

Electrochemical Degradation of Acridine Orange Dye at Pd/graphite Modified Electrode in Aqueous Solution

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Abstract

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

Keywords: Acridine orange; anodic oxidation; Pd/graphite modified electrode; mineralization.

INTRODUCTION

Acridine orange (AO) is a heterocyclic dye containing nitrogen atoms which is widely used in the fields of printing and dyeing, leather, printing ink, and lithography. It has also been used extensively in biological stains. Toxicological investigation indicates that amino acridine has mutagenic potential [1, 2]. The waste water generated by the textile and dyeing industry is rated as the most polluting among all the industrial sectors. The release of this waste water without treatment into water stream is very dangerous, since most of the dyes are carcinogenic in nature and pose a serious threat to the environment. [3]. The release of this colored waste water in the ecosystem is dramatic source of water pollution, eutrophication, and perturbation in aquatic life [4]. Conventional wastewater treatment methods such as precipitation, adsorption, air stripping, flocculation, reverse osmosis, and ultra filtration can be used for color removal from dye-contaminated effluents [5]. However, these methods are non-destructive, since they only transfer the contamination from one phase to another, causing secondary pollution and requiring further treatment [6]. In recent years "advanced oxidation processes" (AOPs) emerged as an alternative to conventional methods. AOPs are based on the generation of very reactive species such as hydroxyl radicals, which oxidize a broad range of organic pollutants quickly and non-selectively [7]. Anodic oxidation and electro-Fenton are the most usual techniques, since they have high degradation efficiency due to electrochemical reaction of OH radical as oxidant [8, 9]. However a limited number of papers have been published for the destruction of dyes by electrochemical methods [10, 11]. Here we have developed the electrochemical method for the degradation of Acridine orange dye with Pd/graphite modified electrode [12, 13]. Electrochemical degradation of organic pollutants has been investigated by many researchers. And it has been proved as a cost-effective technology. Thus electrochemical degradation is a good choice of removing Acridine orange. As a new and attractive technology, electrochemical oxidation of organic pollutants has gained significant attentions over the past two decades [14, 15]. The kinetics of degradation of Acridine orange was studied.

EXPERIMENTAL

A solution of acridine orange (AO) (LOBACHEMIE) was prepared [0.0001M]. The 8cm length and 0.63cm diameter graphite electrode (ALFA AESAR) was used. The 2.5cm length graphite electrode is dipped into the above solution. Prior to experiment, the surface pretreatment of graphite electrode was performed by hand polishing of the electrode surface with successive grades of emery papers down to 3000 grit up to a mirror finish. The polished electrode was then degreased with 1:1 HCL solution, acetone and washed with running doubly distilled water and utilized for further electrodeposition. The experimental setup is shown in the figure (1). Palladium was deposited on Graphite electrode from PdCl₂ (Arora matthey) solution. All chemicals used were of accepted grades of purity. It consists of reaction chamber and a voltage power supply. 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. 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, Pd (II) thin film deposited on a conductive Graphite electrode has taken as anode and Pt electrode as cathode. The experiment was run from 15 to 360 minutes with continuous stirring. The kinetic runs were carried out for different concentration of acridine orange and different applied current. To account for the mineralization of the dye solution COD was measured at regular intervals of time [16]. The pH of the solution before and after electrolysis was measured. A positive voltage was applied by using battery eliminator (NEULITE INDIA) and current output of 2.1mA-6.1mA using rheostat (INSIFINDIA). The decolourisation and disappearance of acridine orange was followed by using spectrophotometer (ELICO SL171).

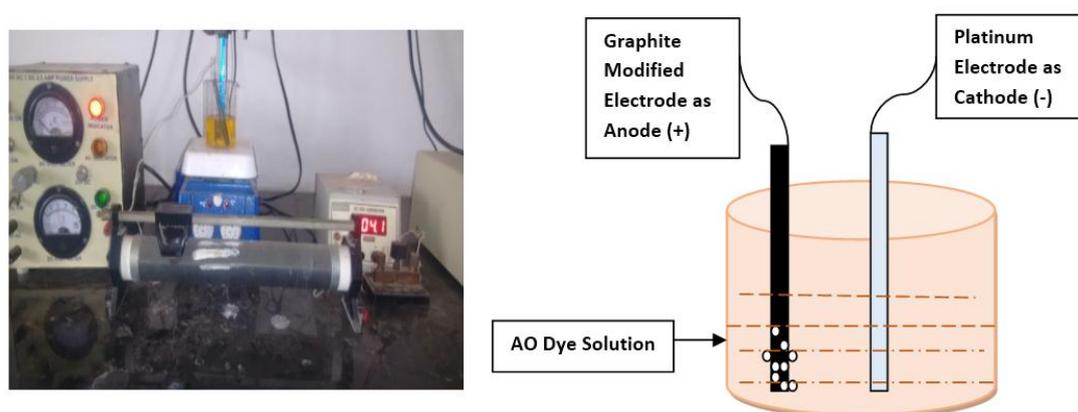


Figure: 1 Experimental set up for electrochemical degradation of AO

RESULTS AND DISCUSSION

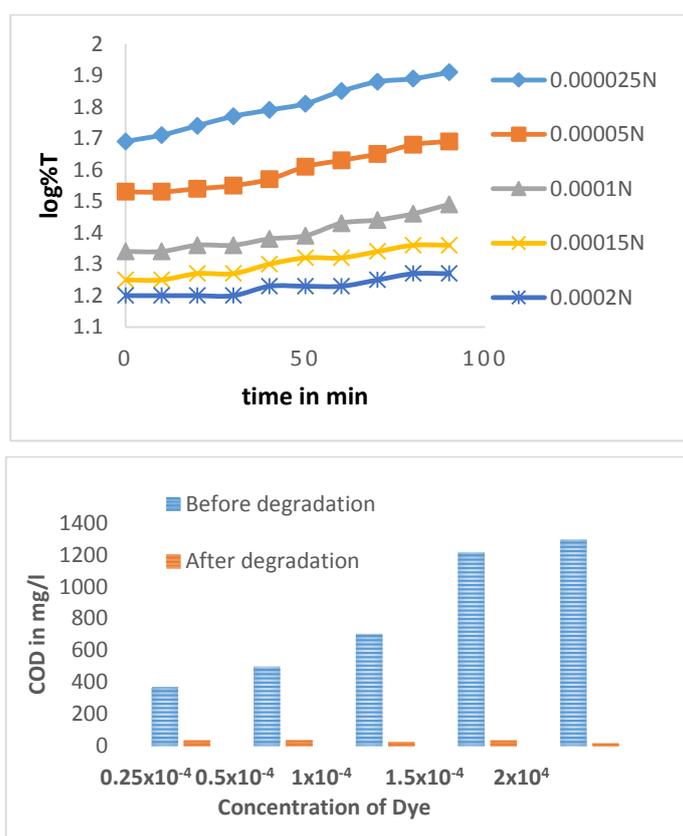
Reaction with graphite as anode electrode

Effect of acridine orange on the rate

The reaction performed in the presence of AO (0.0001M), with constant current (4.1mA). The change in concentration of the acridine orange was recorded by change in color using spectrophotometer. A plot of $\log T$ (percentage transmittance of light) versus time was linear upto 60% of the reaction indicating disappearance of AO follows first order kinetics. The rate constant values are given in table (1). The reaction rate decreased with increase in [AO]. 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 of before and after the electrolysis shows slight increase towards the alkaline pH. The COD for Acridine orange solution before and after electrolysis were measured. The values of rate constants and COD Values were calculated for 50% of degradation during the reaction. (Table-1, Fig-2 and 3).

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

| $10^4[\text{AO}]$ | 10^4k sec^{-1} | Effect of pH | | COD values in mg/l | |
|-------------------|------------------------------|--------------------|-------------------|--------------------|-------------------|
| | | Before degradation | After degradation | Before degradation | After degradation |
| 0.25 | 07.67 | 5.68 | 7.01 | 368 | 32 |
| 0.5 | 08.44 | 6.39 | 7.04 | 496 | 34 |
| 1.0 | 06.90 | 6.70 | 7.20 | 704 | 24 |
| 1.5 | 06.14 | 7.30 | 7.78 | 1216 | 32 |
| 2.0 | 03.45 | 7.39 | 8.0 | 1296 | 16 |

**Figure 2 and 3:** Effect of Concentration of AO on rate of degradation and COD Value**Effect of current on the rate**

At fixed [AO] the rate of reaction increased with increase in applied current. The current is varied from 2.1mA-6.1mA. (Table-2, Fig-4 and 5). The increase of current increases the concentration of oxidizing intermediates and OH radicals, which increases the rate of degradation.

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

| Current in mA | 10^4 k sec^{-1} | COD values in mg/l | |
|---------------|---------------------------|--------------------|-------------------|
| | | Before degradation | After degradation |
| 2.1 | 0.30 | 704 | 32 |
| 3.1 | 0.42 | 704 | 24 |
| 4.1 | 0.65 | 704 | 32 |
| 5.1 | 15.35 | 704 | 28 |
| 6.1 | 16.88 | 704 | 30 |

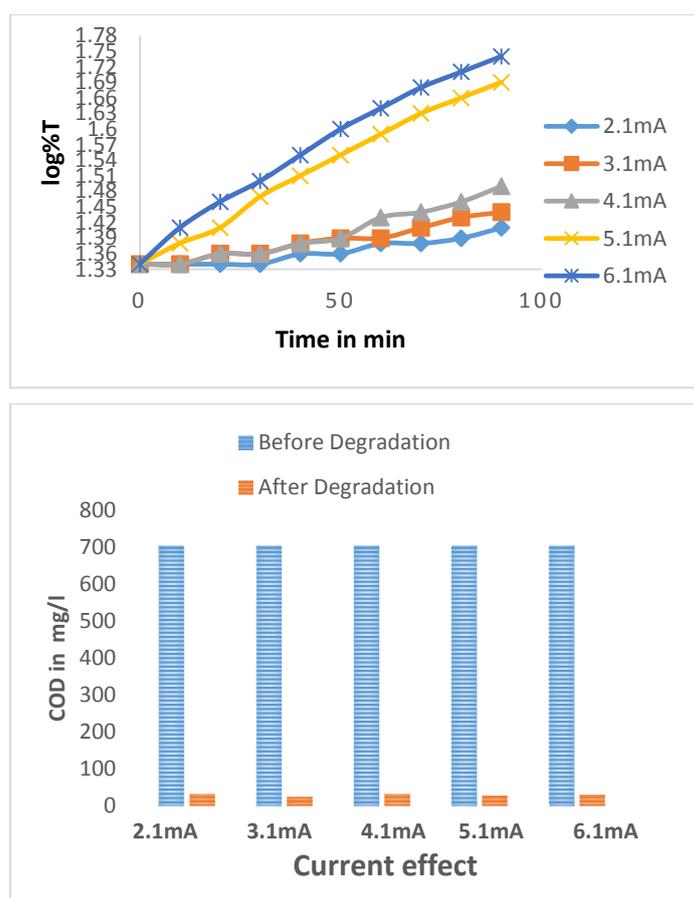


Figure 4 and 5: Effect of current of AO on the rate of degradation and COD Values

Effect of temperature

The rate constant with respect to temperature increases first and then falls off with raising temperature. Indicates variation of chemisorption with temperature. The initial increase shows that, like the chemical reaction Chemisorption also needs activation energy. However the later decrease indicates that at higher temperature desorption

does occur in chemisorption process. Frequently during the high temperature desorption of some atoms of the adsorbent are in a chemically bound form. This indicates at lower temperature increases the adsorption capacity of the graphite. Hence the rate constant at higher temperature the desorption increases and the rate decreases. Thermodynamic parameters for the degradation of AO was calculated.(Table-4 Fig-6)

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

| Temperature in K | $10^4 k \text{ sec}^{-1}$ | COD values in mg/l | |
|------------------|---------------------------|--------------------|-------------------|
| | | Before degradation | After degradation |
| 283 | 03.07 | 704 | 64 |
| 288 | 04.60 | 704 | 48 |
| 293 | 06.25 | 704 | 16 |
| 308 | 03.45 | 704 | 32 |
| 313 | 02.30 | 704 | 16 |
| 318 | 01.91 | 704 | 48 |

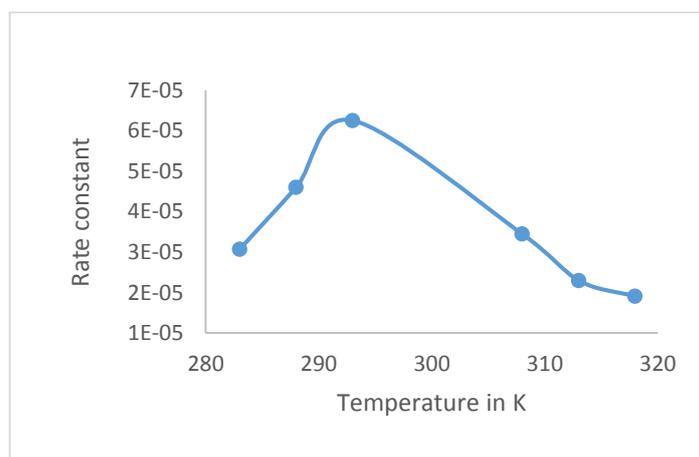


Figure 6: Effect of temperature of AO on the rate of degradation

Table 4: Thermodynamic parameters for the degradation of AO.

| Temperature in K | ΔH | ΔS | ΔG |
|------------------|--------------|-------------|---------------|
| 283 | 46.66 KJ/mol | -166.02 J/k | 93.64 KJ/mol |
| 288 | 46.62 KJ/mol | -146.67 J/k | 88.86 KJ/mol |
| 293 | 46.57 KJ/mol | -147.17 J/k | 89.70 KJ/mol |
| 308 | 46.45 KJ/mol | -160.67 J/k | 95.94 KJ/mol |
| 313 | 46.41 KJ/mol | -166.71 J/k | 98.59 KJ/mol |
| 318 | 46.37 KJ/mol | -170.85 J/k | 100.70 KJ/mol |

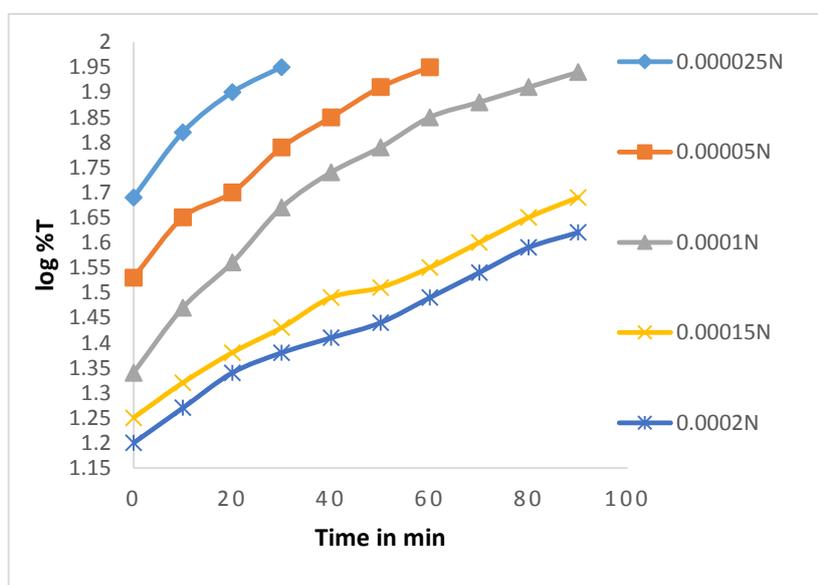
Reaction with palladium- graphite modified electrode (PdGME) as anode electrode

Effect of acridine orange on the rate

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

Table 5: Effect of [AO] on the rate of degradation and COD values for PdGME \

| 10 ⁴ [AO] | 10 ⁴ k sec ⁻¹ | Effect of pH | | COD values in mg/l | |
|-------------------------|--|--------------------|-------------------|--------------------|-------------------|
| | | Before degradation | After degradation | Before degradation | After degradation |
| 0.25 | 33.00 | 5.20 | 7.01 | 368 | 16 |
| 0.5 | 26.48 | 5.68 | 7.06 | 496 | 16 |
| 1.0 | 24.94 | 6.70 | 7.20 | 704 | 16 |
| 1.5 | 18.04 | 7.30 | 7.78 | 1216 | 32 |
| 2.0 | 17.27 | 7.39 | 8.01 | 1296 | 32 |



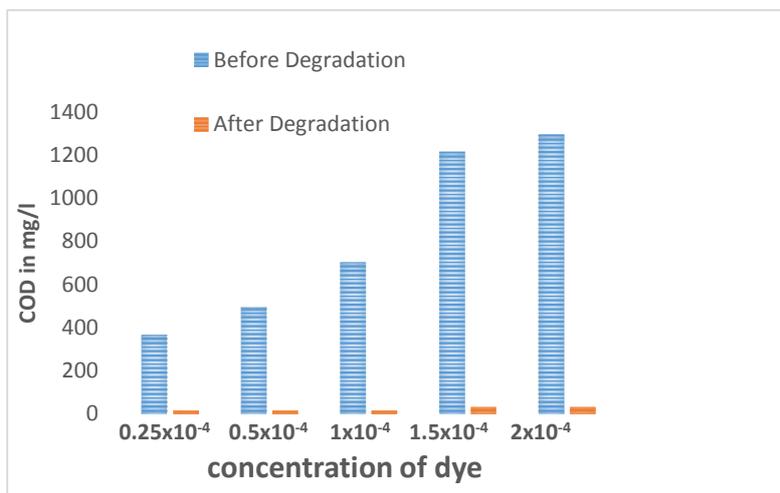


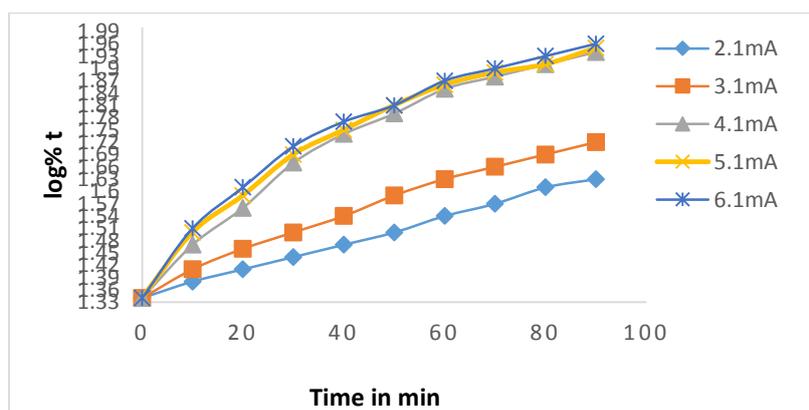
Figure7 and 8: Effect of Concentration of AO on the rate of degradation and COD Values

Effect of current on the rate

At fixed [AO] the rate of reaction increased with increased in applied current. The current is varied from 2.1mA-6.1mA. (Table-6, Fig-9and10). The rate of degradation is higher compared to graphite electrode as anode.

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

| Current in mA | $10^4 k \text{ sec}^{-1}$ | COD values in mg/l | |
|---------------|---------------------------|--------------------|-------------------|
| | | Before degradation | After degradation |
| 2.1 | 12.26 | 704 | 16 |
| 3.1 | 16.11 | 704 | 32 |
| 4.1 | 24.93 | 704 | 16 |
| 5.1 | 24.93 | 704 | 28 |
| 6.1 | 26.11 | 704 | 32 |



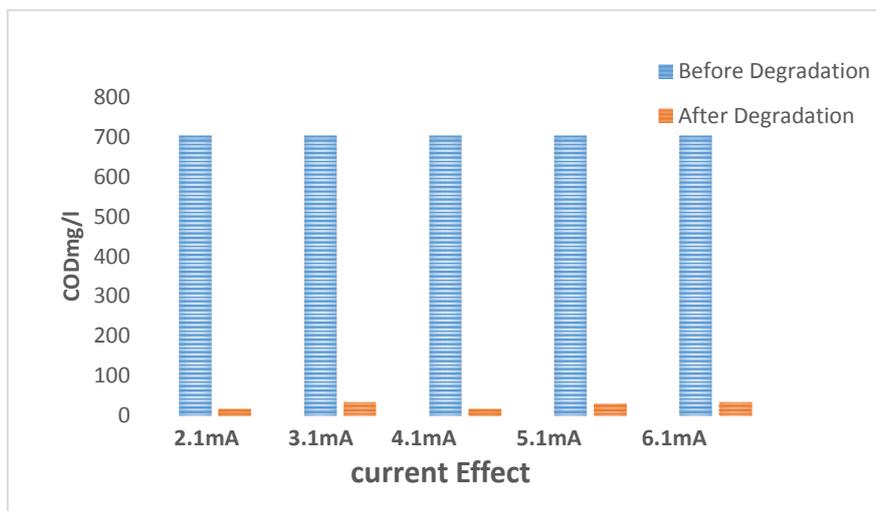


Figure 9 and 10: Effect of current of AO on the rate of degradation and COD Values

Effect of temperature

The rate constant with respect to temperature increases first and then falls off with raising temperature. Indicates variation of chemisorption with temperature. The initial increase shows that, like the chemical reaction chemisorption also needs activation energy. However the later decrease indicates that at higher temperature desorption does occur in chemisorption process. Frequently during the high temperature desorption of some atoms of the adsorbent are in a chemically bound form. This indicates at lower temperature increases the adsorption capacity of the graphite. Hence the rate constant at higher temperature the desorption increases and the rate decreases. The rate constants absorbed for Pd/graphite modified electrode are higher than the reaction taking place for graphite electrode. Similarly to previous observation here also the rate constant increases with temperature and falls of at higher temperature indicating the chemisorption at lower temperature and desorption at higher temperature. Thermodynamic parameters for the degradation of AO for Pd/graphite modified electrode was calculated (Table-8', Fig-11)

Table 7: Effect of Temperature on the rate of degradation and COD values.

| Temperature in K | $10^4 k \text{ sec}^{-1}$ | COD values in mg/l | |
|------------------|---------------------------|--------------------|-------------------|
| | | Before degradation | After degradation |
| 283 | 13.43 | 704 | 16 |
| 288 | 22.25 | 704 | 32 |
| 293 | 18.81 | 704 | 16 |
| 308 | 24.93 | 704 | 32 |
| 313 | 21.11 | 704 | 28 |
| 318 | 19.18 | 704 | 32 |

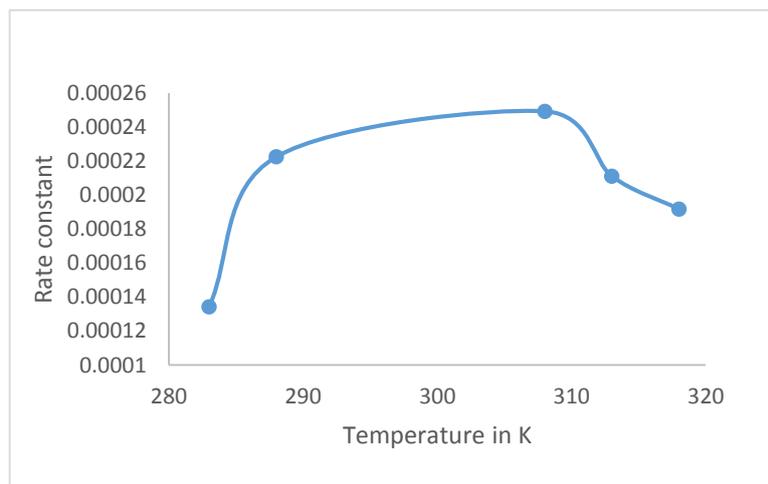


Figure 11: Effect of Temperature of A O on the rate of degradation

Table 8: Thermodynamic parameters for the degradation of AO for PdGME electrode

| Temperature in K | ΔH | ΔS | ΔG |
|------------------|--------------|-------------|---------------|
| 283 | 20.93 kJ/mol | -244.68 J/k | 90.17 kJ/mol |
| 288 | 20.88 kJ/mol | -242.00 J/k | 90.58 kJ/mol |
| 293 | 20.84 kJ/mol | -244.94 J/k | 92.61 kJ/mol |
| 308 | 19.26 kJ/mol | -251.64 J/k | 96.77 kJ/mol |
| 313 | 19.22 kJ/mol | -254.26 J/k | 98.80 kJ/mol |
| 318 | 19.18 kJ/mol | -256.32 J/k | 100.69 kJ/mol |

Production of OH radical

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



The degradation of AO takes place due to sequential electrochemical reduction and oxidation [17]. Graphite electrodes have high affinity for AO 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 $\cdot OH$ Radical, the sequential reduction/oxidation with graphite and pt electrodes which reacts with AO converting into CO₂, H₂O and inorganic ions until their total mineralization is reached [18]. It has been found that Pt electrode possesses greater

O_2^- over voltage (+0.77V), thus generating higher amount of oxidant $OH\cdot$. 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 [19]. The present method can be used for remediation of waste water.

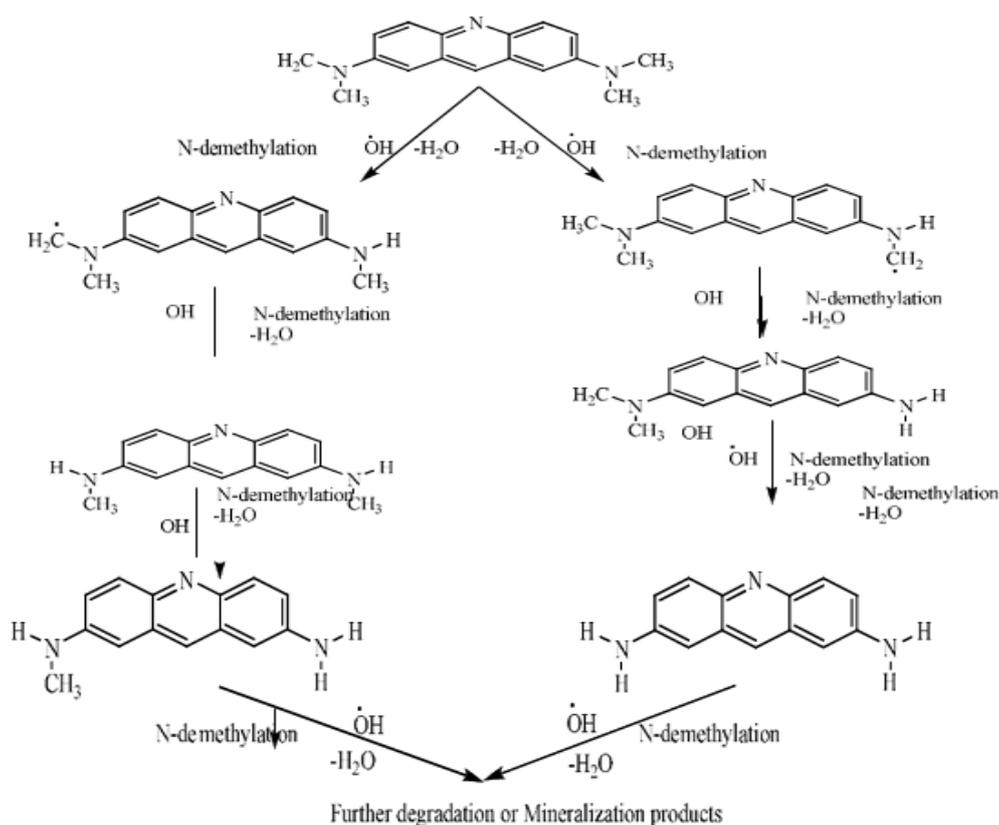
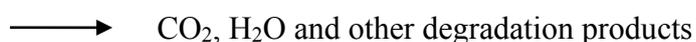


Figure 12: Proposed degradation pathway of acridine orange

Effect on COD of duration of treatment

The effect of rate of dye degradation on COD was determined. During the experiment the initial COD 704mg/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 (13).

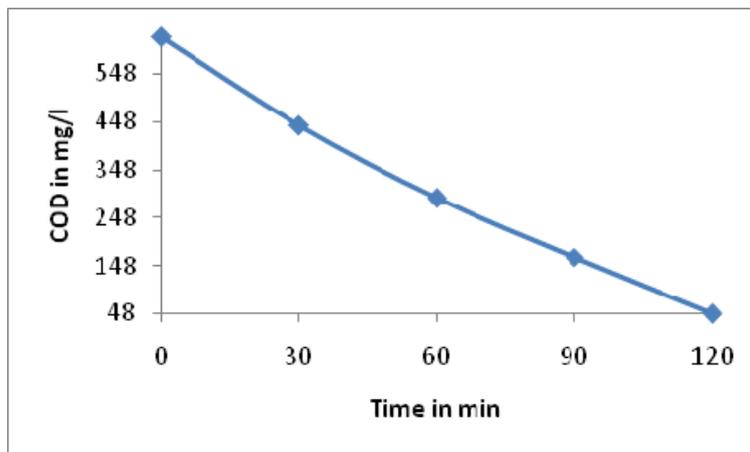


Figure 13: The rate of decrease of COD at different intervals of time.

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

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

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, 't' 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 PdGME anode compared to GE anode.

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

| Concentration of dye 10 ⁻⁴ | Variables | ICE |
|---------------------------------------|-----------|--------|
| | 0.25 | 164.75 |
| | 0.5 | 151.02 |
| | 1.0 | 153.89 |
| | 1.5 | 178.63 |

| | | |
|------------------|-----|--------|
| Current in mA | 2.1 | 140.36 |
| | 3.1 | 139.26 |
| | 4.1 | 153.89 |
| | 5.1 | 145.35 |
| Temperature in K | 283 | 116.29 |
| | 288 | 137.85 |
| | 293 | 192.77 |
| | 308 | 208.11 |
| | 313 | 168.67 |

Table 10: ICE values at different experimental conditions for PdGME electrode.

| | Variables | ICE |
|--|-----------|--------|
| Concentration of dye in 10 ⁻⁴ | 0.25 | 690.40 |
| | 0.5 | 470.81 |
| | 1.0 | 449.81 |
| | 1.5 | 580.56 |
| Current in mA | 2.1 | 493.98 |
| | 3.1 | 522.96 |
| | 4.1 | 449.81 |
| | 5.1 | 517.18 |
| Temperature in K | 283 | 368.02 |
| | 288 | 395.41 |
| | 293 | 449.81 |
| | 308 | 494.26 |
| | 313 | 439.34 |

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 Acridine orange for the degradation process was determined by plotting logT versus time (t). Here 'T' is percentage transmission of the light obtained from spectrophotometer, at $\lambda_{max}490nm$ 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 Palladium Graphite Modified Electrode

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

UV-Visible spectra

Figure 14 (A and B) represents UV-Visible spectra during the electrochemical Degradation of Acridine orange dye. Broad visible colour absorption spectra at 490nm and 470 nm were completely removed at the end of the degradation process.

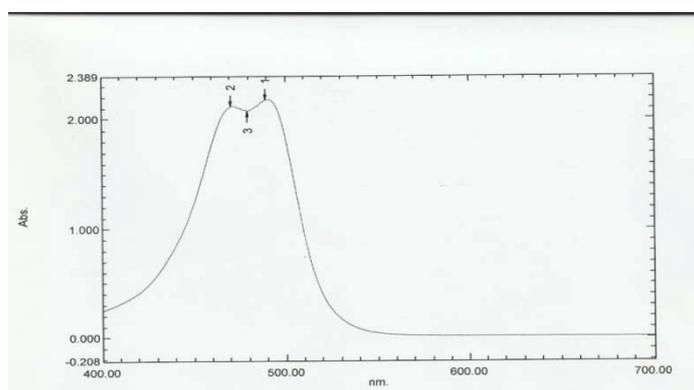


Figure 14 (A): UV-Visible spectra of AO before degradation.

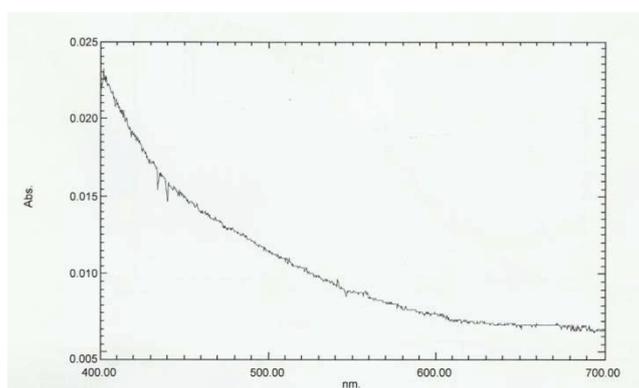


Figure 14 (B): UV-Visible spectra of AO after degradation

CONCLUSION

Electrochemical oxidation in presence of graphite and palladium modified electrode is capable of destroying the chromophore groups of dye found in industrial effluents at short treatment times, low energy consumption and reuse of graphite electrode. This

method can be applied to the remediation of waste water containing dyes and organics. Hence the method is cost effective as graphite electrode is used. The rates of Acridine orange elimination and COD removal were higher on the Pd/graphite modified electrode than that of the graphite electrode.

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REFERENCES:

- [1] Rakesh, S. Ananda* and Sowbhagya. ISSN 0974-3111 Volume 4, Number 3 (2012), pp. 227-239
- [2] Chung-Shin Lu 1,*, Chiing-Chang Chen 2, Ling-Kuen Huang 1, Peir-An Tsai 3, and Hsiao-Fang Lai 4 *Catalysts* 2013, 3, 501-516; doi:10.3390/catal3020501
- [3] BRIJESH PARE*, VIJENDRA SINGH, PRAKASH MORE and T. R. THAPAK *Int. J. Chem. Sci.*: 9(2), 2011, 537-544
- [4] Faisal, M.; Tariq, M. A.; Muneer, M. *Dyes Pigm.* 2007, 72, 233
- [5] Kansal, S. K.; Singh, M.; Sud, D.J. *Hazard. Mater.* 2007, 141, 581
- [6] Chiing-Chang Chen. Ren-Jang Wu. Yi-You Tzeng. Chung-Shin Lu.; *Journal of the Chinese Chemical Society*, 2009, 56, 1147-1155
- [7] Daneshvar, N.; Salari, D.; Khataee, A. R. *J. Photochem. Photobiol. A: Chem.* 2004, 162, 317.
- [8] Guivarch, E., Oturan, N., Oturan, M. A., 2003, Removal of organophosphorous pesticides from water by electrogenerated Fenton's reagent, *Environ. Chem. Lett.*, 1, pp. 165-168
- [9] Brillas, E., Boye, B., Sires, I., Garrido, J. A., Rodriguez, R. M., Arias, C., Cabot, P. L., Comninellis Ch., 2004, Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode, *Electrochemi. Acta.* 49, pp. 4487-4496.
- [10] Wang, A., Qu, J., Ru, J., Liu, H., Ge, J., 2005, Mineralization of an azo dye Acid Red 14 by electro-Fenton's reagent using an activated carbon fiber cathode. *Dyes pigments*, 65, pp. 227-233.
- [11] Salah Ammar, Ridha Abdelhedi, Cristina Flox, Conchita Arias, Enric Brillas., 2006, Electrochemical degradation of the dye indigocarmine at boron-doped diamond anode or waste waters remediation, *Environ. Chem. Lett*, 4, pp. 229-233.
- [12] Song, Y. H., Wei, G and Xiong, R. C., 2007, *Electrochim. Acta*, 52, pp. 7022.

- [13] Feng, Y.J., Cui, Y.H., Logan, B. and Liu, Z.Q., 2008, *Chemosphere*, 70, pp. 1629.
- [14] S.M.pawar, A.V.Moholkar, P.S.Shinde, K.Y.Rajpure, C.H.Bhosale, *Journal of Alloys and Compounds*, 459(2008)515
- [15] J.Vazquez-Arenas, R.Cruz, L.H.Mendoza-Huizar, *Electrochimica Acta*, 52 (2006) 892
- [16] APHA, standard methods for the examination of water and waste water, America.Wastewater.Association, New, New York(1989).
- [17] Mei Sun,[†] Danny D. Reible,[§] Gregory V. Lowry,^{†,‡} and Kelvin B. Gregory,^{†,*} [dx.doi.org/10.1021/es300048y](https://doi.org/10.1021/es300048y) | *Environ. Sci. Technol.* 2012, 46, 6174–6181
- [18] Sowbhagya, *S. Ananda and Rakesh ISSN 0973-1792 Volume 8, Number 2 (2012) pp. 141-152
- [19] Qing Hao, Yonggang Zhang* Electrochemical degradation of formaldehyde with a novel Pd/GO modified graphite electrode *Int. J. Electrochim. Sci.*, 11 (2016) 1496 - 1511