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Electrochemical Degradation of Indigocarmine Dye at Ni/Graphite Modified Electrode in Aqueous Solution

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Abstract

Nickel Graphite modified electrode (Ni/GME) was prepared by electrochemical method and degradation of Indigocarmine (IC) dye was carried out. An investigation between the efficiency of degradation by graphite electrode and the Ni/graphite modified electrode has been carried out. The different effects of concentration, current density and temperature on the rate of degradation were studied. This study shows that the rate of the degradation is more for Ni doped modified graphite electrode. UV-Visible spectra before and after degradation of the dye solution were observed. The thin film formation of Ni or encapsulated in graphite rod is observed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM & EDAX). The instantaneous current effectiveness values of different experimental conditions are evaluated. The anodic oxidation by Ni/ graphite modified electrode showed the complete degradation of aqueous solution indigocarmine, which is confirmed by UV-Visible and chemical oxygen demand (COD) measurements. The dye is converted into CO_2, H_2O and simpler inorganic salts. The results observed for reuse of modified electrodes indicate that the Ni/graphite modified electrode would be a promising anode for electrochemical degradation of indigocarmine. This method can be applied for the remediation of waste water containing organics, cost-effective and simple.

Keywords

Indigocarmine (IC) Dye, Nickel Graphite Modified Electrode (Ni/GME), Chemical Oxygen Demand (COD), Instantaneous Current Efficiency (ICE)

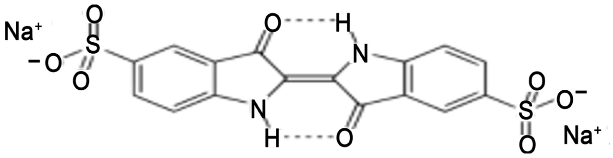
1. Introduction

The industrial revolution has influenced the quality of available fresh water. Many industries like textiles, refineries, chemical, plastic and food-processing plants produce wastewater characterized by a perceptible content of organics with strong colour. A typical textile dyeing processing unit consisting of desizing, scouring, bleaching, dyeing, finishing and drying operations produces wastewater contains high amounts of pollution load along with huge quantities of dyes. With the increasing demand for the textile products, the wastewater of textile industry is rising proportionally, making it one of the main sources of severe pollution problems globally. In particular, the release of coloured effluents into the environment is undesirable, not only because of their colour, but also because many dyes and their breakdown products are toxic and/or mutagenic to aquatic life [1]-[5]. Pollution of water resources by wastewater containing synthetic colour compounds, especially 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 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 colourful compounds, as well as the intermediates produced by their degradation, are considered as a major health hazard to the human environment and other organisms, especially aquatic life [6]. The industry uses lots of water in the textile dyeing processes. Thus it leaves a great amount of effluent to be treated. This is because the effluents are toxic, mutagenic, have low ability to biodegrade, high COD value, pH and temperature. One of the most vivid indicators of textile industrial wastewater pollution is colour. At very low dye concentrations, their strong colour is still visible and disturbs the solubility of gas in water bodies. The highly coloured effluents can cause severe problems when disposing and discharging the wastewater into the water system without proper treatment; hence this will cause serious problems for the environment. The strong colour is caused by the unfixed dyes [7] [8]. Dyes are bright coloured because of the chromosphere and azo group. The most problematic dye to be treated is reactive, water-soluble, acidic and brightly coloured. These kinds of dye cannot be treated by conventional treatment methods. The complexity of the aromatic molecular structure of the dyes may affect the stability and biodegradability of compounds. The electrode material selection is very important to obtain the desired result in the electrochemical oxidation process. In this study, graphite was used as the main ingredient in electrode fabrication. It is known as a carbon-based metallic composite electrode since metals are also used to increase colour removal efficiency [9]-[11]. Electrochemical oxidation has been applied for remediation of pollutants in recent years. The electron has the main role in this technique; hence, it is a clean and eco-friendly process. Electrochemical oxidation has advantages of no chemical involvement in the treatment process, no sludge generation, besides cost-effectiveness and requirement of small area [12]-[16].

2. Experimental

Indigocarmine (LOBACHEMIE) solution was prepared [0.0001 M] using double distilled water. The 8.9 cm length and 0.55 cm diameter graphite electrode (ALFA AESAR) was used. The 1.5 cm length graphite electrode is dipped into the above indigocarmine solution. The surface pre-treatment of graphite terminal was performed by hand cleaning of the electrode surface with progressive grades of every paper down to 3000 coarseness up to a mirror finish. The cleaned terminal was then degreased with 1:1 HCl arrangement, acetone and washed with running doubly distilled water and used for additional electrodeposition. The experimental setup is shown in **Figure 1**. Nickel was coated on a graphite electrode with $NiCl_2$ (Arora matthey) solution. All the chemicals used were of acknowledged grades of virtue. A balanced out DC power supply was utilized as the wellspring of electricity flow for the investigations. The current and voltage varied between 3.6 mA - 6.6 mA and 0 - 60 V 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 situated upward and corresponding to one another with a terminal distance of 1 cm. These electrodes were dipped in the indigocarmine dye solution. The electrode system consists of a graphite electrode as anode and a Pt electrode as a cathode in case of degradation of dye by anodic oxidation with graphite electrode **Figure 2**. The degradation kinetic runs were carried out with a graphite electrode alone as anode. For another situation, Ni (II) thin film coated on a conductive graphite (Ni/Graphite) electrode is used as anode and an Pt electrode as a cathode. The trial was run from 10 to 360 minutes with constant mixing. The kinetic runs were followed with various concentrations of indigocarmine dye and a distinctive applied current. To represent the mineralization of the dye solution, COD was estimated at regular intervals of time. The pH of the dye solution before degradation and after degradation was measured. A positive voltage was applied by utilizing a battery eliminator (NEULITE INDIA) and a current yield of 3.6 mA - 6.6 mA utilizing rheostat (INSIFINDIA). The decolourization and degradation of indigocarmine was followed by measuring % transmittance using spectrophotometer (ELICO SL171) of $\lambda_{max} = 610$ nm.

3. Properties of Indigocarmine Dye



Molecular formula: $C_{16}H_8N_2Na_2O_8S_2$;
Molar mass: 466.36 g/mol;
Absorption maximum (water): 608 - 612 nm;
Bulk density: 700 - 900 kg/m^3.

4. Results & Discussion

Degradation using Graphite as anode electrode

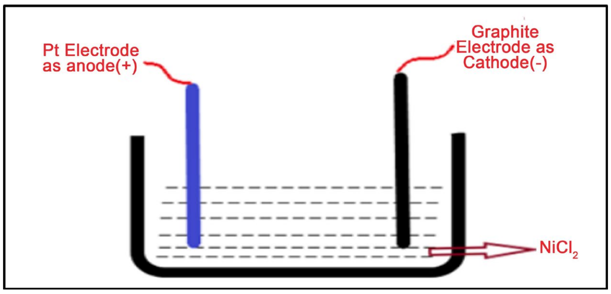


Figure 1. Synthesis of Ni/GME by electrochemical method.

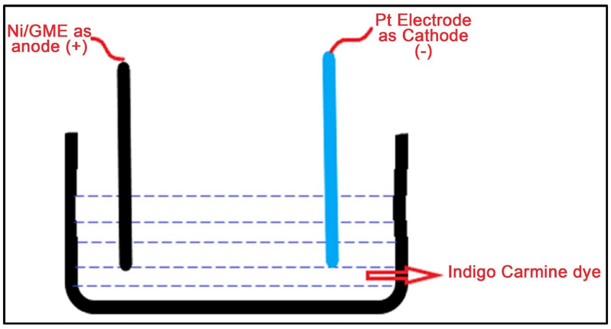


Figure 2. Experimental set up for electrochemical degradation of indigocarmine Dye using Ni/GME as anode.

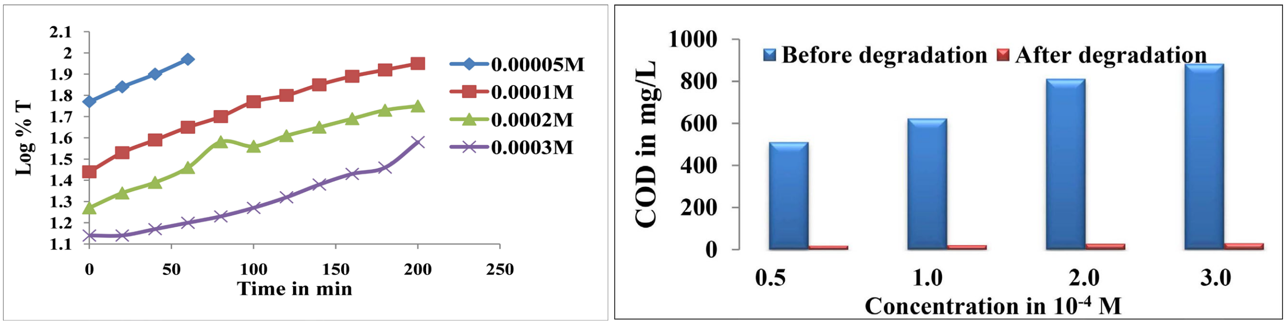
4.1. Effect of Concentration of Indigocarmine on the Rate of Degradation

The experiment was performed by taking different concentrations of IC dye solution (E-Merck) varying from [0.5×10^{-4} to 2.0×10^{-4} M] with constant current (4.6 mA). The change in concentration of the Indigocarmine was recorded by a change in % transmittance using a spectrophotometer. A plot of log%T (percentage transmittance of light) versus time was linear. Up to 60% of the reaction indicating degradation of IC follows first order kinetics. The rate constant values are given in **Table 1**. The reaction rate decreased with the increase in [IC]. This is due to the accumulation of Indigocarmine molecules at the outermost layer of graphite anode as a result of the graphite electrode. Which decreases the concentration of OH free radicals. The pH value before and after the electrolysis remain constant. The COD for Indigocarmine solution before and after electrolysis was measured (**Table 1**, **Figure 2** and **Figure 3**).

Table 1. Effect of [Indigocarmine] on the rate of degradation and COD values by GE.

Conc of Indigo carmine in 10^{-4} M	10^4 k in sec^{-1}	Measured pH		COD Values in mg/L	
		Before degradation	After degradation	Before degradation	After degradation
0.5	1.266	6.44	6.40	512	20
1.0	0.959	6.91	6.85	624	22
1.5	0.921	7.05	6.96	812	28
2.0	0.806	7.22	7.11	884	32

Applied Current = 4.6 mA, Temperature = 303 K, λ_{max} = 610 nm.



(a) (b)

Figure 3. Effect of concentration of indigocarmine dye on rate of degradation [a] and COD values [b].

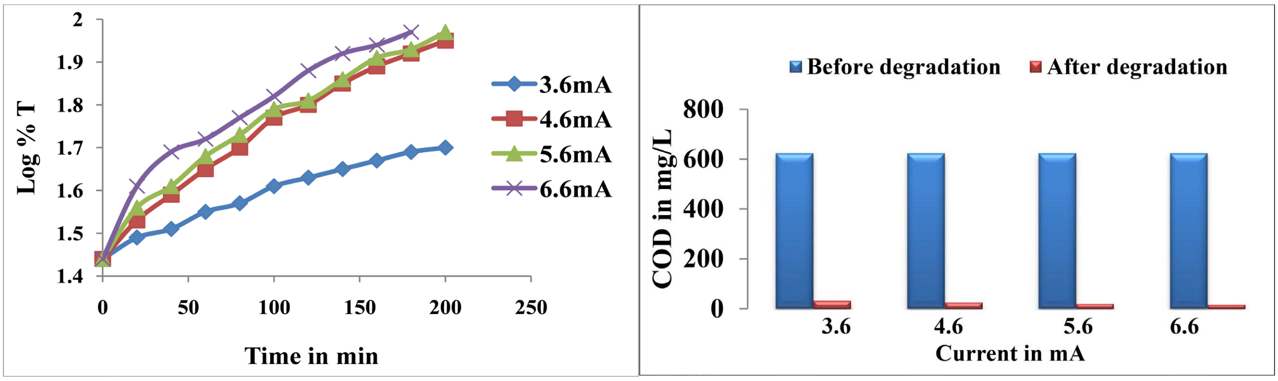
4.2. Effect of Current Density on the Rate of Degradation

To investigate the impact of applied current, the experiment was conducted using four distinct current density ranging from 3.6 mA to 6.6 mA, while maintaining a constant 0.0001M Indigocarmine dye concentration. Notably, as the applied current increased, it observed a corresponding increase in the reaction rate. This phenomenon can be attributed to the higher current levels leading to elevated concentrations of oxidizing intermediates and OH free radicals, ultimately resulting in an accelerated degradation rate. The corresponding rate constant values can be found in Table 2. Additionally, they conducted COD measurements for the Indigocarmine dye solution in various applied currents, both before and after degradation, with the results presented in Table 2 and Figure 4.

Table 2. Effect of current density on the rate of degradation and COD values by GE.

Current in mA	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
3.6	0.522	624	32
4.6	0.959	624	26
5.6	0.997	624	20
6.6	1.036	624	16

[IC] = 1×10^{-4} M, Temperature = 303 K, λ_{max} = 610 nm.



(a) (b)

Figure 4. Effect of current density of indigocarmine dye on the rate of degradation [a] and COD values [b].

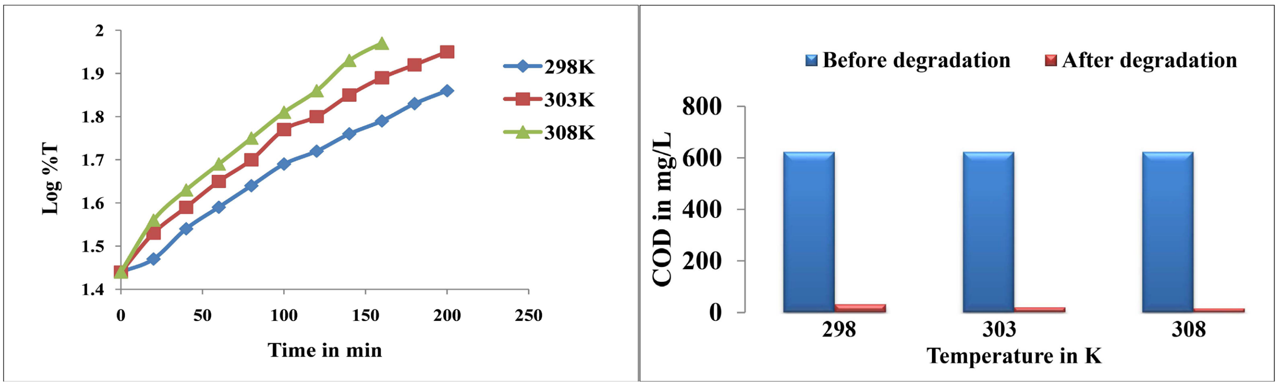
4.3. Effect of Temperature on the Rate of Degradation

To investigate the effect of temperature, the experiments were conducted at three distinct temperatures. As the temperature increased, it is observed that the rate of the reaction increased. It is observed that the rate of degradation of dye is not very significant at lower temperatures, however the reaction is more significantly influenced at higher temperatures. We determined the rate constant for degradation and COD values for both before and after degradation for the indigocarmine dye solution and these results are presented in **Table 3** and **Figure 5**. The increase in temperature can be attributed to an enhanced diffusion rate, potentially leading to a higher degradation rate. Thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ are calculated and are reported in **Table 4**.

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

Temperature in K	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
298	0.806	624	32
303	0.959	624	20
308	1.228	624	16

[IC] = 1 × 10^{-4} M, Current = 4.6 mA, λ_{max} = 610 nm.



(a)

(b)

Figure 5. Effect of temperature of Indigocarmine dye on the rate of degradation [a] and COD values [b].

Table 4. Thermodynamic parameters for the degradation of indigocarmine dye.

Temperature in K	ΔH# kJ/mol	ΔS# J/K/mol	ΔG# kJ/mol	Ea kJ/mol
298	96.84	−290.82	96.46	99.28
303	96.80	−290.00	97.57	
308	96.75	−287.87	98.58	

4.4. Reaction with Nickel Doped Graphite Modified (Ni/GME) as Anode Electrode Effect of [Indigocarmine] on the Rate of Degradation and COD Values by Ni/GME

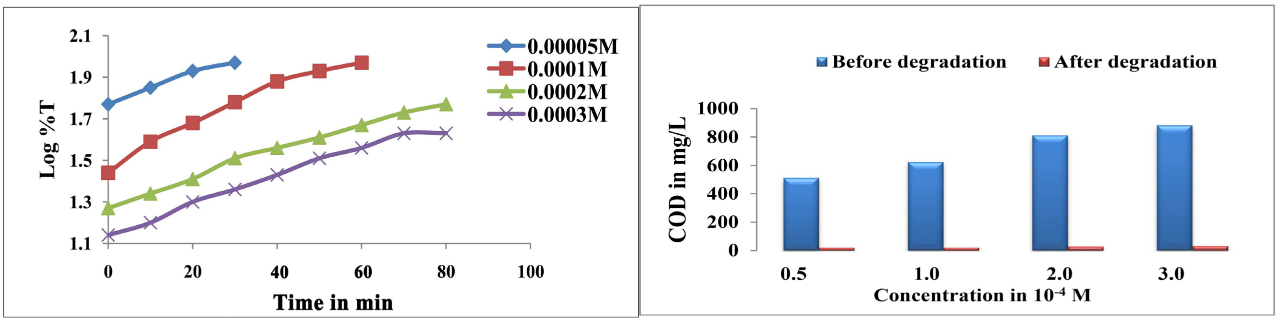
The reaction has been carried out in the presence of Indigocarmine dye solution

(0.0001 M), by keeping the applied current as constant (4.6 mA). The change in concentration of the Indigocarmine was recorded by a change in % transmittance of light using a spectrophotometer at λ_{max} = 610 nm. A plot of log%T (percentage transmittance of light) versus time was linear. Up to 65% of the reaction indicating the disappearance of Indigocarmine follows first order kinetics. The rate constant values are reported in Table 5. The rate of the reaction is decreased with an increase in the concentration of Indigocarmine dye and the values of rate constants were higher compared to the graphite electrode as an anode. pH value was almost constant before and after degradation. The COD was measured for Indigocarmine solution before and after degradation and the values were reported in Table 5 and Figure 6.

Table 5. Effect of [Indigocarmine] on the rate of degradation and COD values by Ni/GME.

[IC] 10^{-4} M	10^4 k in sec^{-1}	Measured pH		COD Values in mg/L	
		Before degradation	After degradation	Before degradation	After degradation
0.5	3.377	6.48	6.42	512	16
1.0	2.610	6.96	6.92	624	20
1.5	2.494	7.12	7.02	812	26
2.0	2.418	7.24	7.19	884	32

Applied Current = 4.6 mA, Temperature = 303 K, λ_{max} = 610 nm.



(a)

(b)

Figure 6. Effect of concentration of indigocarmine dye on rate of degradation [A]and COD values [B] by Ni/GME.

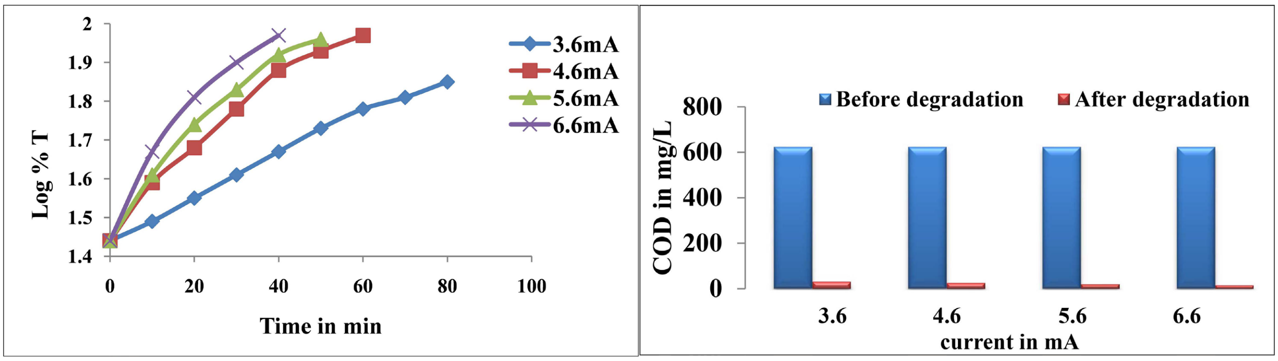
4.5. Effect of Current Density on the Rate of Degradation

At constant [IC] the rate of reaction increased with increase in applied current. The current density varies from 3.6 mA - 6.6 mA. The increment of applied current builds the concentration of oxidizing intermediates and OH free radicals, which increases the rate of degradation. The rate of degradation efficiency was higher in Ni doped graphite modified electrode compared to the graphite electrode. The rate constant values are higher compared to graphite electrodes and are reported in Table 6 and Figure 7(a). The COD was measured for both before and after degradation of dye solutions and is reported in Table 6 and Figure 7(b).

Table 6. Effect of current density on the rate of degradation and COD values by Ni/GME.

Current in mA	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
3.6	2.034	624	32
4.6	2.610	624	26
5.6	3.953	624	20
6.6	4.951	624	16

[IC] = 1 × 10^{-4} M, Temperature = 303K, λ_{max} = 610 nm.



(a) (b)

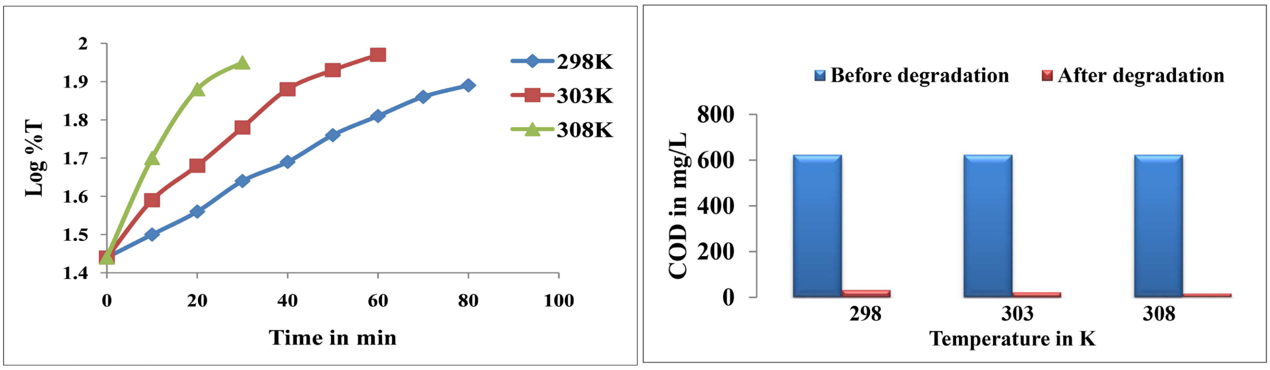
Figure 7. Effect of current of indigocarmine dye on the rate of degradation [a] and COD values [b] by Ni/GME.

4.6. Effect of Temperature on the Rate of Degradation

To investigate the effect of temperature, the degradation was carried out at three unique temperatures. Obviously, the increase in temperature increases the rate of reaction and shows that the rate of degradation is not extremely at low temperatures. However, the reaction was significantly increased at higher temperatures. The degradation efficiency was high for Ni/GME compared to graphite electrodes. Since the diffusion rate is increased with temperature, an increase in temperature could bring about an increase in the degradation rate. The rate constant values and COD values for before and after degradation are reported in Table 7 and Figure 8. Thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ are calculated and are reported in Table 8.

Table 7. Effect of temperature on the rate of degradation and COD values by Ni/GME.

Temperature in K	10^4 k in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
298	2.226	624	32
303	4.610	624	22
308	6.563	624	16



(a) (b)

Figure 8. Effect of temperature on the rate of degradation of indigocarmine dye [A] and COD values [B] by Ni/GME.

Table 8. Thermodynamic parameters for the degradation of Indigocarmine by Ni/GME.

Temperature in K	ΔH# kJ/mol	ΔS# J/K/mol	ΔG# kJ/mol	Ea kJ/mol
298	54.12	−296.0	93.79	
303	54.08	−295.85	95.04	56.60
308	54.04	−288.61	94.29	

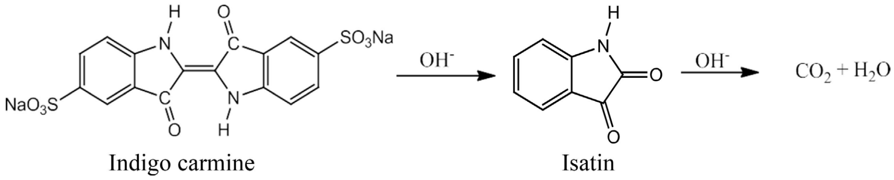
4.7. Production of OH Radical

The electrochemical degradation of Indigocarmine dye solution was carried out by anodic oxidation. Further, the experiment was done in the presence of electrodes with platinum as cathode graphite or Ni/GME as anode. In the electrochemical method, OH free radical is formed by direct electrolysis and formed as an intermediate at the surface of a high O_2^- overvoltage anode from oxidation of water.

$$H_2O \rightarrow .\, OH_{ads} + H^+ + e^-$$

The degradation of the IC takes place due to sequential electrochemical reduction and oxidation [17]. Graphite electrodes have the high affinity for IC with the implication that it will adversely affect electrode performance because of competitive adsorption and interaction such as electron shuttling may increase interactions. The strong oxidizing agent OH free radical, the sequential reduction and oxidation with graphite and the Pt electrodes. It has been found that Pt electrode possesses greater O_2 over voltage (+0.77 V), thus generating higher amounts of oxidant OH free radical. This reacts with IC converting into CO_2, H_2O and inorganic salts, until their total mineralization is reached. A colourless solution is obtained after degradation, which indicates the absence of formation of insoluble metal oxides. This suggests that oxidizing intermediates which are formed result in degradation of the dye. The graphite electrodes (GE) advantages such as commercial availability, low costs and easy modification [18] [19]. The present method can be used for remediation of waste water (**Scheme 1**).

$$O_2^{\cdot} + H_2O \longrightarrow HO_2^{\cdot} + OH\bullet$$
$$HO_2^{\cdot} + H_2O \longrightarrow OH^{\cdot} + H_2O_2$$
$$H_2O_2 \longrightarrow 2\ OH^{\cdot}$$
$$OH^{\cdot} + IC \longrightarrow \text{Intermediate proucts}$$
$$\longrightarrow \text{Degradation products}$$
$$O_2^{\cdot} + IC \longrightarrow \text{Intermediate proucts}$$
$$\longrightarrow CO_2 + H_2O$$



Scheme 1. Proposed degradation pathway of Indigocarmine.

4.8. Effect on COD for Duration of Treatment

The effect of the degradation rate of the dye on COD was determined. During the experiment, the initial COD was 392 mg/L which led to 40 mg/L, of COD after degradation, a 95% decrease in COD was achieved. The COD level obtained after degradation was within the allowed permitted level of 250 mg/L. A graph showing COD decrease versus treatment time is displayed in **Figure 9**.

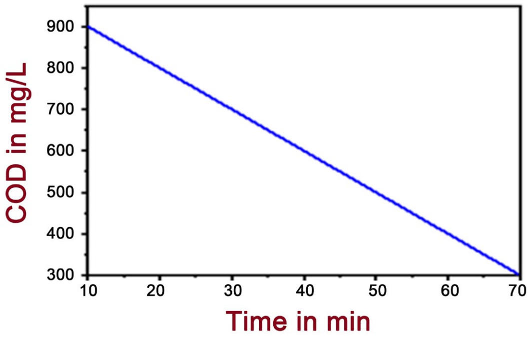


Figure 9. The rate of decrease of COD at different intervals of time.

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

$$\text{ICE}(\%) = \frac{(\text{COD}_i - \text{COD}_f)}{8\text{It}} \times \text{FV}$$

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 is the treatment time and "8" is the oxygen equivalent mass (geq − 1). The ICE data in **Table 9**, **Table 10** shows the efficiency of the process linearly related to ICE and indicates higher efficiency of the process for Ni/GME anode compared to GE anode [20] [21].

Table 9. ICE values at different experimental conditions for graphite electrode.

	Variables	ICE
Concentration of Dye 10^{-4} M	0.5	433.55
	1.0	177.14
	2.0	160.56
	3.0	159.58
Current in mA	3.6	152.58
	4.6	177.14
	5.6	154.07
	6.6	144.26
Temperature in K	298	114.99
	303	177.14
	313	199.29

Table 10. ICE values at different experimental conditions for Ni/GME.

	Variables	ICE
Concentration of Dye 10^{-4} M	0.5	867.10
	1.0	531.44
	2.0	379.51
	3.0	297.89
Current in mA	3.6	330.60
	4.6	531.44
	5.6	523.85
	6.6	540.98
Temperature in K	298	238.82
	303	523.85
	313	1062.89

4.9. Kinetics of Degradation

The degradation of dye takes place in the absence of electrolyte HCl or NaOH. The degradation of dye depends on [dye], current density (I) and the surface active sites [S]. Since [S] remains constant, the rate of degradation in the present case is given by

$$-\frac{\mathrm{d}c}{\mathrm{d}t}=\frac{k[I]}{[dye]}$$

The rate constant for the degradation of the indigocarmine process was determined by plotting log%T versus time (t). Here "T" is the percentage transmission of the light obtained from a spectrophotometer, at $\lambda_{\max}$ 610 nm and it is inversely proportional to the concentration of the dye. A straight line was obtained for 60%

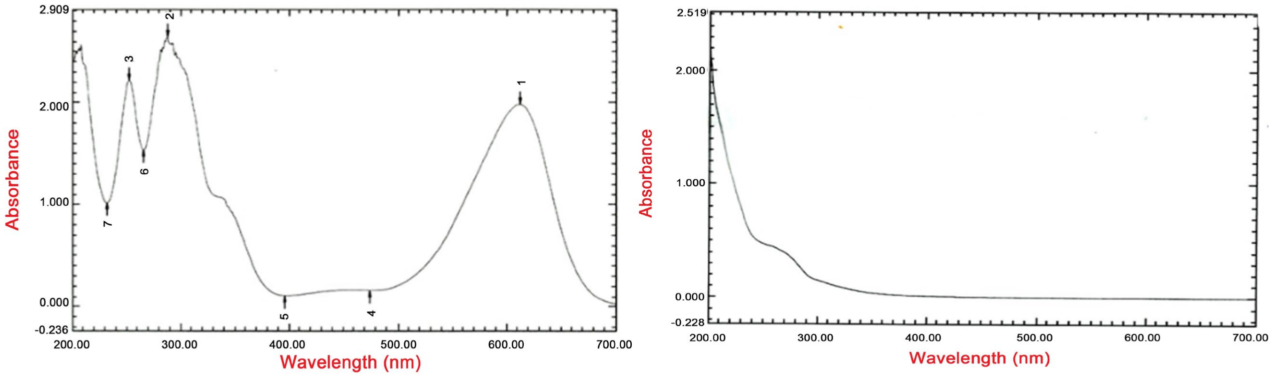
of the degradation reaction and afterward deviation in linearity was observed.

4.10. Reuse of Nickel Graphite Modified Electrode

The possibility of reusing the Ni/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 washed with double distilled water and afterward reused for the degradation by taking the fresh dye solution. From the degradation study it is clear that the reuse of the graphite modified electrode to degrade the dye solution showed little less efficiency.

4.11. UV-Visible Spectra

Figure 10(a) and **Figure 10(b)** represents UV-Visible spectra during the electrochemical degradation of Indigocarmine dye. A broad visible colour absorption spectra at 620 nm were totally eliminated at the end of the degradation cycle. However, the absorption in the UV-region indicates a less intense small peak which shows the presence of a minute concentration of organics (<48 mg/l COD).



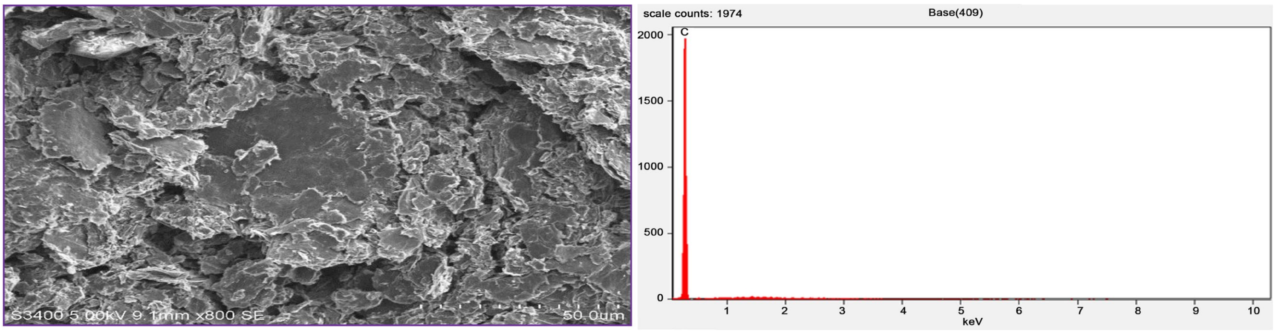
(a) (b)

Figure 10. (a): UV-Visible spectra of IC before degradation; (b): UV-Visible spectra of IC after degradation.

4.12. Scanning Electron Microscopy (SEM) & Energy Dispersive X-Ray Spectroscopy (EDX)

Figure 11(a) & **Figure 11(b)** shows the SEM image of a graphite flake and its corresponding EDX profile. From the micrograph, the layered and homogenous nature of graphite was seen in different diameters. It is clear from **Figure 11(a)** before deposition, just graphite flakes are found. The observed size of the graphite flake ranged from 10 to 50 μm. From the EDX profile, the presence of carbon and oxygen content indicates the graphite present in the pure form in **Figure 11(b)**.

Figure 12(a) and **Figure 12(b)** show the SEM and EDX profile of Nickel encapsulated in a graphite rod. The SEM image of a nickel encapsulated graphite rod can clearly be distinguished from the graphite rod. Further, the heterogeneous block dots were seen on the surface, which show the nickel doped or encapsulated inside the graphite rod in **Figure 12(a)**. The corresponding EDX plot as shown in **Figure 12(b)**. From the EDX plot, we clearly noticed the presence of nickel peaks in different oxidation states along with graphite carbon peaks (Table 11 and Table 12).

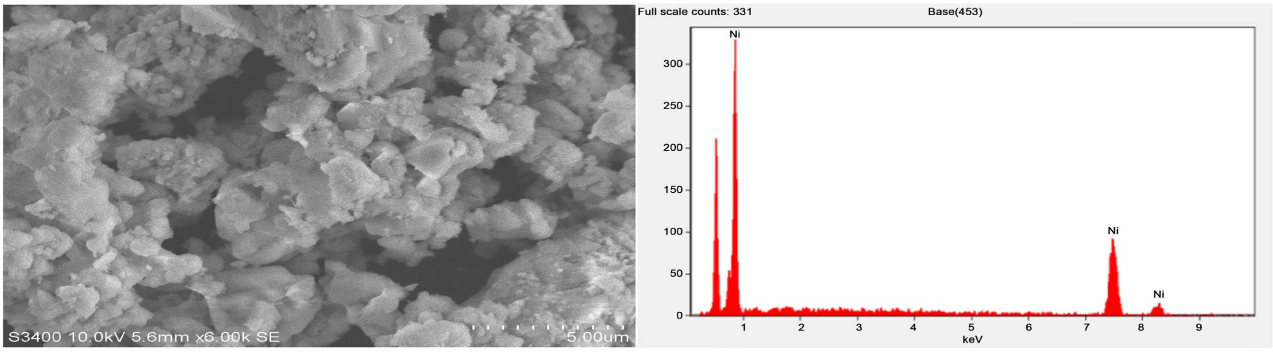


(a) (b)

Figure 11. (a): SEM micrographs of graphite electrode; (b): Energy-dispersive X-ray spectroscopy (EDS) for 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



(a) (b)

Figure 12. (a): SEM micrographs of Ni/graphite modified electrode; (b): Energy-dispersive X-ray spectroscopy (EDS) for Ni/GME.

Table 12. Quantitative results for nickel graphite modified electrode.

Element Line	Weight %	Weight % Error	Atom %
C K	---	---	---
O K	13.04	± 2.11	5.64
Ni L	50.60	± 1.30	80.25
Ni M	36.36	±3.41	14.11
Total	100.00		100.00

5. Conclusion

In this work, electrochemical oxidation in the presence of a graphite electrode and Ni/GME was capable of destroying the chromophore groups of dye and organic moiety found in industrial effluents at short treatment times, low energy utilization and reuse of graphite electrode. This method can be applied to the remediation of wastewater containing colours and organics and the technique is cost-effective as a graphite electrode was utilized. The rates of IC elimination and COD removal were higher on the Ni/GME compared to the graphite electrode.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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