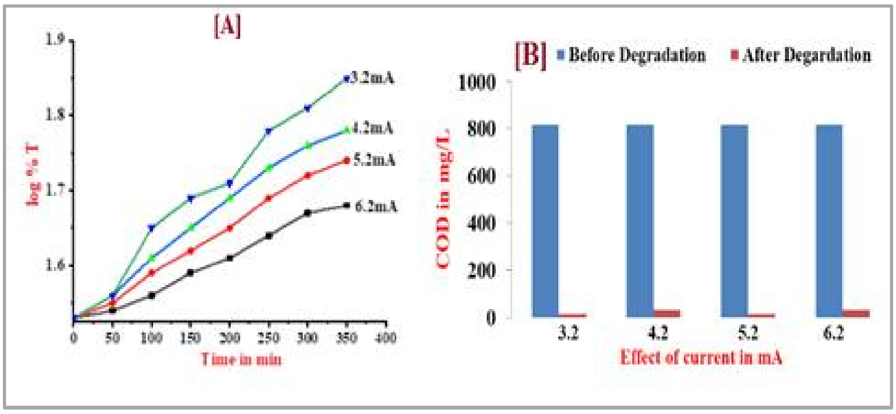


Figure 4. Effect of current of Rhodamine-b on the rate of degradation and COD Values.

Effect of Temperature: To examine the effect of temperature the experiments is carried out at three different temperatures, the increase of temperature the rate of the reaction is increased. It is observed that the rate of removal of colour is not very significant at low temperature. However the reactions is more significantly influenced at higher temperature, the rate constant and COD for before and after degradation of dye are reported in table 4 and figure 5. Since the diffusion rate is increased with temperature, an increase of temperature could bring about an increase in the degradation rate. Thermodynamic parameters are calculated and are reported in table 5.

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

Temperature in K	10^4k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
298	0.153	816	32
303	0.307	816	16
313	0.345	816	16

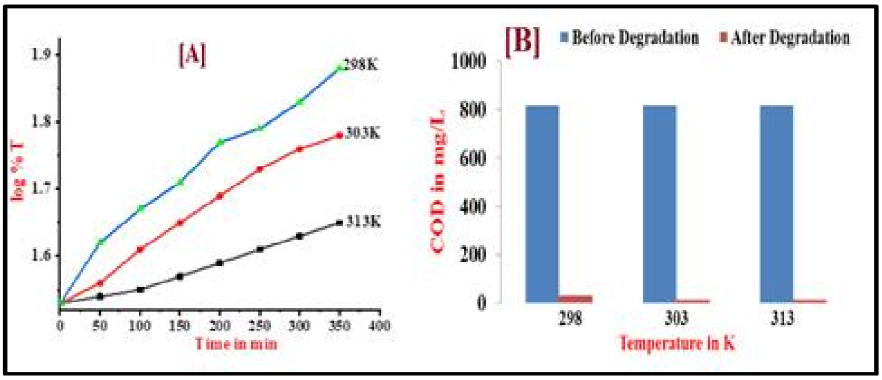


Figure 5. Effect of temperature of Rhodamine-b on the rate of degradation and COD Values.

Table 5. Thermodynamic parameters for the degradation of Rhodamine-b

ΔH$^{\#}$ kJ mol^{-1}	ΔS$^{\#}$ J K^{-1} mol^{-1}	ΔG$^{\#}$ kJ mol^{-1}	Ea
45.34	-183.29	99.98	47.86 kJ mol^{-1} (11.441x 10^3cal mol^{-1})

Reaction with Stannous graphite Modified (Sn/GME) as anode electrode

Effect of Rhodamine-bon the rate: The reaction has been carried out in the presence of Rhodamine-b (0.0001M), by keeping constant current 5.2 mA. The change in concentration of the Rhodamine-b was recorded by change in colour using spectrophotometer. A plot of log%T (percentage transmittance of light) versus time was linear upto 65% of the reaction indicating disappearance of Rhodamine-b follows first order kinetics. The rate constant values are given in table 6. The reaction rate decreased with increase in Rhodamine-b and the values of rate constants were higher compared to graphite electrode as anode. The pH value of before degradation slightly increases and after the electrolysis shows slight increase towards the alkaline pH. The COD for Rhodamine-b solution before and after electrolysis were measured. (Table 6, Figure 6).

Table 6. Effect of [Rhodamine-b] on the rate of degradation and COD values for Sn/GME

[Rb] 10^{-4} M	10^4 k in sec^{-1}	Effect of pH		COD Values in mg L^{-1}	
		Before degradation	After degradation	Before degradation	After degradation
0.5	2.034	6.67	6.73	446	16
1.0	1.919	6.96	7.16	816	16
1.5	1.343	7.09	7.21	992	48
2.0	0.959	7.15	7.23	1224	64

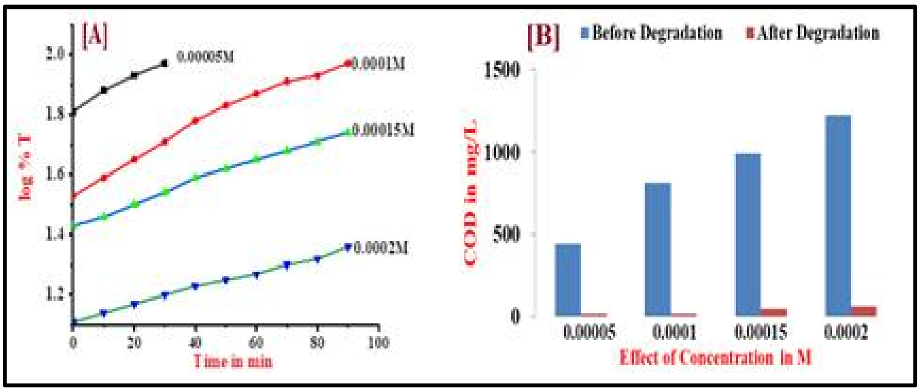


Figure 6. Effect of Concentration of Rhodamine-b on rate of degradation and COD Value.

Effect of current on the rate: At fixed [RB] the rate of reaction increased with increase in applied current. The current is varied from 3.2 mA-6.2 mA. The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of degradation. The rate of degradation was higher compared to graphite electrode because of the catalytic activity of Sn. The rate constant values are reported in table 7 and figure 7 (A).The COD values for before and after degradation were measured and reported in table 7 and figure 7(B).

Table 7. Effect of Current on the rate of degradation and COD values for Sn/GME

Current in mA	10^4k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
3.2	1.151	816	48
4.2	1.650	816	32
5.2	1.919	816	16
6.2	2.379	816	32

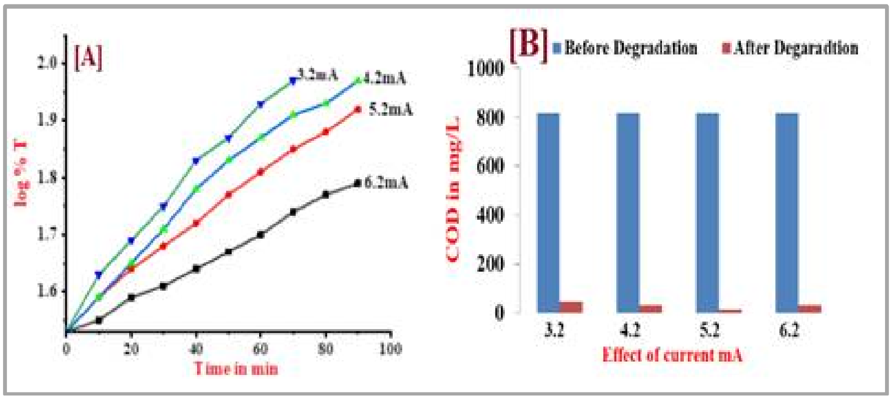


Figure 7. Effect of current of Rhodamine-b on the rate of degradation and COD Value.

Effect of Temperature: To investigate the effect of temperature, the experiments were carried out at three different temperatures. It is clear that, the increase of temperature increases the rate of the reaction, and observed that, the rate of removal of degradation is not very significant at low temperature. However the reaction was more significantly influenced at higher temperature. The degradation efficiency was high for Sn/GME compare to graphite electrode. The rate constant values and COD values for before and after degradation are reported in table 8 and figure 8. Since the diffusion rate is increased with temperature, an increase of temperature could bring about an increase in the degradation rate. Thermodynamic parameters for the degradation of Rhodamine-b by Sn/GME electrode were measured and reported in table 9.

Table 8. Effect of Temperature on the rate of degradation and COD values for Sn/GME

Temperature in K	10^4k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
298	1.305	816	32
303	1.919	816	16
313	2.533	816	16

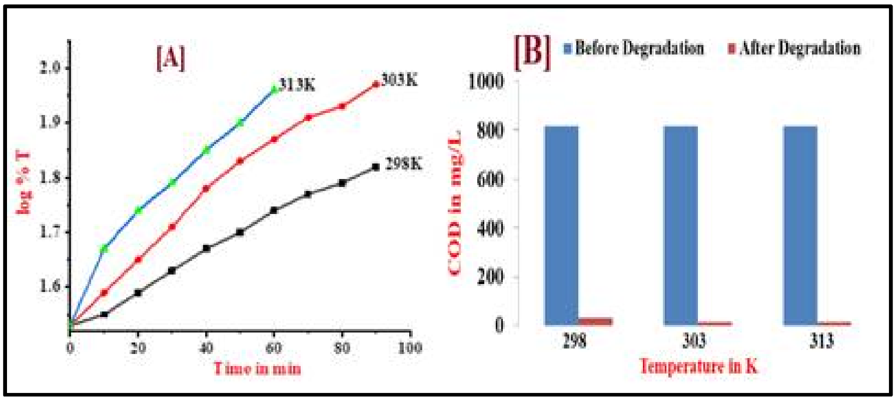


Figure 8. Effect of temperature of Rhodamine-b on the rate of degradation and COD Values.

Table 9. Thermodynamic parameters for the degradation of Rhodamine-b for Sn/GME

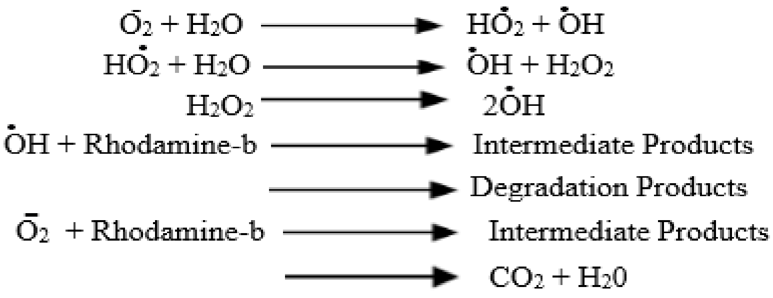
$\Delta H^{\#}$ kJ/mol	$\Delta S^{\#}$ J/K/mol	$\Delta G^{\#}$ kJ/mol	Ea
31.98	-210.70	95.16	32.23kJ mol^{-1} (7.705x10^{3}cal mol^{-1})

Production of OH radical: The degradation of Rhodamine-b 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 theelectrochemical technique .OH formed by direct electrolysis and absorbed as intermediate at the surface of high O_2^-overvoltage anode from oxidation of water.

$$H_2O \longrightarrow OH_{ads} + H^+ + e^- \qquad ...1$$

The degradation of Rhodamine-b takes place due to sequential electrochemical reduction and oxidation [16]. Graphite electrodes have high affinity for Rhodamine-b 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 Rhodamine-b converting into CO_2, H_2O and inorganic salts like bromides. Until their total mineralization is reached [17]. It has been found that Pt electrode possesses greaterO_2^- 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 electrodes (GE) advantages such as commercial availability, low costs and easy of modification [18]. The present method can be used for remediation of waste water.

Effect on COD of duration of treatment: The effect of rate of dye degradation on COD was determined. During the experiment the initial COD 446 mg L^{-1} which gave rise to 40 mg L^{-1} of COD, a 95% reduction in COD was achieved. The COD level obtained after degradation was within the permitted limit of 250 mg L^{-1}. A graph showing COD reduction versus treatment time is shown in figure 9.



Scheme 1. Proposed degradation pathway of Rhodamine-b.

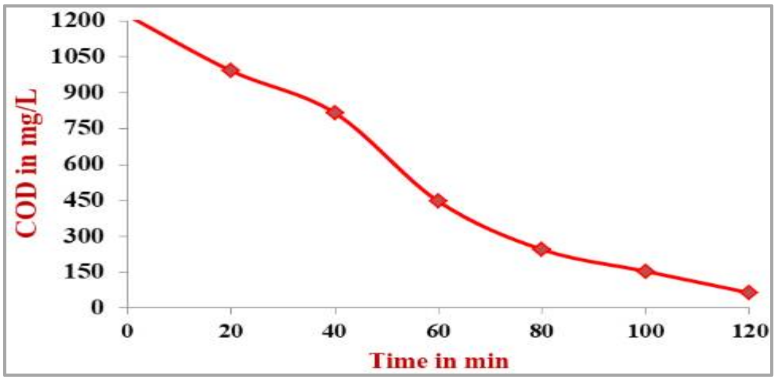


Figure 9. The rate of decrease of COD at different intervals of time.

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 Rhodamine-b dye was calculated from the values of the COD using the equation,

$$\boxed{ICE(\%) = \frac{(CODi - CODf)}{8It} \times FV}$$

Here; CODi and CODf are the chemical oxygen demands before and after degradation respectively, 'I' the current, 'F' the Faraday constant, 'V' the volume of the electrolytethe treatment time and '8' is the oxygen equivalent mass (geq-1). The ICE data in tables 10 and 11 indicates, the efficiency of the process linearly related to ICE and indicates higher efficiency of the process for Sn/GME anode compared to GE anode.

Table 10. ICE Values at different experimental conditions for Graphite Electrode

	Variables	ICE
Concentration of Dye 10^{-4}M	0.5	181.35
	1.0	123.71
	1.5	118.36
	2.0	131.26
Current in mA	3.2	172.32
	4.2	145.26
	5.2	123.71
	6.2	138.66
Temperature in K	298	101.03
	303	123.71
	313	161.37

Table 11. ICE Values at different experimental conditions for Sn/GME

	Variables	ICE
Concentration of Dye 10^{-4}M	0.5	664.98
	1.0	412.39
	1.5	291.97
	2.0	283.24
Current in mA	3.2	413.57
	4.2	375.27
	5.2	412.39
	6.2	435.80
Temperature in K	298	279.79
	303	412.39
	313	618.58

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

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

The rate constant for the disappearance of Rhodamine-b for the degradation process was determined by plotting log%T versus time (t). Here'T' is percentage transmission of the light obtained from spectrophotometer, at λ_{max}510 nm 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.

Reuse of Stannous Graphite Modified Electrode: The possibility of reusing the Sn/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 lesser efficiency.

UV-Visible spectra: Figure 10 (A and B) represents UV-Visible spectra during the electrochemical degradation of Rhodamine-b dye. Broad visible colour absorption spectra at 510 nm were completely removed at the end of the degradation process.

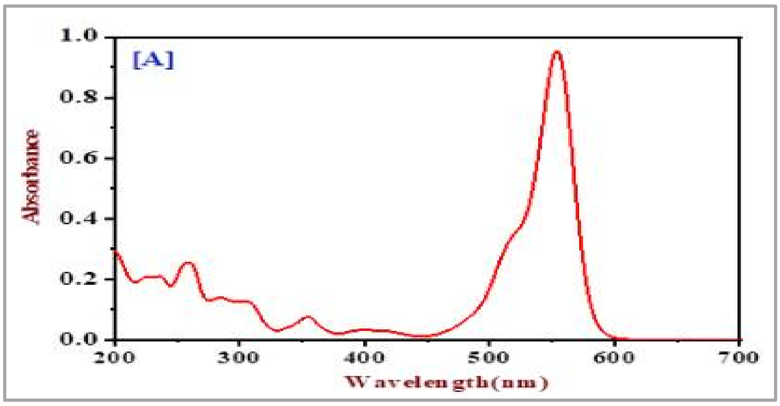


Figure 10(A). UV-Visible spectra of Rhodamine-bbefore degradation.

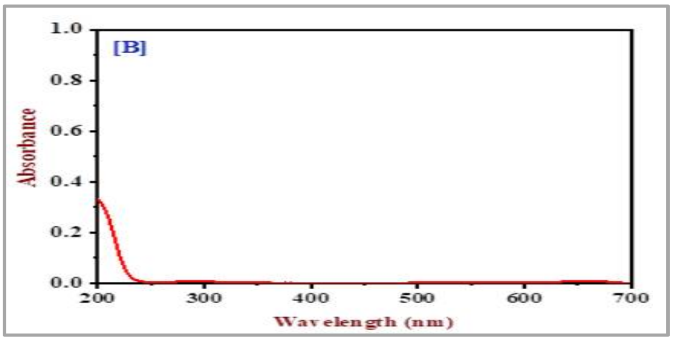


Figure 10(B). UV-Visible spectra of Rhodamine-bafter degradation.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS): Scanning electron microscopy (SEM) is used to differentiate the Stannous (Sn) deposited graphite electrode and bare graphite electrode. Figure 11(A) and 11(B) shows the SEM image of graphite flake and its corresponding EDX profile. From the micrograph, the layered and homogenous nature of graphite was observed in different diameter. It is clear from the figure 11(A) before deposition only graphite flakes are found. The observed size of graphite flake was ranging from 10 to 50µm. From the EDX profile, the presence of carbon and oxygen content indicated the graphite present in the pure form figure 11(B).

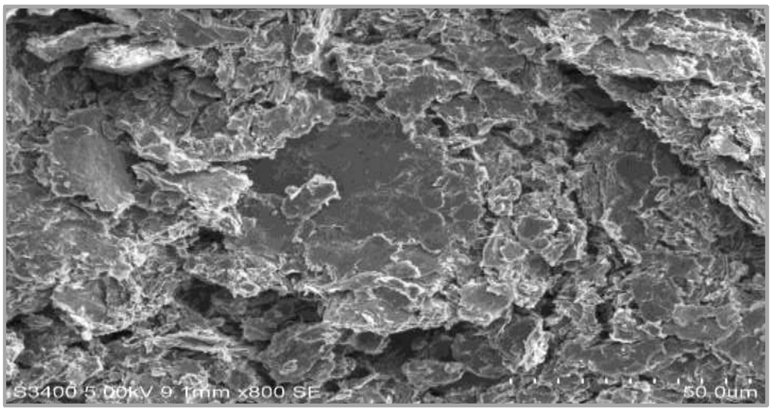


Figure 11(A). SEM micrographs of graphite Electrode.

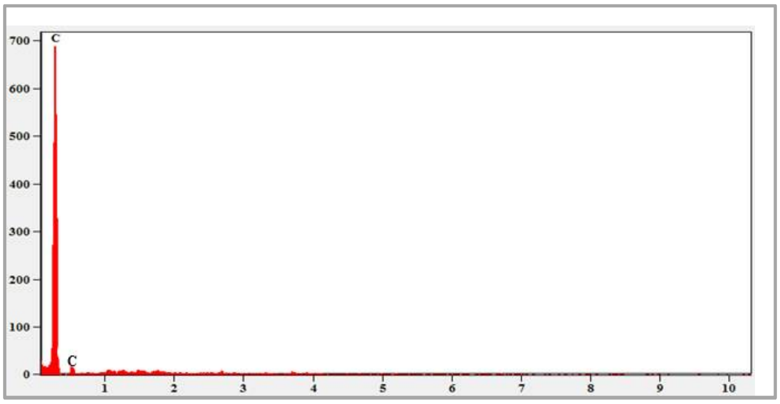


Figure 11(B). EDAX spectra of graphite Electrode.

Table 12. Quantitative results for graphite Electrode

Element Line	Weight %	Weight % Error	Atom %
C K	100.00	± 2.20	100.00
C K	0.00	---	0.00
Total	100.00		100.00

Figure 12(A) and (B) shows the SEM and EDX profile of stannous encapsulated in graphite rod. The SEM image of stannous encapsulated graphite rod can clearly distinguish from graphite rod. Further, the heterogeneous block dots were observed on the surface, which indicates the stannous doped or encapsulated inside the graphite rod figure 12(A). The corresponding EDX plot as shows in figure 12 (B). From the EDX plot, we clearly noticed the presence of stannous peaks in different oxidation states along with graphite carbon peak.

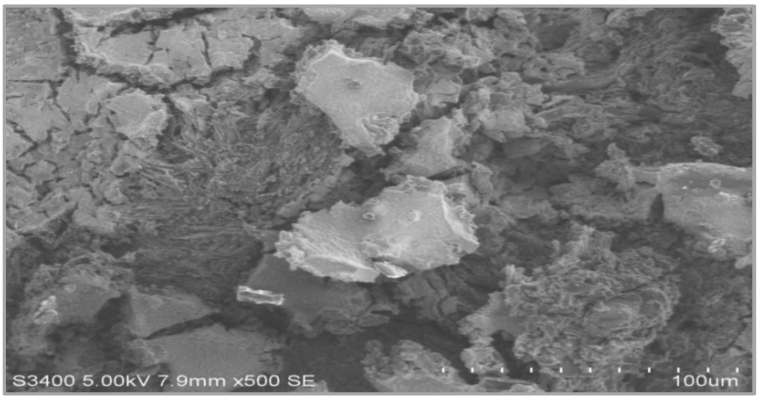


Figure 12(A). SEM micrographs of stannous graphite modified electrode.

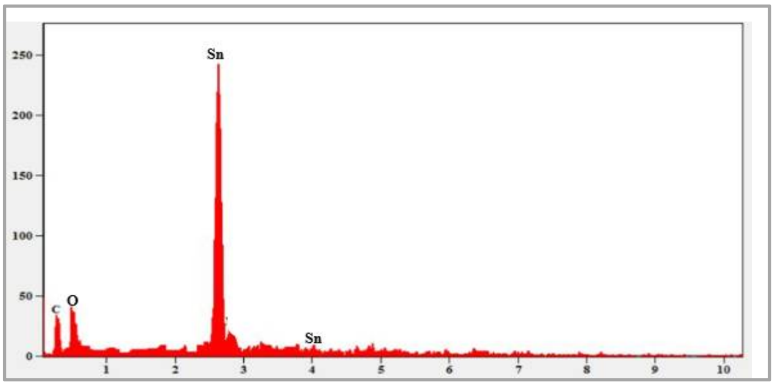


Figure 12(B). EDAX spectra of Sn/GME

Table 13. Quantitative results for stannous graphite modified Electrode

Element Line	Weight %	Weight % Error	Atom %
C K	---	---	---
O	10.67	± 0.56	47.00
Sn L	89.33	± 1.44	53.00
Sn M	---	---	---
Total	100.00		100.00

APPLICATION

This method can be applied to the remediation of wastewater containing dyes and organics and the method is cost effective as graphite electrode was used.

CONCLUSION

In this paper, electrochemical oxidation in presence of graphite electrode and Sn/GME was 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 and the method is cost effective as graphite electrode was used. The rates of Rhodamine-b elimination and COD removal were higher on the Sn/GME compare to graphite electrode.

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