Electrochemical Degradation of Phenothiazine- 5-ium, 3, 7-bis (dimethyl amino) Dye at Sn/graphite Modified Electrode in Aqueous Solution

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Abstract
In the present study, the electrochemical degradation of Methylene blue dye from its aqueous solution by synthesized Sn/graphite modified electrode. The comparison between the kinetics of degradation by graphite and Sn/graphite modified electrode has been studied systematically. The effects of various parameters like 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 methylene blue, 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 methylene blue. This dye is converted into CO_2, NO_2, H_2O and simpler inorganic salts. This method can be applied for the remediation of waste water containing organics, cost effective and simple. The results of the study prove that the method is a potential technique for the treatment of azo dye wastewater.
Keywords: *Methylene Blue, Stannous graphite modified electrode (Sn/GME)*

I.   Introduction

Decomposition of water resources by wastewater encompass synthetic color compounds, specifically in the textile industry, is a major environmental concern. Today, more than 100,000 types of commercial dyes have an annual production rate of about 700,000 tons. Of these, approximately 15% of the dye compounds used in industry enter the effluent during the production and processing stages and are eventually discharged into the environment. Most of the colorful compounds, as well as the intermediates produced by their degradation, are considered as a major health hazard for the human environment and other organisms, especially aquatic life [1].At the moment, several biological, physical and chemical processes are used to treat dye effluents. However, conventional sewage plant treatments are usually ineffective for dye removal because of their high biochemical stability, their relatively high molecular weight and the presence of aromatic rings. Physical methods such as precipitation, coagulation, filtration, adsorption, although effective in decolourisation have the disadvantage of sludge formation which requires the regular regeneration of the adsorbents. Chemical oxidation with ozone, Fenton's reagent and advanced oxidation processes are quite expensive and present operational problems [2-4]. Generally, a conventional wastewater treatment scheme consists of a pre-treatment step followed by primary, secondary, and tertiary treatments that involve physical, chemical, and biological processes, which are selected and designed based on the characteristics of the wastewater and the target contaminants. However, conventional wastewater treatment methods are often ineffective or insufficient for the removal of recalcitrant organic compounds and they may cause the formation of hazardous or even more toxic transformation products. Most of the recent research has been focused on the development of advanced oxidation processes (AOPs) . These processes are based on the in situ generation of a sufficient quantity of highly reactive oxidizing agents such as ozone or hydroxyl radicals that are efficient in breaking down persistent organic contaminants. Electrochemical advanced oxidation processes (EAOPs) are capable of degrading organic materials to CO_2 and H_2O through reaction with hydroxyl radicals (HO$\cdot$) [5-7]. In recent years, electrochemical oxidation has attracted more attention owing to its wide application, simple equipment, easy operation, high efficiency, and environmental compatibility, Azo dyes are the largest group of dyes, and they are widely used in the textile industry [8, 9].

Methylene blue (MB) is classified in the cationic dye group, which is used in various applications including chemistry, biology, medical sciences, and dyeing. Long-term exposure to this dye leads to vomiting, nausea, anemia, and hypertension. Carbon materials have been widely used in both analytical and industrial electrochemistry. The advantages of carbon electrodes are low cost, wide potential window, inert and electrocatalysis activity for a variety of redox reaction. Carbon electrode is superior material of noble metals for oxidation and reduction of organic and biological molecules in both aqueous and nonaqueous media [10-12]. Graphite modified electrodes represent a modern approach to electrochemical system. The two major approaches for the synthesis of GMEs are to understand the mechanism of electron transfer at the electrode surface and to study the chemical specificity of the modified electrode which is unavailable at the unmodified graphite electrodes [13].

II.   Experimental

A solution of Methylene blue (LOBACHEMIE) was prepared [0.0001M].The 8.9cm length and 0.55cm diameter graphite electrode (ALFA AESAR) was using. The 1.6cm 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 electrodeposition.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. A stabilized dc power supply was used as the source of electric current for the experiments. The current and voltage were adjustable between 3.6mA -6.6mA and 0-60V with digital displays. The experiments were conducted by a batch process. An undivided cell of 50 mL capacity (glass beaker) was used throughout the study. The anode and cathode were positioned vertically and parallel to each other with an inter electrode gap of 1 cm. These electrodes were dipped in the methylene blue dye solution. The electrode system consists of a graphite modified electrode as anode and a Pt electrode as cathode in case of degradation of dye by anodic oxidation with graphite electrode figure (2) . 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 Pt electrode as cathode. The experiment was run from 10 to 380 minutes with continuous stirring. The kinetic runs were carried out for different concentration of methylene blue 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 3.6mA-6.6mA using rheostat (INSIFINDIA).The decolourization and disappearance of methylene blue was followed by using spectrophotometer (ELICO SL171).
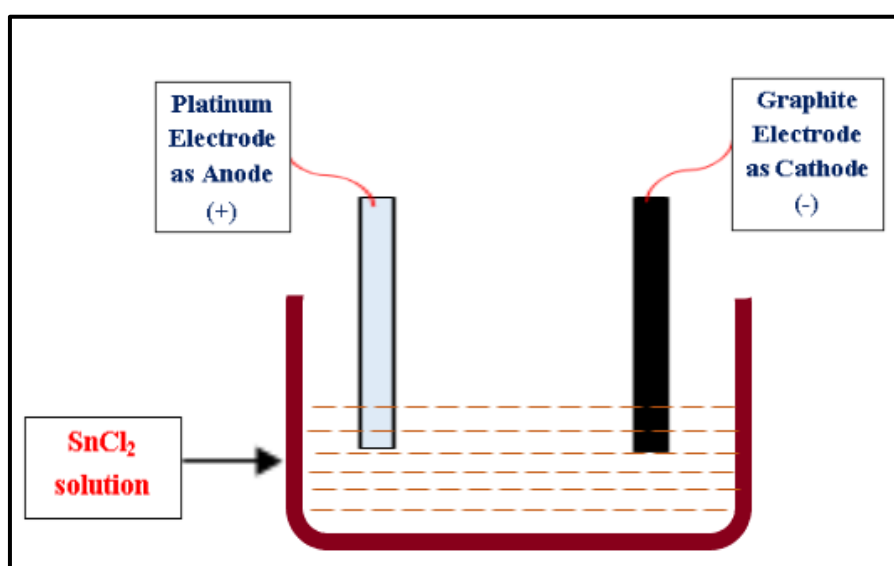

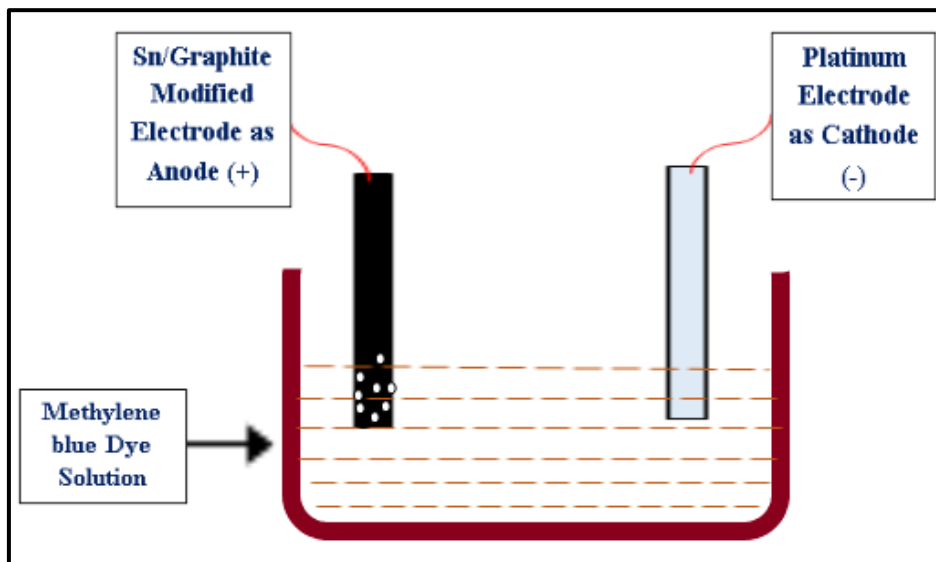**Figure 1 :** Synthesis of Sn/GME by electrochemical method

Figure: 2 Experimental set up for electrochemical degradation of methylene blue Dye

III. Results & Discussion

3.1 Reaction with graphite as anode electrode

3.1.1 Effect of Methylene blue on the rate

The reaction performed in the presence of Methylene blue (0.0001M), with constant current (4.6mA). The change in concentration of the Methylene blue 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 Methylene blue follows first order kinetics. The rate constant values are given in table 1.The reaction rate decreased with increase in Methylene blue. 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 Methylene blue solution before and after electrolysis were measured. (Table-2, Fig-3).

Table 1: Effect of Methylene blue on the rate of degradation and COD values

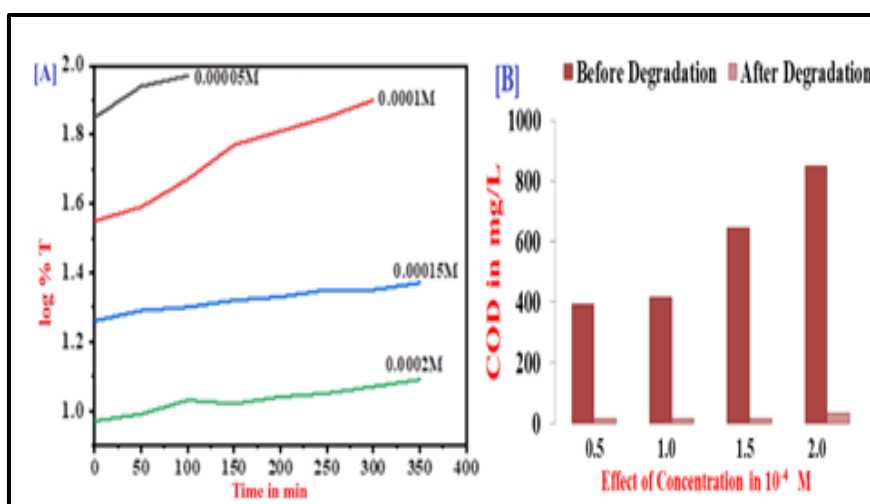| Conc of Methylene blue in 10^{-4} M	10^4 k in sec^{-1}	Effect of pH		COD Values in mg/L	
		Before degradation	After degradation	Before degradation	After degradation
0.5	0.460	6.67	6.71	392	16
1.0	0.422	6.96	7.13	416	16
1.5	0.115	7.09	7.19	645	16
2.0	0.089	7.15	7.23	848	32

Figure 3: Effect of Concentration of Methylene blue on rate of degradation [A] and COD Value [B]

3.1.2 Effect of current on the rate

To examine the effect of applied current the experiment is carried out for four different current varied from 3.6mA-6.6 mA and keeping Methylene blue 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 2. The COD for different current of Methylene blue dye solution before and after electrolysis were measured.(Table-2, Fig-4).

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

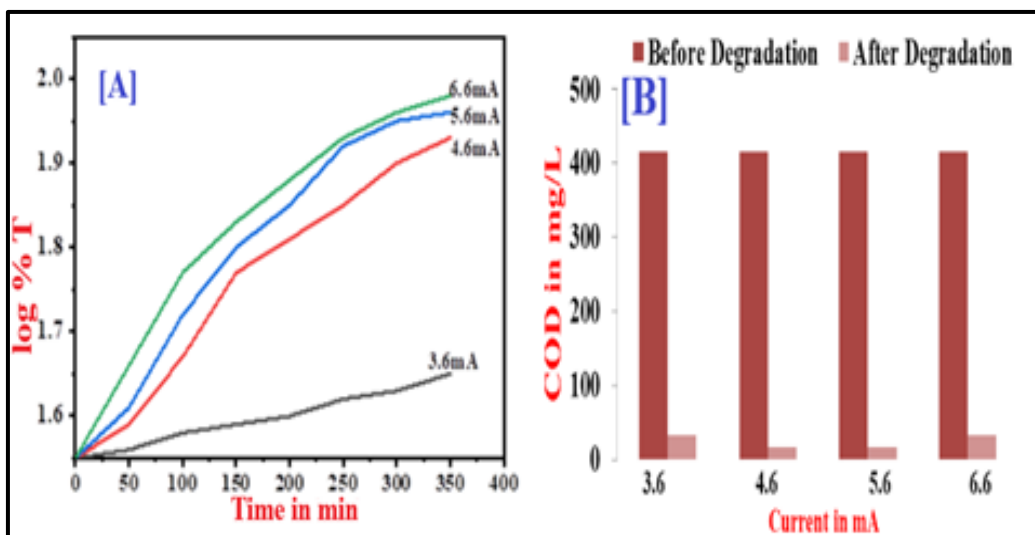| Current in mA	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
3.6	0.115	416	32
4.6	0.422	416	16
5.6	0.498	416	16
6.6	0.537	416	32

Figure 4: Effect of current of Methylene blue on the rate of degradation[A] and COD Values[B]

3.1.3 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 reaction is more significantly influenced at higher temperature, the rate constant and COD for before and after degradation of dye are reported in table 3 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 4.

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

Temperature in K	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
298	0.191	416	32
303	0.422	416	16
308	0.575	416	16

Table 4: Thermodynamic parameters for the degradation of Methylene blue

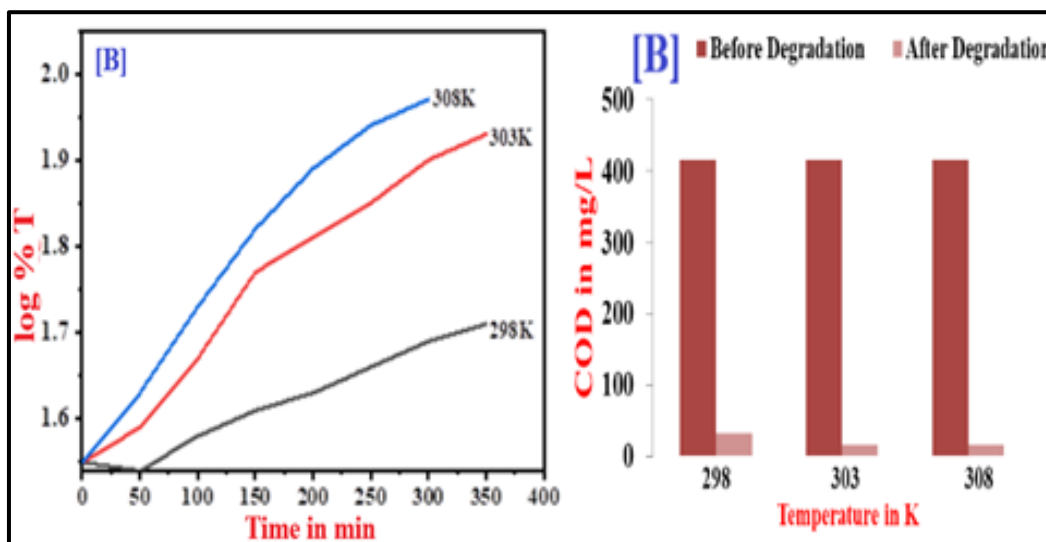| ΔH# kJ/mol	ΔS# J/K/mol	ΔG# kJ/mol	Ea
56.64	-311.47	100.04	81.87kJ/mol (19.56x 10^3 cal/mol)

Figure 5: Effect of temperature of Methylene blue on the rate of degradation[A] and COD Values[B]

3.2 Reaction with Stannous graphite Modified (Sn/GME) as anode electrode
3.2.1 Effect of Methylene blue on the rate

The reaction has been carried out in the presence of Methylene blue (0.0001M), by keeping constant current 4.6mA. The change in concentration of the Methylene blue 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 Methylene blue follows first order kinetics. The rate constant values are given in table 5.The reaction rate decreased with increase in Methylene blue 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 Methylene blue solution before and after electrolysis were measured. (Table-5, Fig-6).

Table 5: Effect of [Methylene blue] on the rate of degradation and COD values for Sn/GME

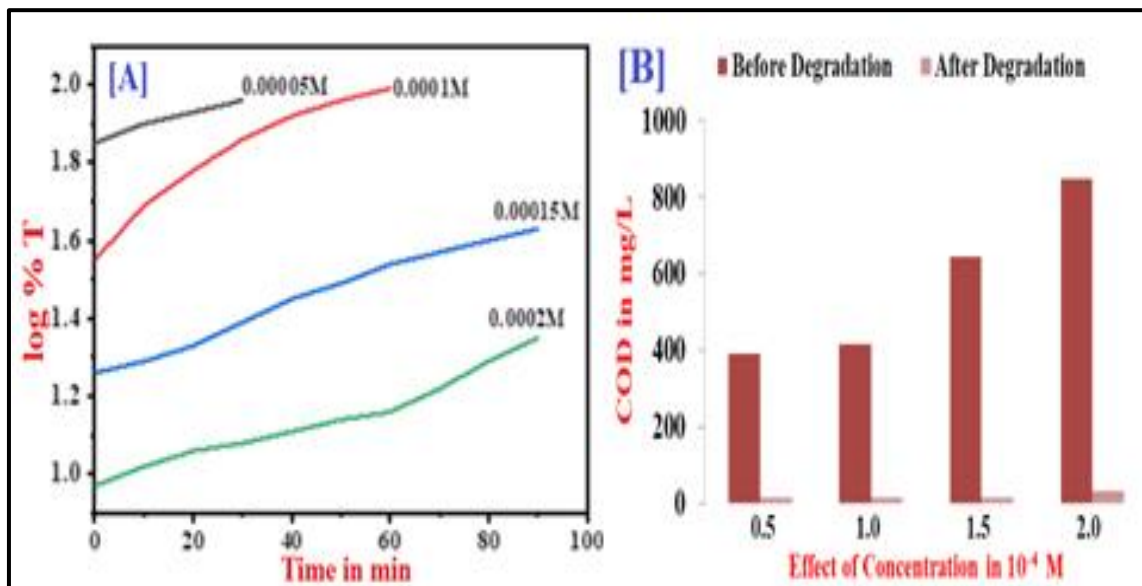| [MB] 10^{-4} M	10^4 k in sec^{-1}	Effect of pH		COD Values in mg/L	
		Before degradation	After degradation	Before degradation	After degradation
0.5	3.147	6.67	6.73	392	16
1.0	2.763	6.96	7.16	416	16
1.5	1.688	7.09	7.21	645	16
2.0	1.458	7.15	7.23	848	32

Figure 6: Effect of Concentration of Methylene blue on rate of degradation [A]and COD Value [B]

3.2.2 Effect of current on the rate

At fixed [MB] the rate of reaction increased with increase in applied current. The current is varied from 3.6mA-6.6mA.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 6 and figure 7 (A).The COD values for before and after degradation were measured and reported in table 6 and figure 7(B).

Table 6: Effect of Current on the rate of degradation and COD values for Sn/GME

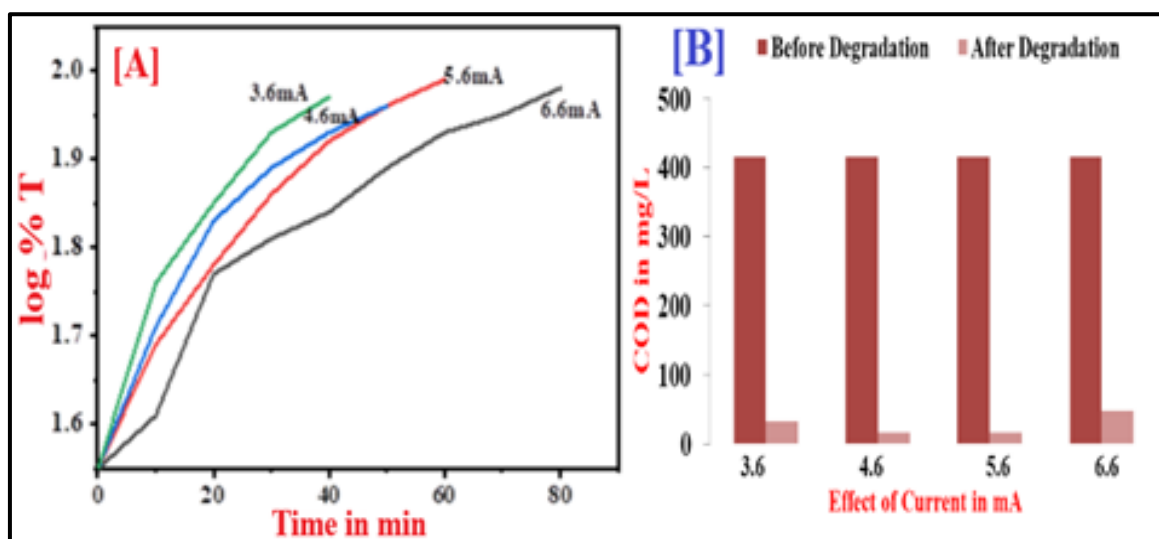| Current in mA	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
3.6	1.99	416	32
4.6	2.763	416	16
5.6	3.032	416	16
6.6	3.876	416	48

Figure 7: Effect of current of Methylene blue on the rate of degradation [A] and COD Value [B]

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 7 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 t h e degradation of methylene blue by Sn/GME electrode were measured and reported in table 8.

Table 7: Effect of Temperature on the rate of degradation and COD values for Sn/GME

Temperature in K	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	**After degradation**
298	1.727	416	48
303	2.763	416	16
308	3.109	416	16

Table 8: Thermodynamic parameters for the degradation of methylene blue for Sn/GME

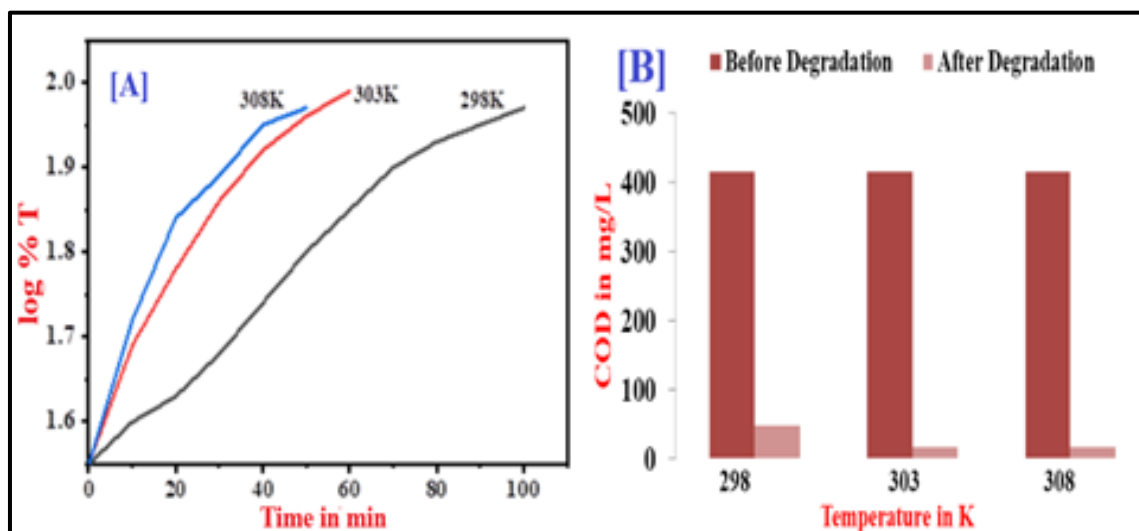| $\Delta H^{\#}$ kJ/mol	$\Delta S^{\#}$ J/K/mol	$\Delta G^{\#}$ kJ/mol	Ea
35.77	-196.10	95.18	38.29kJ/mol (9.153×10^3 cal/mol)

Figure 8: Effect of temperature of Methylene blue on the rate of degradation [A] and COD Values[B]
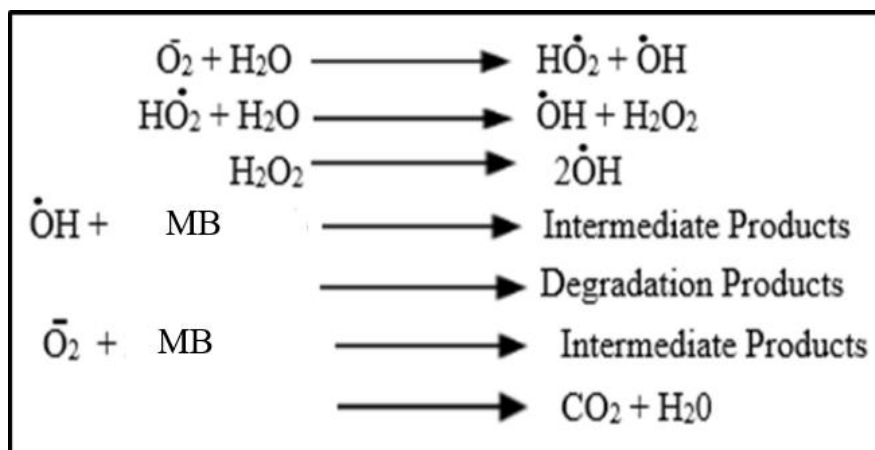
Production of OH radical

The electrochemical degradation of Methylene blue dye solution was bringing 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 and absorbed as intermediate at the surface of high O_2^- overvoltage anode from oxidation of water.

$$H_2O \longrightarrow \dot{O}H_{ads} + H^+ + e^-$$

[1]
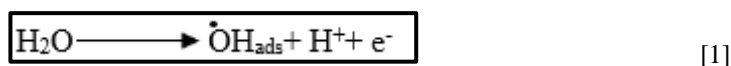
The degradation of Methylene blue takes place due to sequential electrochemical reduction and oxidation [14].Graphite electrodes have high affinity for methylene blue with implication that it will adversely affect electrode performance by competitive adsorption and interaction such as electron shuttling may increase the reactivity. The strong oxidizing agent .OH Radical, the sequential reduction/oxidation with graphite and pt

electrodes which reacts with methylene blue converting into CO_2, H_2O and inorganic salts like bromides. Until their total mineralization is reached [15]. It has been found that Pt electrode possesses greater O_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 [16]. The present method can be used for remediation of waste water.

$$\dot{\bar{O}}_2 + H_2O \longrightarrow H\dot{O}_2 + \dot{O}H$$
$$H\dot{O}_2 + H_2O \longrightarrow \dot{O}H + H_2O_2$$
$$H_2O_2 \longrightarrow 2\dot{O}H$$
$$\dot{O}H + MB \longrightarrow \text{Intermediate Products}$$
$$\longrightarrow \text{Degradation Products}$$
$$\bar{O}_2 + MB \longrightarrow \text{Intermediate Products}$$
$$\longrightarrow CO_2 + H_2O$$

Scheme 1: Proposed degradation pathway of Methylene blue

Effect on COD of duration of treatment

The effect of rate of dye degradation on COD was determined. During the experiment the initial COD 392 mg/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 (9).
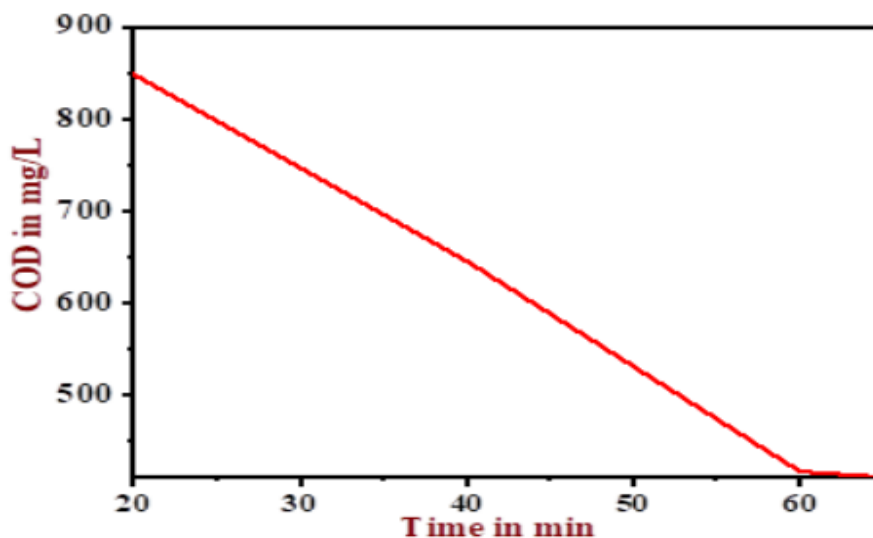

Figure 9: The rate of decrease of COD at different intervals of time.

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 methylene blue dye was calculated from the values of the COD using the equation,

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

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 electrolyte the treatment time and '8' is the oxygen equivalent mass (geq-1). The ICE data in tables (9,10) 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 9: ICE Values at different experimental conditions for Graphite Electrode

	Variables	ICE
Concentration of Dye 10^{-4}M	0.5	197.19
	1.0	59.93
	1.5	86.81
	2.0	104.37
Current in mA	3.6	65.98
	4.6	59.93
	5.6	59.42
	6.6	66.83
Temperature in K	298	51.63
	303	59.93
	313	91.20

Table 10: ICE Values at different experimental conditions for Sn/GME

	Variables	ICE
Concentration of Dye 10^{-4}M	0.5	657.31
	1.0	349.63
	1.5	235.63
	2.0	251.73
Current in mA	3.6	321.66
	4.6	349.63
	5.6	344.64
	6.6	336.28
Temperature in K	298	193.00
	303	349.63
	313	524.45

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 methylene blue 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} 660nm 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 11 (A and B) represents UV-Visible spectra during the electrochemical degradation of methylene blue dye. Broad visible colour absorption spectra at 660 nm were completely removed at the end of the degradation process.
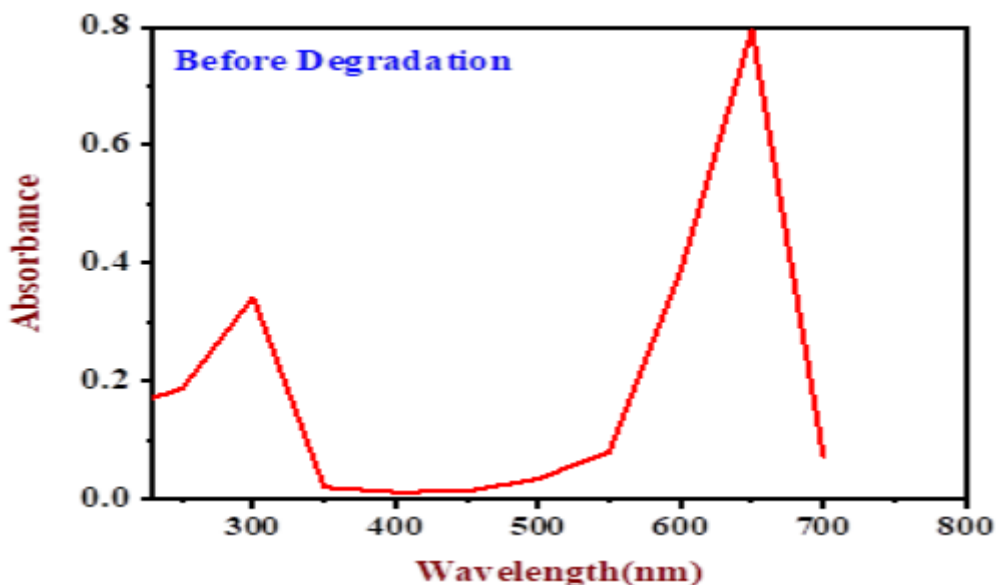
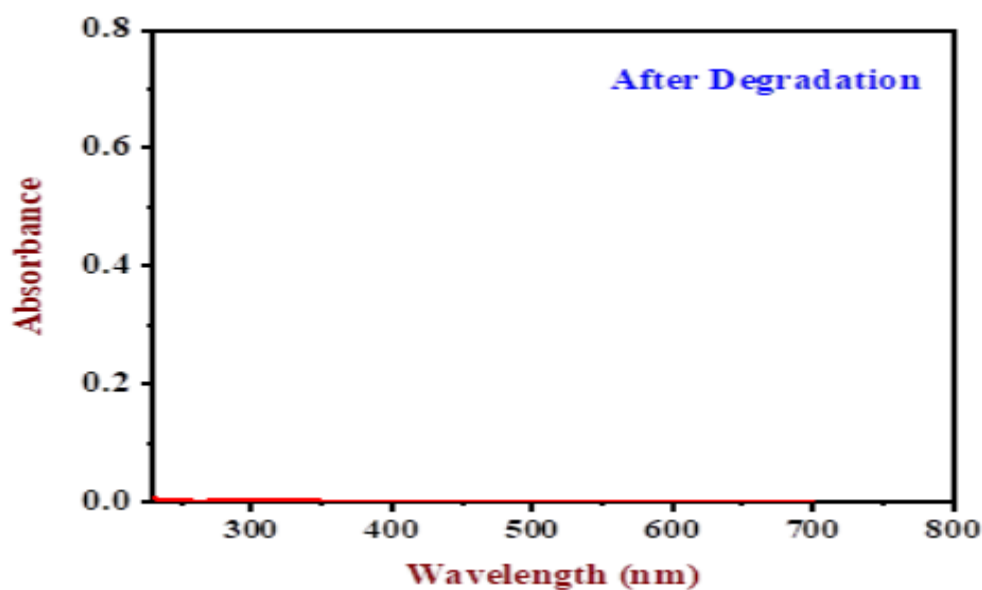**Figure 10(A):** UV-Visible spectra of methylene blue before degradation

Figure 10(B): UV-Visible spectra of methylene blue after degradation

Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray spectroscopy (EDS)

Scanning electron microscopy (SEM) is used to differentiate the Stannous (Sn) deposited graphite electrode and bare graphite electrode. Fig.11 (A) &11 (B) shows the SEM image of graphite flake and its corresponding EDAX profile. From the micrograph, the layered and homogenous nature of graphite was observed in different diameter. It is clear from the Fig 11(A) before deposition only graphite flakes are found. The observed size of graphite flake was ranging from 10 to 50μm. From the EDAX profile, the presence of carbon and oxygen content indicated the graphite present in the pure form Fig 11(B)
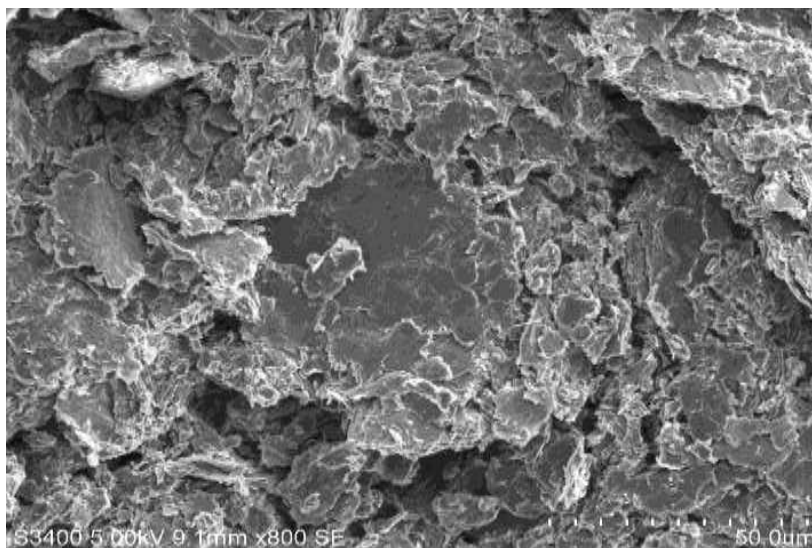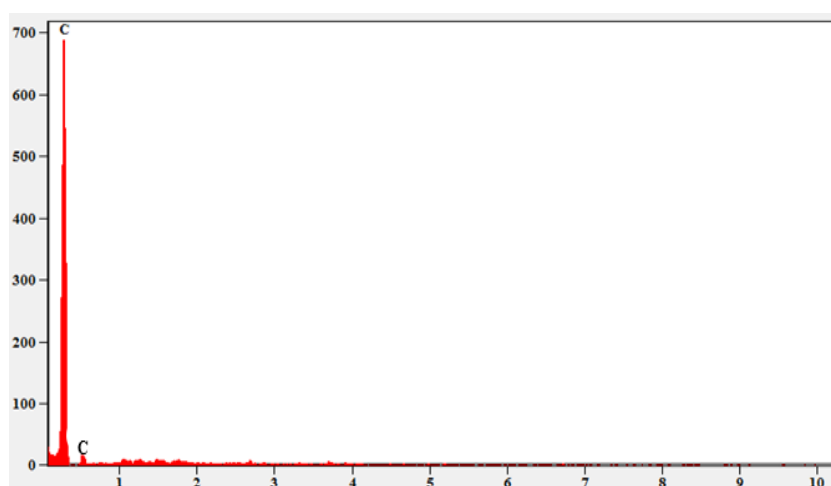
Fig. 11(A): SEM micrographs of graphite Electrode

Fig. 11(B): EDAX spectra of graphite Electrode

Table 11: 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
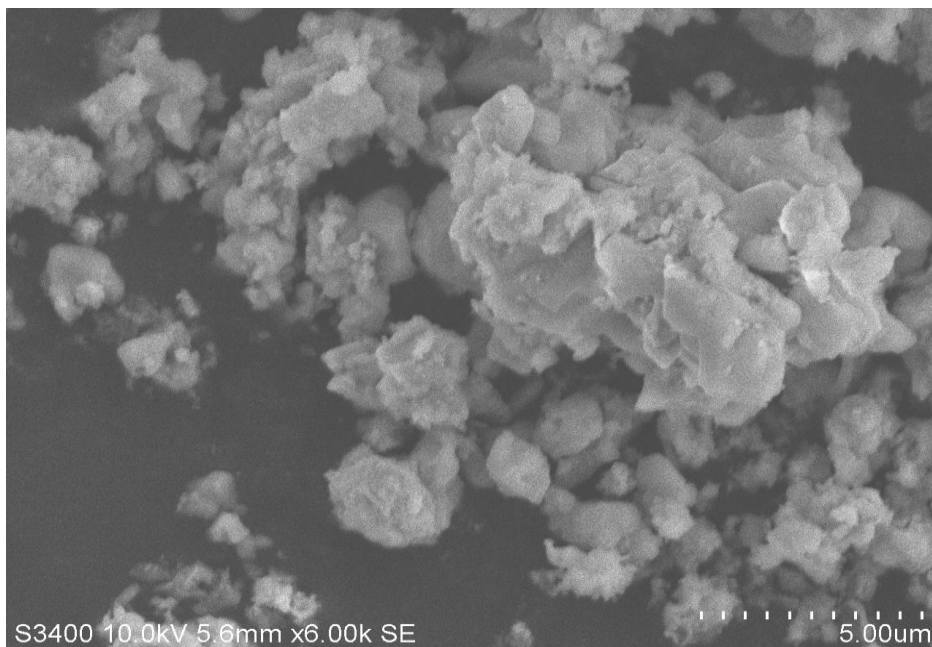
Fig. 12(A): SEM micrographs of stannous graphite modified electrode
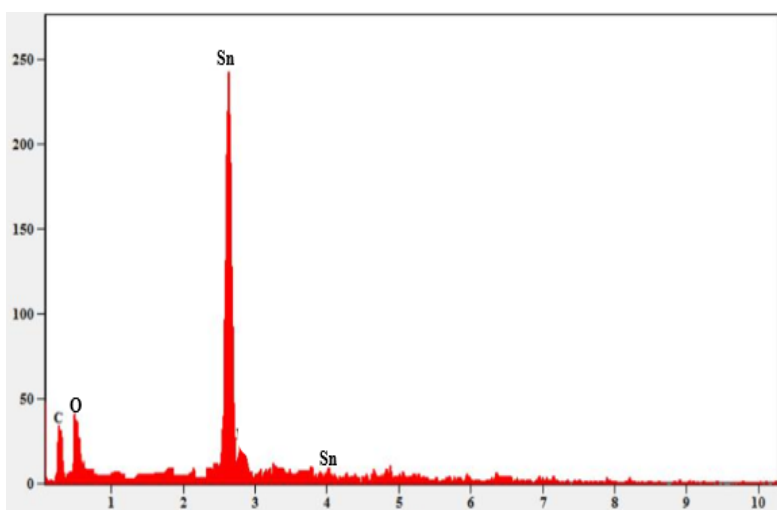

Fig. 12(B): EDAX spectra of Sn/GME

Table 12: 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

Fig 12(A) & (B) shows the SEM and EDAX 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 Fig 12(A). The corresponding EDAX plot as shows in Fig12 (B). From the EDAX plot, we clearly noticed the presence of stannous peaks in different oxidation states along with graphite carbon peak.

IV.   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 methylene blue elimination and COD removal were higher on the Sn/GME compare to graphite electrode.

Acknowledgements

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