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Electrochemical Degradation of 3-(dimethylamino)-7-(methylamino) phenothiazin-5-ium chloride Dye at Barium/Graphite Modified Electrode in Aqueous Solution

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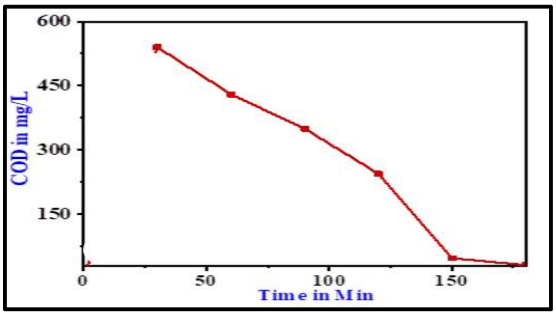
ABSTRACT

In this work Barium/Graphite modified electrode(Ba/GME)has been successfully developed by electrochemical method which is simple and inexpensive method. The developed graphite modified electrode was used for electrochemical degradation of wastewater containing azure B dye. The kinetics study of the dye degradation by graphite and Ba/graphite modified electrode are compared. Azure B[AB] is one of the most important textile dye. The developed modified electrode was characterized by SEM/EDAX, UV-Visible spectra. The thin film formation of Ba or encapsulated in graphite rod is observed from SEM/EDAX .The effect of concentration of the dye, effect of current and effect of temperature on the kinetics of degradation were studied. The degradation rate increases with increasing current and electrochemical degradation of azure B at Ba/GME follows 1st order kinetics up to 70% of the reaction. Electrochemical oxidation in presence of unmodified graphite electrode and Ba/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. The Instantaneous current efficiency (ICE) values of different experimental conditions are evaluated. The thermodynamic parameters for graphite and Ba/GME were studied. The anodic oxidation by Ba/GME showed the complete degradation of water containing azure B, which is confirmed by UV-Visible spectra and COD measurements. The dye is converted into CO_2, H_2O and simpler inorganic salts. The results observed for reuse of modified electrodes indicates that the Ba/GME would be promising anode for electrochemical degradation of azure B dye. The rates of elimination of azure B and COD decreases were higher on the Ba/GME compare to graphite electrode. This method can be applied for the remediation of waste water containing organics and cost effective.

Graphical Abstract



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

Keywords: Azure B [AB], Barium/graphite modified electrode (Ba/GME).

INTRODUCTION

In electrochemical oxidation process the electrode materials plays an important role [1]. However, in many researchers have investigated that numerous electrode materials such as Pd [2], Au [3], Pt-Ru alloys [4] and IrO_2 [5] are used in the oxidation process. The usage of these electrode materials in electrochemical oxidation showed good activities, but these materials are high cost. Therefore, the utilization of low cost materials like carbon, iron etc., is very important [6]. The utilization of metallic materials in the catalytic process have some limited applications due to their corrosive property. Hence the utilization of carbon materials like graphite, exfoliated graphite are excellent source to overcome the corrosion problem, because graphite have some typical properties like corrosion resistance, compatibility, large surface area, temperature resistance , flexibility, good conductivity , porosity and stability to aggressive media [7-9]. The graphite electrode is used as anode in the electrochemical degradation of textile effluents due to its excellent results and low cost material [10]. The water pollution is mainly due to the presence of environmental and industrial pollutants in water [11, 12]. Dyes are frequently used in many industries like paper, textile, plastic, rubber and dye manufacturing industries. These industries discharged the dyes along with wastewater to environment [13-15]. Dyes are the major pollutants of aquatic forms and they are most dangerous to aquatic life. The dyes contained water not only affects the aquatic life, but it also affects the human and terrestrial animals. It is also affects the photosynthesis in plants by inhibitory action of dyes on plants [16, 17]. The presence of small quantities dyes in water bodies may cause skin irritation, mutations, skin allergy and cancer [18]. It is very difficult to remove the dyes from industrial effluents due to their complex structures [19]. In this context, the removal of dyes from the wastewater is very essential need, based on this need researchers employed plenty of methods such as ion exchange, adsorption, ozonization, biological, precipitation, photocatalytic, coagulation and electrochemical oxidation [20]. The electrochemical oxidation is most accepted method due to its versatility, low cost, energy efficiency, giving excellent results and less time consuming [21-25]. Azure B is a blue colored dye and it belongs to the thiazine class of dye and it is classified into four types namely Azure A,B,C and II, with colour varies from green and blue to red. Azure B is a blue coloured dye and it is also called trimethylthionine chloride and it is a oxidative product of methylene blue. Azure B is used frequently in many dyeing industries such as ink, wood, paper, silk and it can be used for biological staining [26]. In present scenario, Azure B is a major water polluting dye [27]. The removal of the Azure B dye from industrial effluents is very important due to its carcinogenic nature.

MATERIALS AND METHODS

Preparation of Barium/Graphite Modified Electrode: The 6.5 cm length and 0.63 cm diameter graphite electrode (ALFA AESAR) was used for the experiment. Prior to experiment the surface pre-treatment 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 double distilled water and utilized for further electro deposition. The experimental set up is shown in the figure 1. Barium was deposited on graphite electrode from $BaCl_2$ (Arora matthey) solution in 0.1M. During electrolysis the potential ranged from 8 to 12 V, electrode position was carried out for 90 min.

Electrolysis: Azure B (lobachemie) solution was prepared [0.00002M]. All chemicals were used of accepted grades of purity. The experimental apparatus is shown in figure 2. It consists of reaction chamber and a voltage power supply. The electrode system consists of a Ba/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 2 cm. The kinetic runs were carried out with graphite electrode alone as anode. In another case, Ba(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 540 min with continuous stirring. The kinetic runs were carried out at different concentration of azure B with 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 degradation was measured. A positive voltage was applied by using battery eliminator (NEULITE INDIA) and current output of 2.5-5.5 mA using rheostat (INSIF INDIA). The decolourization and disappearance of azure B was followed by using spectrophotometer (ELICO SL 171).

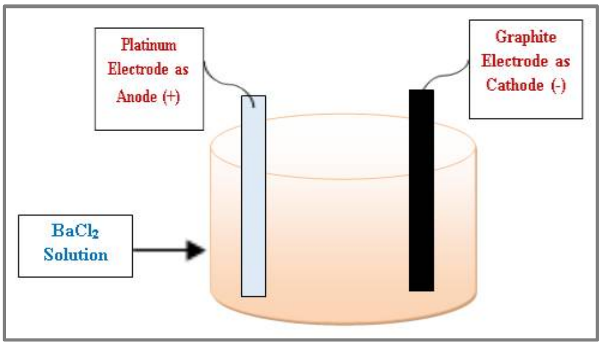
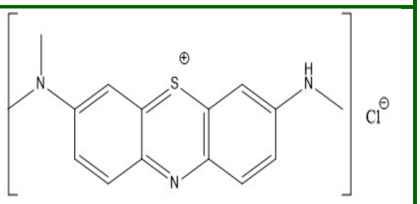


Figure 1. Synthesis of Ba/GME by electrochemical method.

Table 1. Properties of Azure B Dye

Dye	Chemical Formula	Molar Mass	Wavelength	Structure
Azure B	**$C_{15}H_{16}ClN_3S$**	305.83 g·mol^{-1}	645-650 nm	

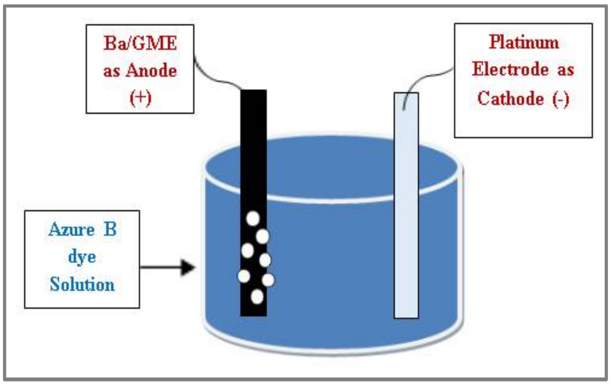


Figure 2. Experimental set up for electrochemical degradation of Azure B Dye.

RESULTS AND DISCUSSION

Degradation Reaction with graphite as anode electrode

Effect of Azure B on the rate: The degradation reaction was carried in the presence of azure B (0.00002 M), with constant current (3.5 mA). The change in concentration of the azure B was recorded by change in colour using spectrophotometer. A plot of log%T (percentage transmittance of light) versus time was linear upto 70% of the reaction indicating disappearance of azure B follows 1st order kinetics. The rate constant values are given in table 2. The degradation reaction rate decreased with increase in azure B dye. The degradation rate at higher concentration is decrease 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 azure B solution before and after electrolysis were measured and as shown in table 2 and figure 3.

Table 2. Effect of [Azure B] on the rate of degradation and COD values

[Azure B] 10^{-5}M	10^5 k in sec^{-1}	Effect of pH		COD Values in mg L^{-1}	
		Before degradation	After degradation	Before degradation	After degradation
1.0	6.52	8.48	8.52	460	24
2.0	6.14	8.61	8.65	590	16
3.0	5.75	8.91	8.94	750	32
4.0	4.98	8.96	8.98	816	48

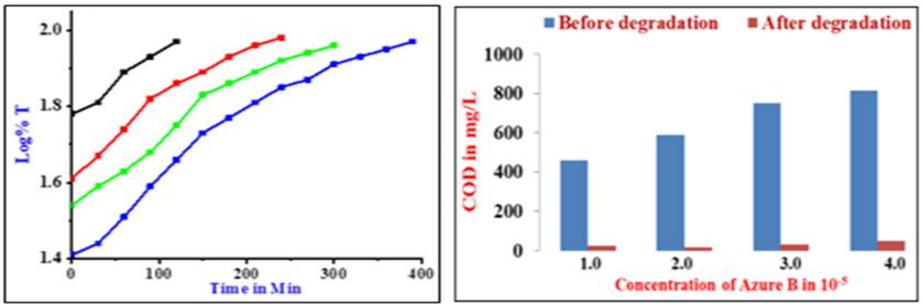


Figure 3. Effect of Concentration of Azure B on rate of degradation and COD Values.

Effect of current on the rate: In effect of current study it was observed that the rate of degradation reaction increases with increasing in applied current at fixed 0.00002M [Azure B]. The rate constant values are given in table 3. The current is varied from 2.5-5.5 mA. The increase of current increases

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

Current in mA	10^5k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
2.5	4.22	590	32
3.5	6.14	590	16
4.5	6.52	590	24
5.5	6.90	590	32

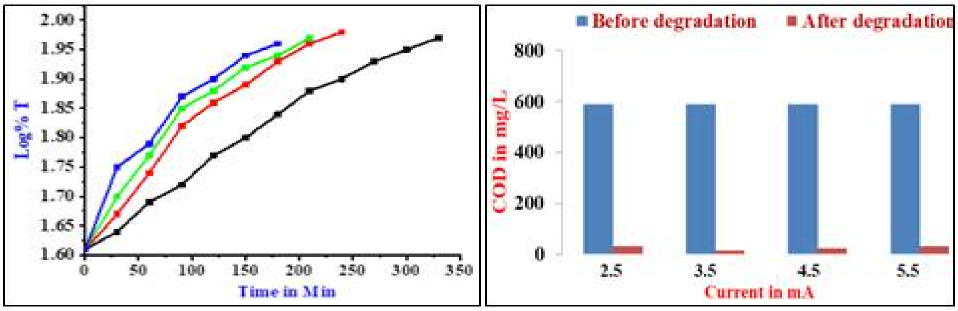


Figure 4. Effect of current of Azure B on the rate of degradation and COD Values.

the concentration of oxidizing intermediates and OH radicals, which increases the rate of the degradation. The COD for different current of azure B solution before and after electrolysis were measured and as shown in table 3 and figure 4.

Effect of temperature: The removal process was carried out by graphite electrode by varying three different temperatures [298K, 303K, 313K]. It was found that the rate of removal of colour is not very significant at low temperature. However the degradation reaction is more significantly influenced at higher temperature, since the diffusion rate is increased with temperature, an increase of temperature could bring about an increase in the degradation rate. The rate constant and COD for before and after degradation of dye were measured and are reported in table 4 and figure 5. 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	10^5k In sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
298	4.22	590	24
303	6.14	590	16
313	7.67	590	32

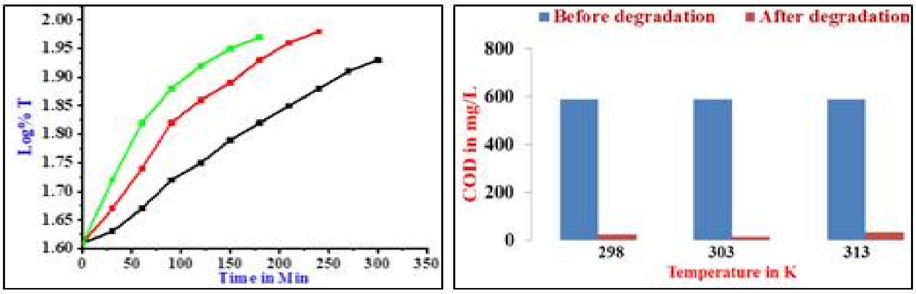


Figure 5. Effect of temperature of Azure B on the rate of degradation and COD Values.

Thermodynamic Parameters: Based on Arrhenius theory, Ea can be evaluated by determining the rate constant of the reaction at different temperatures. In the activated complex theory or transition state theory, the reactants are assumed to combine to form an energy rich activated complex which will be in equilibrium with the molecules of the reactants. This activated complex disproportionate with a certain rate to give products. It is this rate determines the overall rate of the reaction. The thermodynamic parameters enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), and free energy of activation ($\Delta G^{\#}$) are shown in table 5.

Table 5. Thermodynamic parameters for the degradation of Azure B

Temperature in K	ΔH# KJ/mol	ΔS# J/K/mol	ΔG# KJ/mol	Ea
298	43.86	-181.49	97.93	46.31KJ
303	43.81	-181.10	98.69	(11.07x10^3 Calories)
313	43.73	-184.43	101.46	

Degradation Reaction with Barium/Graphite Modified Electrode (Ba/GME) as anode Effect of Azure Bon the rate: The reaction was performed with different concentration of azure B dye by Ba/GME by keeping all other experimental conditions constant. It was observed that the rate of degradation reaction decreased with increase of concentration. The change in concentration of the azure B was recorded by change in colour using spectrophotometer. A plot of log%T (percentage transmittance of light) versus time was linear upto70% of the reaction indicating disappearance of azure B follows 1storder kinetics. The rate constant values are given in table 6. The reaction rate decreased with increase in azure 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 azure B solution before and after electrolysis were measured and are reported in table 6 and figure 6.

Table 6. Effect of Azure B on the rate of degradation and COD values for Ba/GME

[AB] 10^{-5}M	10^4 k in sec^{-1}	Effect of pH		COD Values in mg L^{-1}	
		Before degradation	After degradation	Before degradation	After degradation
1.0	3.64	8.48	8.56	460	32
2.0	1.65	8.61	8.71	590	16
3.0	1.07	8.91	8.97	750	32
4.0	0.99	8.96	9.03	816	24

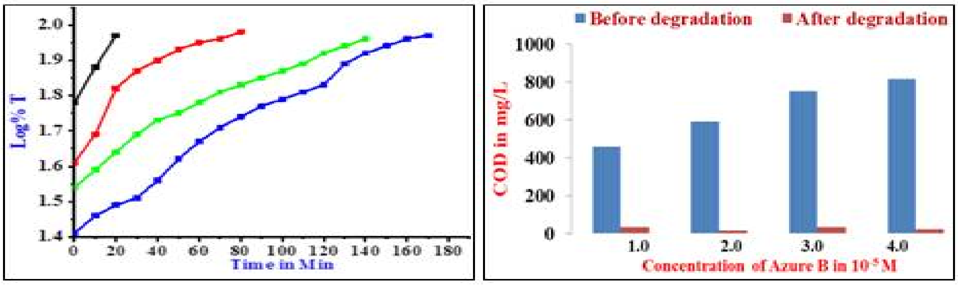


Figure 6. Effect of Concentration of Azure B on rate of degradation and COD Values.

Effect of Current on the rate: In the effect of current study the current is varied from 2.5-5.5 mA and keeping all other experimental conditions constant. It was noticed that the rate of degradation reaction increases with increasing in applied current at fixed 0.00002 M [Azure B]. The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of the degradation. The rate constant values are given in table 7. The COD for different current of azure B solution before and after electrolysis were measured and are reported in table 7 and figure 7.

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

Current in mA	10^4 k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
2.5	1.34	590	24
3.5	1.65	590	16
4.5	2.30	590	32
5.5	3.26	590	24

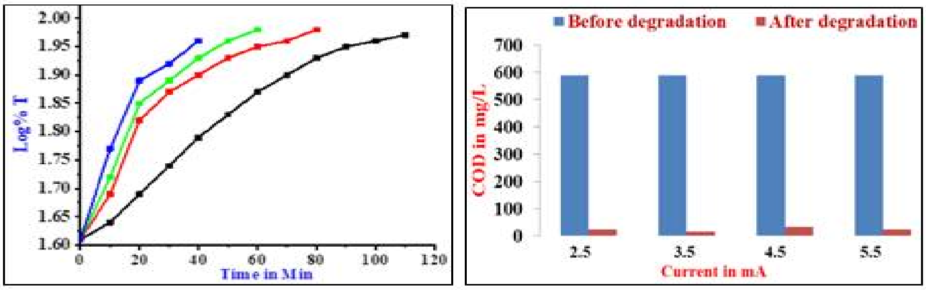


Figure 7. Effect of current of Azure B on the rate of degradation and COD ValueS.

Effect of Temperature: The azure B removal process was carried out by Ba/GME by varying three different temperatures [298K, 303K, 313K]. 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. Since the diffusion rate is increased with temperature, an increase of temperature could bring about an increase in the degradation rate. The degradation efficiency was high for Ba/GME compare to graphite electrode. The rate constant values and COD values for before and after degradation were measured and are reported in table 8 and figure 8. Thermodynamic parameters for the degradation of azure B by Ba/GME electrode were measured and reported in table 9.

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

Temperature in K	10^4 k in sec^{-1}	COD Values in mg L^{-1}	
		Before degradation	After degradation
298	0.88	590	24
303	1.65	590	16
313	3.41	590	16

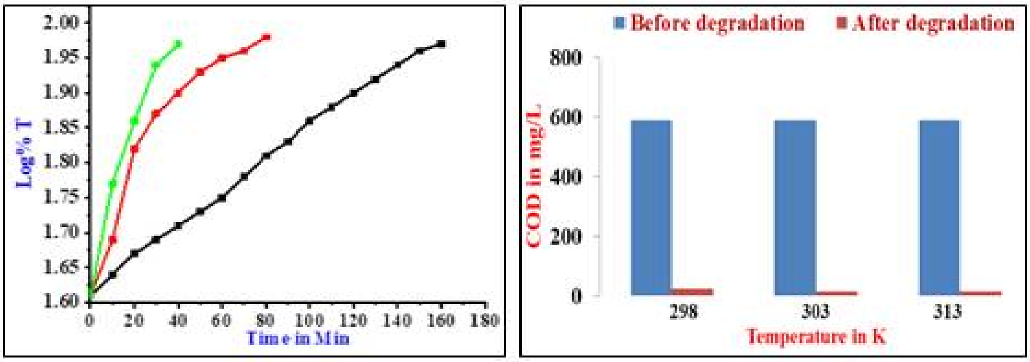


Figure 8. Effect of temperature of Azure B on the rate of degradation and COD Values.

Table 9. Thermodynamic parameters for the degradation of Azure B for Ba/GME

Temperature in K	ΔH# KJ mol^{-1}	ΔS# J $K^{-1}mol^{-1}$	ΔG# KJ mol^{-1}	Ea
298	29.82	-203.38	90.41	32.30 KJ (7.721x 10^3 Calories)
303	29.78	-219.19	96.18	
313	29.70	-216.77	97.55	

Production of OH radical: The degradation reaction of azure B solutions was 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 radical formed by direct electrolysis and absorbed as intermediate at the surface of high O_2^-overvoltage anode from oxidation of water.

$$H_2O^{\cdot} \longrightarrow OH_{ads} + H^+ + e^- [1]$$

The degradation of azure B takes place due to sequential electrochemical reduction and oxidation [28]. Graphite electrodes have high affinity for azure 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 azure B converting into CO_2, H_2O and inorganic salts. Until their total mineralization is reached. It has been found that Pt electrode possesses greaterO_2^- over voltage (+0.77V), thus generating higher amount of oxidant $OH^{\cdot}$.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 [29]. The present method can be used for remediation of waste water.

$$\begin{aligned}
O_2^- + H_2O &\longrightarrow HO_2^- + {}^{\bullet}OH \\
HO_2^- + H_2O &\longrightarrow {}^{\cdot}OH + H_2O_2 \\
H_2O_2 &\longrightarrow 2{}^{\bullet}OH \\
{}^{-}OH + [AB] &\longrightarrow \text{Intermediate products} \\
&\longrightarrow \text{Degradation products} \\
O_2^- + [AB] &\longrightarrow \text{Intermediate products} \\
&\longrightarrow CO_2 + H_2O
\end{aligned}$$

Scheme 1. Proposed degradation pathway of Azure B.

Effect on COD of duration of treatment: The effect of rate of dye degradation on COD was determined. During the experiment the initial COD 590 mg L^{-1} which gives rise to 48 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.

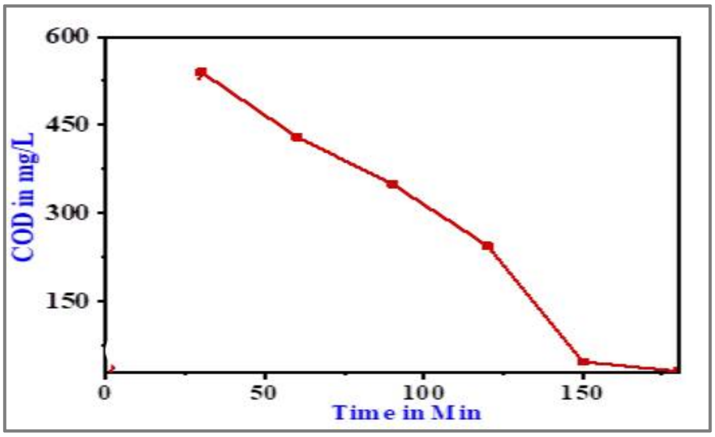


Figure 9. The rate of decrease of COD at different intervals of time.

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 azure Bdye was calculated from the values of the COD using the equation,

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

Here; CODi and CODf are the chemical oxygen demands before and after degradation respectively, 'I' is the current, 'F' is the Faraday constant, 'V' is the volume of the electrolyte the 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 Ba/GME anode compared to GE anode.

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

	Variables	**ICE**
Concentration of Dye 10^{-5}M	1.0	250.44
	2.0	164.85
	3.0	164.96
	4.0	135.73
Current in mA	2.5	163.17
	3.5	164.85
	4.5	144.49
	5.5	135.97
Temperature in K	298	130.04
	303	164.85
	313	213.67

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

	Variables	**ICE**
Concentration of Dye 10^{-5}M	1.0	1475.07
	2.0	494.56
	3.0	353.50
	4.0	303.28
Current in mA	2.5	496.53
	3.5	494.56
	4.5	498.58
	5.5	620.67
Temperature in K	298	243.83
	303	494.56
	313	989.12

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

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

The rate constant for the disappearance of azure 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}645-650 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 Barium/Graphite Modified Electrode (Ba/GME): The possibility of reusing the Ba/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 of azure B dye before and after degradation. Broad visible colour absorption spectra at 645-650 nm were completely removed at the end of the degradation process.

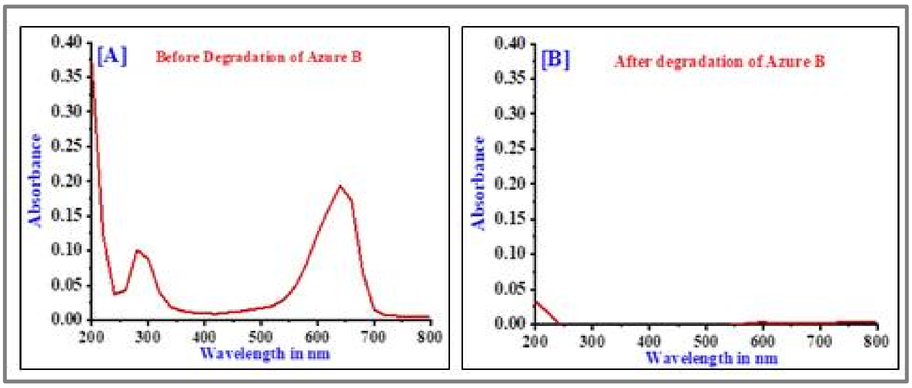


Figure 10. UV-Visible spectraof azure B [A] before degradation [B] After degradation.

Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Analysis (EDAX): Scanning electron microscopy (SEM) is giving morphological examination with direct visualization. The techniques based on electron microscopy offer several advantages in morphological and sizing analysis. The sample is scanned with a focused fine beam of electrons. The surface characteristics of the sample are obtained from the secondary electrons emitted from the sample surface. Figure11 (A) shows the SEM image of graphite flake and its corresponding EDAX profile. From the image, the layered and homogenous nature of graphite was observed. It is clear from the figure 11(A) before deposition only graphite flakes are found. From the corresponding EDAX profile, the presence of carbon content indicated the graphite present in the pure form as shown in figure 11(B) and corresponding quantitative results as shown in table 12. Figure 12(A) shows SEM image of Ba/GME shows the deposited Ba on graphite electrode. The Ba are deposited in the needle shape with aggregates. The corresponding EDAX spectra show the existence of high percentage of Barium (Ba). It also shows the presence of Cl, O and C as impurities probably obtained from the electrolyte solution as shown in figure 12(B) and corresponding quantitative results are shown in table 13.

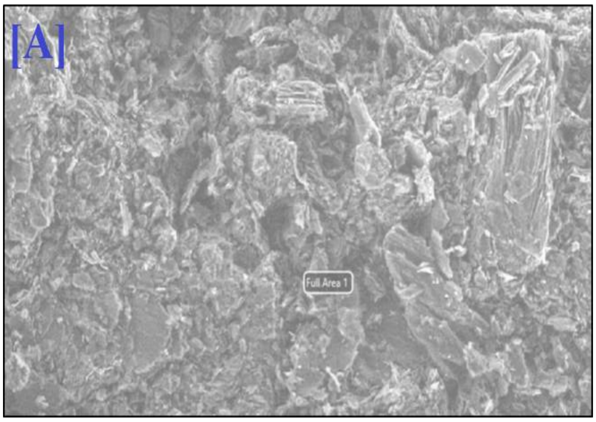


Figure 11(A). SEM micrographs of graphite Electrode.

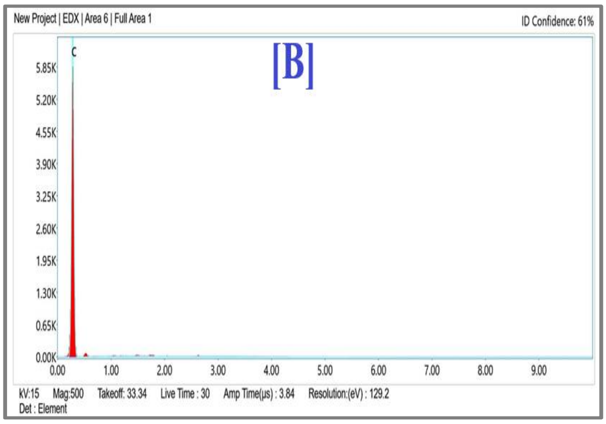


Figure 11(B). Energy-dispersive X-ray Analysis (EDAX) for graphite Electrode.

Table 12. Quantitative Results for: Base (472)

Element	Weight %	Atomic %	Error %
C K	100.0	100.0	7.6

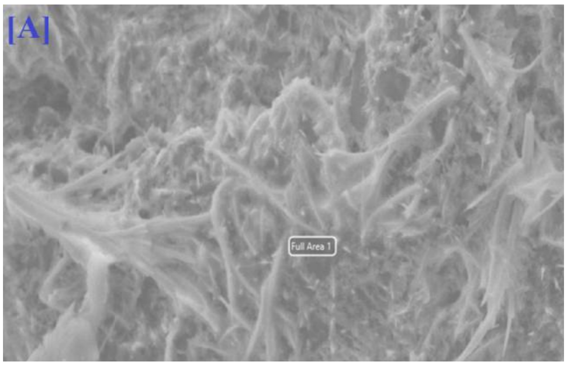


Figure 12(A). SEM micrographs of Barium/graphite modified Electrode.

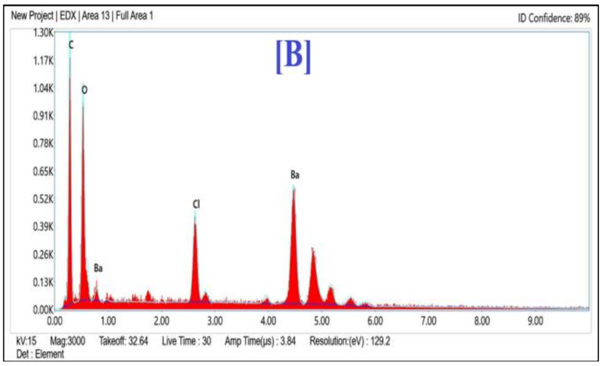


Figure 12(B). Energy-dispersive X-ray Analysis (EDAX) for Barium/graphite modified Electrode.

Table 13. Quantitative Results for: Base (472)

Element	Weight %	Atomic %`	Error %
C K	30.2	62.0	11.1
O K	16.5	25.5	10.7
Cl K	5.7	4.0	6.3
Ba L	47.5	8.5	5.1

CONCLUSION

In this paper, electrochemical oxidation in presence of graphite electrode and Ba/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 azure B elimination and COD removal were higher on the Ba/GME compare to graphite electrode.

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