



ELECTROCHEMICAL DEGRADATION OF 5, 5-INDIGODISULFONIC ACID SODIUM SALT DYE AT COPPER/GRAPHITE MODIFIED ELECTRODE IN AQUEOUS SOLUTION

Chandrashekar¹, Charan Kumar H.C*¹, Raghavendra M.P², Prashanth P.A¹, Shilpa.R³, Ananda.S³

1, Department of Chemistry, PES College of Engineering Mandya 571401, Karnataka

2. Department of Microbiology, Maharani Science College for Women, Mysuru, Karnataka

3. Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysuru. Karnataka

Abstract: An anodic oxidation process with graphite anode coated with Cu was optimized for the degradation of IC dye. The Cu/GME was prepared by the electrochemical method. The comparison between the kinetics of degradation by graphite and Cu/GME has been studied systematically. The effect of four independent variables like dye concentration, pH, current density and different temperature, degradation rate is to be studied. The anodic oxidation by Cu/GME showed the complete degradation of aqueous solution IC, which is confirmed by UV-vis and COD measurement. The experimental removal efficiencies of IC using Cu/GME and graphite anodes were 97.8% and 60.3% respectively. The electrochemical removal of IC using both Cu/GME and graphite anodes well followed the 1st order kinetics. This process is one of the advanced oxidation processes (AOPs). It generates hydroxyl free radicals ($\cdot\text{OH}$) which attack the dye molecules, resulting in degradation of the dye molecules. The thin film formation of Cu or encapsulated in graphite rod is observed from SEM/EDAX. The ICE values of different experimental conditions are calculated. These results indicated that the Cu/GME would be promising anode for electrochemical degradation of indigo carmine. This dye is converted into CO_2 , SO_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: Indigo carmine, copper graphite modified electrode (Cu/GME)

Introduction:

Azo dyes are extensively used in textile manufacture, which is one of the maximum polluting sectors in the unique human activities. A considerable amount of the dye (among 1–15%) is discharged into wastewaters after the dyeing technique. Indigo carmine is a natural salt derived from indigo by using sulfonation, which renders the compound soluble in water. It is authorized to be used as a food colorant within the America and E.U. It has the E range E132. Moreover, many dyes are prone to producing toxicity inside the aquatic organisms in addition to in humans. Similarly, the aromatic structures of those chemical compounds are very refractory and, consequently, proof against being degraded in wastewater treatment plant life because they continue to be unaffected in the direction of daylight, oxidizing retailers and microorganisms [1-8]. Pollutants of water resources by wastewater containing synthetic color compounds, specially inside the fabric industry, is a main environmental concern. Nowadays, more than 100,000 kinds of industrial dyes have an annual production fee of about seven-hundred,000 tons. Of these, approximately 15% of the dye compounds used in industry input the effluent at some point of the manufacturing and processing ranges and are eventually discharged into the surroundings. Maximum of the colorful compounds, as well as the intermediates produced via their degradation, are considered as a primary fitness risk for the human environment and different organisms. Electrochemical advanced oxidation procedures (EAOPs) are capable of degrading natural substances to CO_2 and H_2O thru response with hydroxyl radicals ($\text{HO}\cdot$). The simplicity of gadget and clean operation, low fee of construction, no sludge generation, mineralization of pollutants, and advancing reaction by means of electron are some of the advantages of EAOP. In EAOP/anodic oxidation (AO), natural pollutants

are degraded by way of each direct and oblique oxidation. In direct oxidation, electrons are transferred from the natural pollutant to the anode floor. In indirect oxidation, the electroactive species produced in the solution act as mediators for pollutant degradation. studies demonstrates that the primary mechanism of oblique oxidation is the mineralization of natural depend with HO radical. Based totally on the interactions of produced HO radical with the surface of the anode, the anodes are labeled into businesses, i.e., the active anode and the non-energetic anode. Lively anodes have low oxygen evolution potential and result in incomplete oxidation of organic pollution. but, non-energetic anodes have excessive oxygen evolution ability and the natural compound can be completely mineralized to H_2O and CO_2 [9-12]. Nowadays, researchers from around the world strive to enhance the typically used wastewater treatment methods so as to lessen their overall costs, optimize performance, and to diminish the production of intermediate pollutants. Some of the most promising effects were received via electrochemical removal of impurities from sewage [13-15]. A spread of different approaches has been carried out in order to do away with the dyestuffs from wastewater, artificial dyestuffs are broadly utilized in various sorts of industries, however specifically in fabric enterprise and paper manufacturing. Dyestuffs can be classified into numerous companies primarily based on their chemical shape. From among all colorants, azo dyes are the most commonly used, with their manufacture constituting around 70% of general dyestuffs manufacturing. , the dyes used for fabric dyeing are solid beneath daylight, resistant to finish organic degradation. Textile enterprise is characterized by means of a high call for water which, in flip, generates the big volumes of wastewater containing the dyestuff residue. The fabric wastewater is characterized with the aid of robust color, due to the fact even 15% of used dyestuffs become in it. Such wastewater incorporates high concentrations of natural compounds which frequently translate into very excessive chemical oxygen demand for (COD) [16-20]. Powerful and monetary remedy of azo dye effluents have emerge as a serious concern during the last few many years. No unmarried traditional treatment system is adequate for degrading the dye structure. Currently, tons research has targeted on chemically and physically degrading azo dyes in wastewater. These techniques are occasionally coupled with UV light/sound wave exposure to boom the colour removal. Other techniques involve adsorption, reverse osmosis, coagulation/flocculation or excessive energy irradiation. a lot of these technologies are nonetheless questionable with regard to their economic viability in massive waste streams. Azo dyes frequently skip via activated sludge facilities with very little reduction in color. Although a few researchers have found mild color discounts, their findings are in large part outweighed by means of those who've not. Discounts within the carbon content material and oxygen call for of azo dye wastewater following cardio treatment are well cited. even though anaerobic treatment of azo dyes shows coloration discount by forming intermediates , this technique is not often preferred because of the fact that a higher percentage of these intermediates were identified as cancer causing agents [21-25].

II. EXPERIMENTAL

A solution of IC (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). Copper was deposited on graphite electrode from $CuCl_2$ (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, Cu (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 indigo carmine 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 indigocarmine was followed by using spectrophotometer (ELICO SL171).

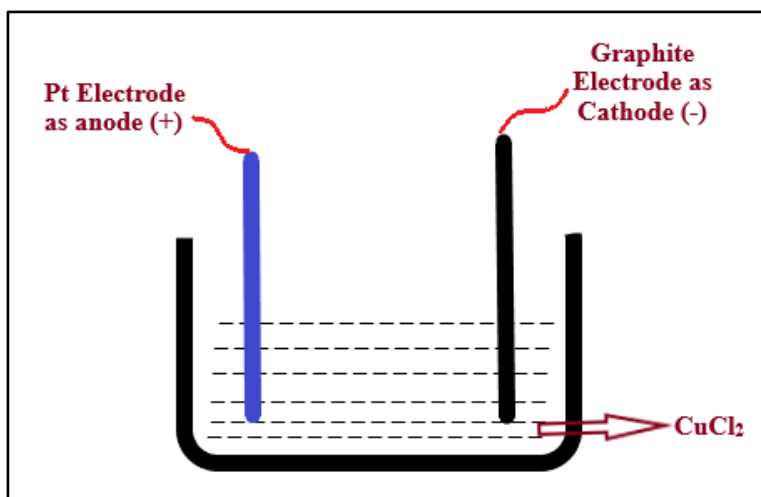


Figure 1: Synthesis of Cu/GME by electrochemical method

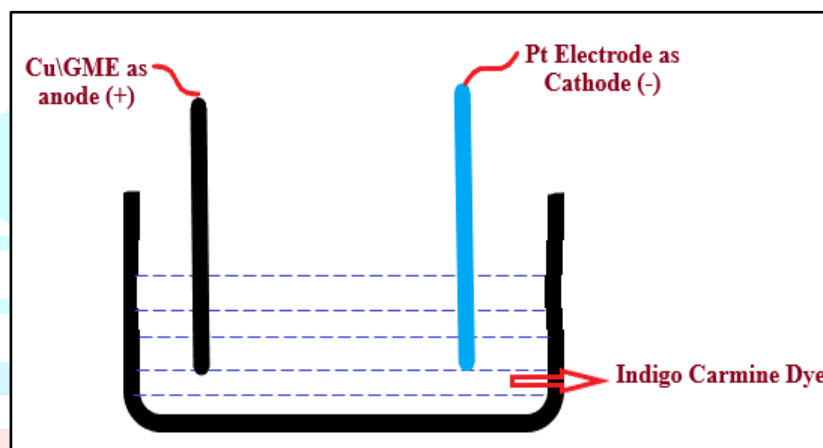


Figure: 2 Experimental set up for electrochemical degradation of indigo carmine Dye

III. RESULTS & DISCUSSION

3.1 Reaction with graphite as anode electrode

3.1.1 Effect of Indigo carmine on the rate

The kinetic degradation was performed in the presence of indigocarmine dye (0.0001M), using constant current (4.6mA). The change in concentration of indigocarmine 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 indigocarmine follows 1st order kinetics. The rate constant values are given in table 1. The rate of the reaction decreased with increase in indigocarmine. The rate of the reaction is decrease at higher concentration 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 indigocarmine solution before and after electrolysis were measured. (Table-1, Fig-3).

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

Conc of indigocarmine 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	0.103	6.59	6.65	512	16
1.0	0.997	6.93	6.98	624	16
1.5	0.882	7.12	7.17	816	32
2.0	0.729	7.26	7.31	992	48

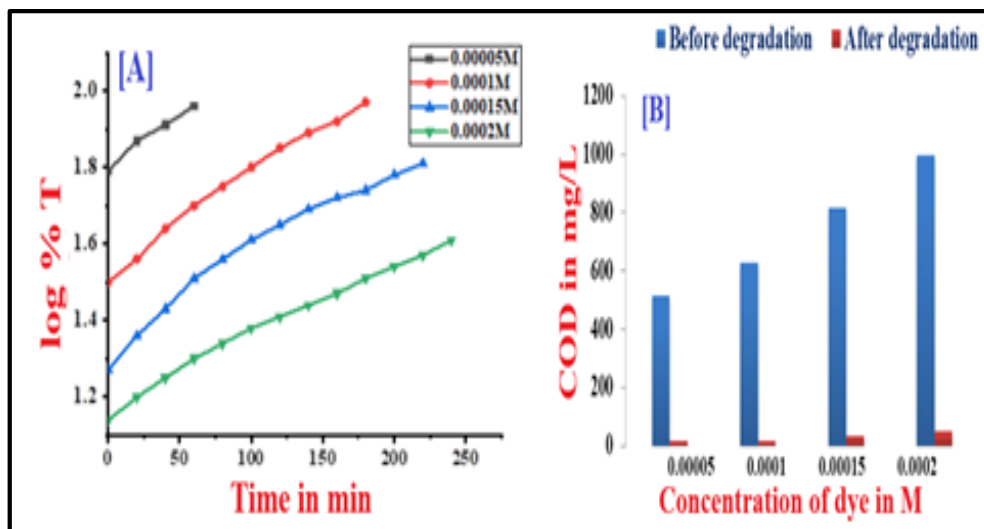


Figure 3: Effect of Concentration of indigocarmin on rate of degradation [A] and COD Value [B]

3.1.2 Effect of current on the rate

To investigate the effect of applied current the experiment is carried out four different current varied from 3.6mA-6.6 mA and keeping indigocarmin dye concentration as constant .when we increased the current the rate of the reaction is increased. 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 indigocarmin 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	0.422	624	16
4.6	0.997	624	16
5.6	1.151	624	48
6.6	1.343	624	32

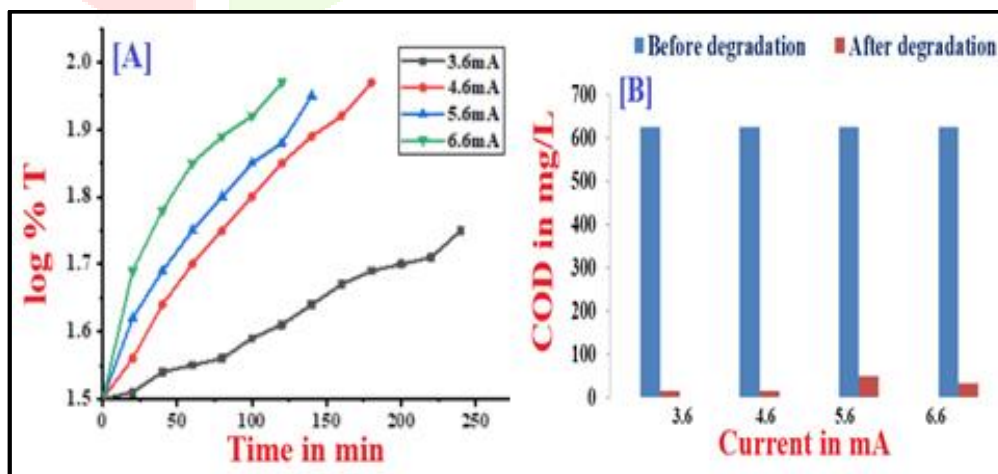


Figure 4: Effect of current of indigocarmin on the rate of degradation [A] and COD Values [B]

3.1.3 Effect of Temperature

To explore the effect of temperature the experiments is carried out at three different temperatures, when temperature increases 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, 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 values for before and after degradation of dye is reported in table 3 and figure 5. 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	0.729	624	32
303	0.997	624	16
313	1.189	624	16

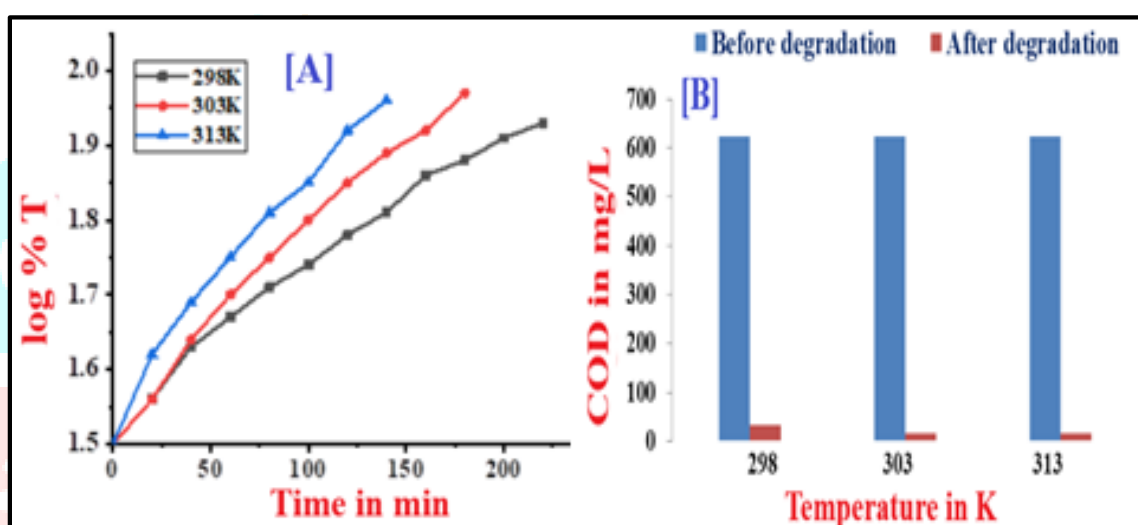


Figure 5: Effect of temperature of indigocarmine on the rate of degradation [A] and COD Values [B]

Table 4: Thermodynamic parameters for the degradation of indigocarmine

$\Delta H^\#$ kJ/mol	$\Delta S^\#$ J/K/mol	$\Delta G^\#$ kJ/mol	Ea
86.04	-300.23	100.08	111.38kJ/mol (26.62×10^3 cal/mol)

3.2 Reaction with copper graphite Modified (Cu/GME) as anode electrode

3.2.1 Effect of Indigo carmine on the rate

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

Table 5: Effect of indigo carmine on the rate of degradation and COD values for Cu/GME

[IC] 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	3.454	6.59	6.65	512	16
1.0	3.723	6.93	6.98	624	16
1.5	2.149	7.12	7.17	816	32
2.0	1.804	7.26	7.31	992	48

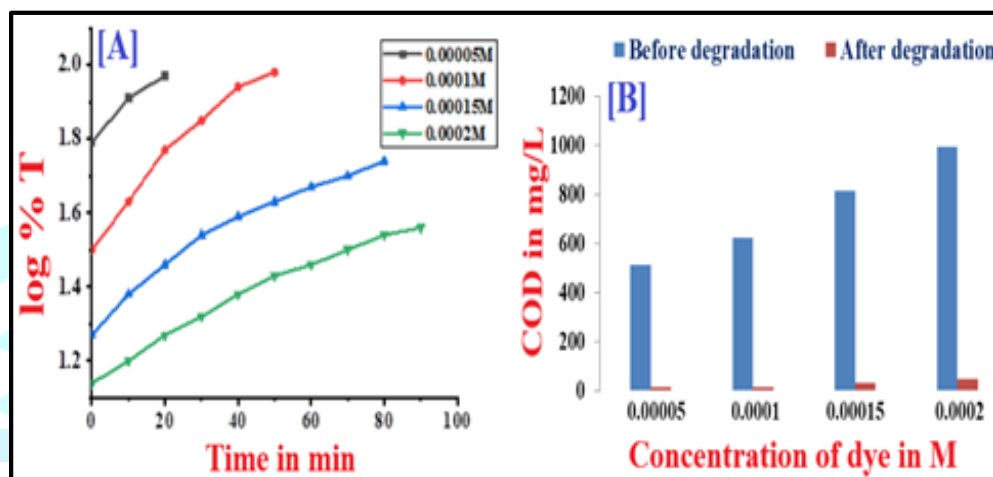


Figure 6: Effect of Concentration of indigocarmine on rate of degradation [A] and COD Value [B]

3.2.2 Effect of current on the rate

At fixed [IC] 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 Cu. 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 Cu/GME

Current in mA	10 ⁴ k in sec ⁻¹	COD Values in mg/L	
		Before degradation	After degradation
3.6	2.072	624	16
4.6	3.723	624	16
5.6	4.414	624	16
6.6	5.757	624	32

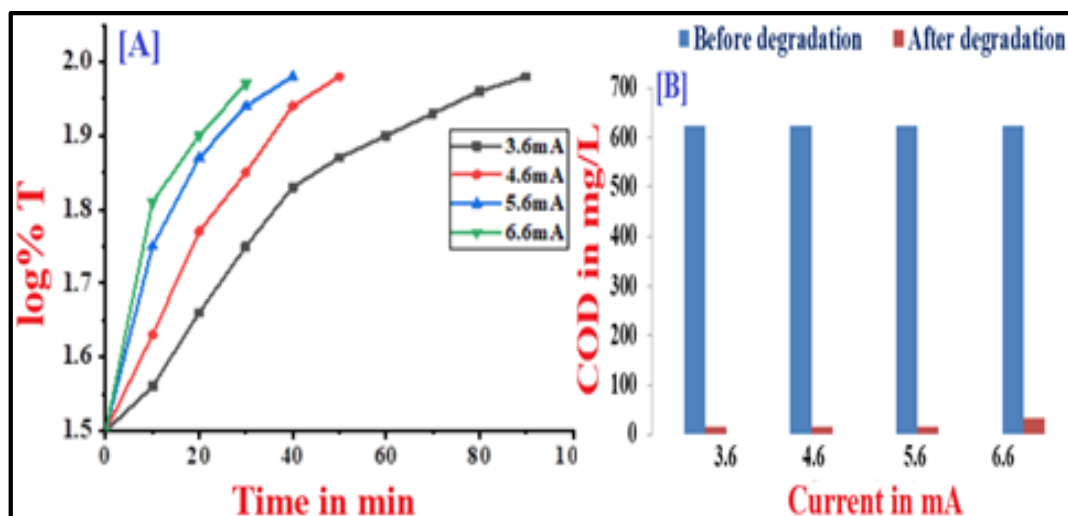


Figure 7: Effect of current of indigocarmine on the rate of degradation [A] and COD Value [B]

Effect of Temperature

To investigate the effect of temperature, the experiments were carried out at three different temperatures. It is clear that, when temperature increases the rate of the reaction is increased, 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 Cu/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 the degradation of indigo carmine by Cu/GME electrode were measured and reported in table 8.

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

Temperature in K	$10^4 k$ in sec^{-1}	COD Values in mg/L	
		Before degradation	After degradation
298	1.727	624	32
303	3.723	624	16
313	4.183	624	16

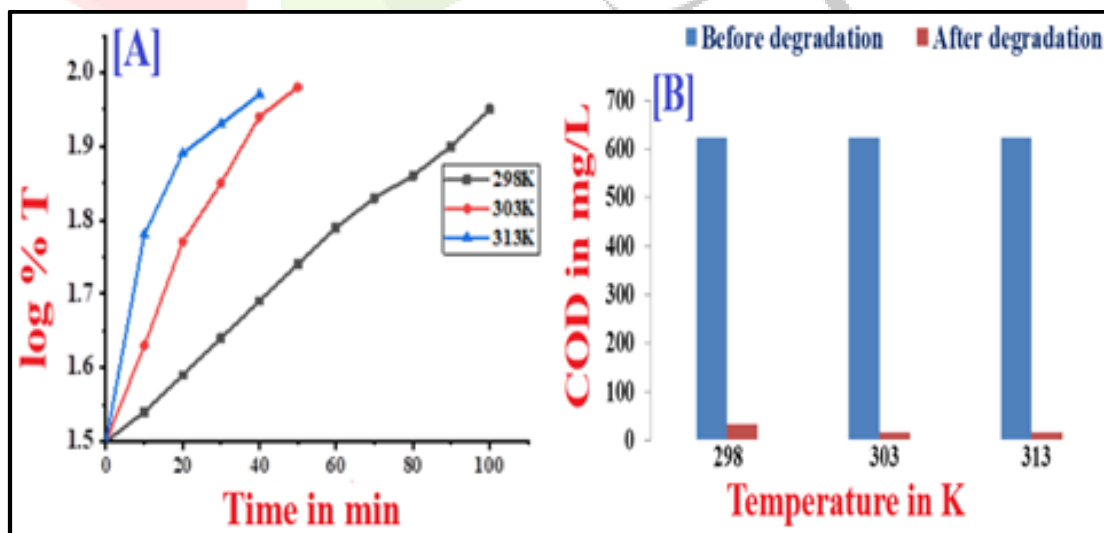


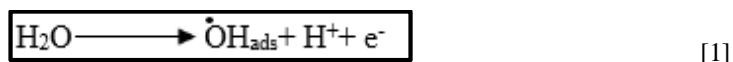
Figure 8: Effect of temperature of indigocarmine on the rate of degradation [A] and COD Values [B]

Table 8: Thermodynamic parameters for the degradation of indigo carmine for Cu/GME

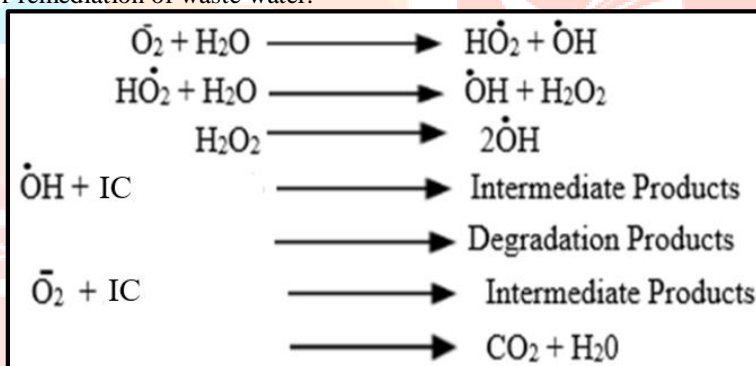
ΔH^\ddagger kJ/mol	ΔS^\ddagger J/K/mol	ΔG^\ddagger kJ/mol	Ea
36.24	-193.47	95.21	40.43kJ/mol (9.665x10 ³ cal/mol)

Production of OH radical

The electrochemical degradation of indigocarmine 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 O₂⁻ overvoltage anode from oxidation of water.



The degradation of indigocarmine takes place due to sequential electrochemical reduction and oxidation [26]. Graphite electrodes have high affinity for indigocarmine 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 indigocarmine converting into CO₂, H₂O and inorganic salts like bromides. Until their total mineralization is reached [27]. It has been found that Pt electrode possesses greater O₂⁻ 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 [28]. The present method can be used for remediation of waste water.



Scheme 1: Proposed degradation pathway of indigocarmine

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).

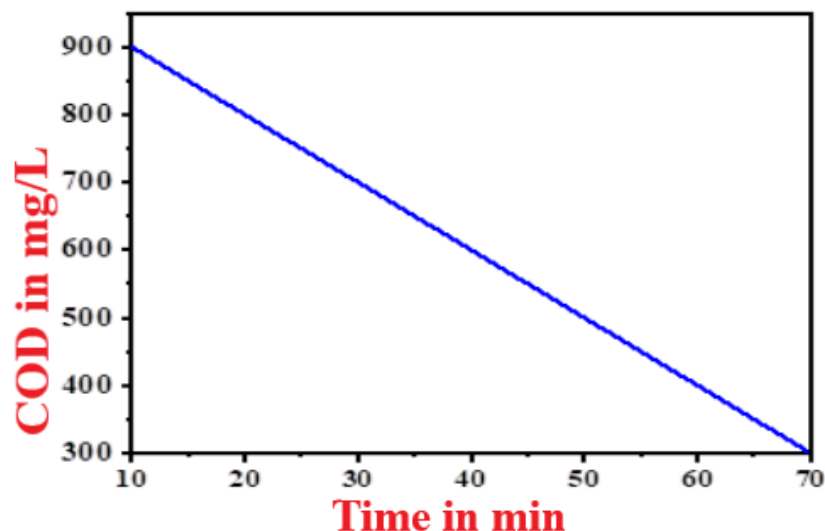


Figure 9: The rate of decrease of COD at different intervals of time.

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 indigocarmine dye was calculated from the values of the COD using the equation,

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

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 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 Cu/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	433.55
	1.0	177.14
	1.5	186.89
	2.0	206.28
Current in mA	3.6	169.76
	4.6	177.14
	5.6	155.08
	6.6	154.56
Temperature in K	298	141.12
	303	177.14
	313	227.76

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

	Variables	ICE
Concentration of Dye 10^{-4} M	0.5	1300.65
	1.0	637.73
	1.5	466.18
	2.0	412.57
Current in mA	3.6	452.71
	4.6	637.73
	5.6	654.82
	6.6	721.31
Temperature in K	298	310.47
	303	637.73
	313	797.17

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} 610nm 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 Copper Graphite Modified Electrode

The possibility of reusing the Cu/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 indigocarmine dye. Broad visible colour absorption spectra at 610 nm were completely removed at the end of the degradation process.

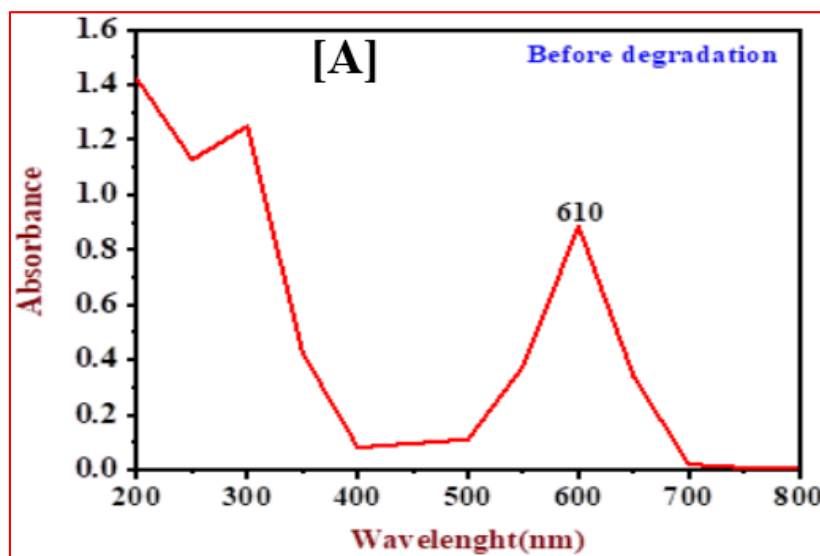


Figure 10(A): UV-Visible spectra of indigocarmine before degradation

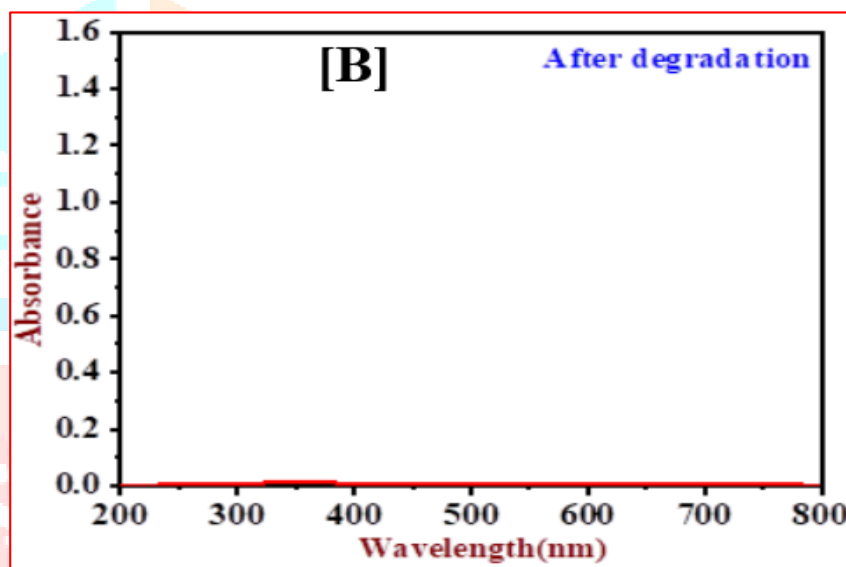


Figure 10(B): UV-Visible spectra of indigocarmine after degradation

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

Scanning electron microscopy (SEM) is used to differentiate the Copper (Cu) 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 50 μ m. From the EDAX profile, the presence of carbon and oxygen content indicated the graphite present in the pure form Fig 11(B)

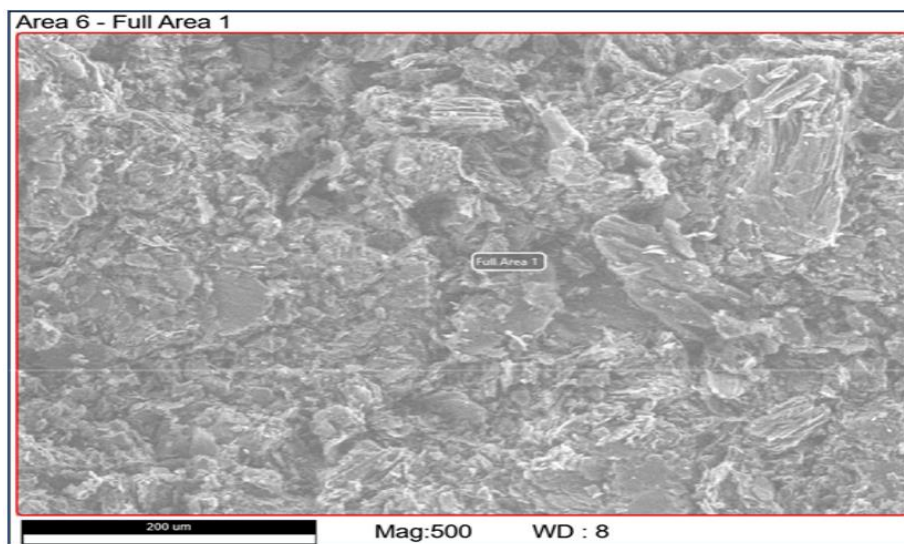


Fig. 11(A): SEM micrographs of graphite Electrode

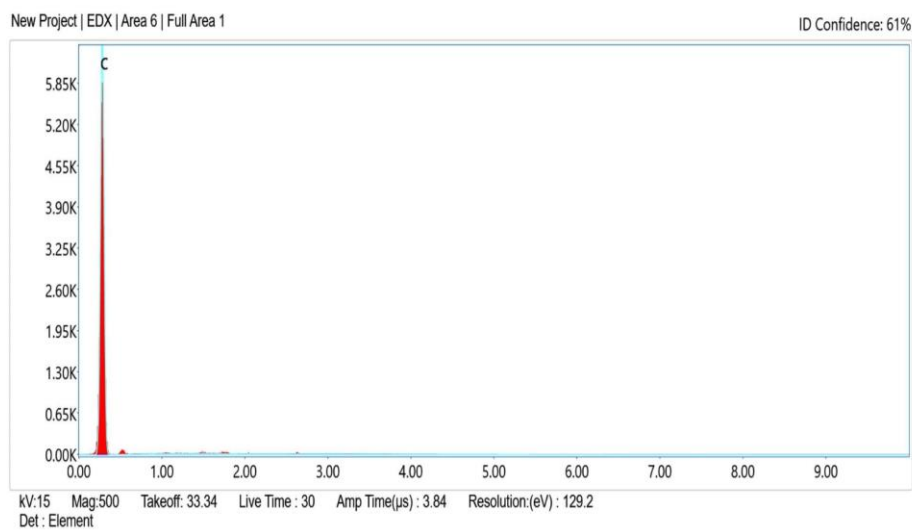


Fig. 11(B): EDAX spectra of graphite Electrode

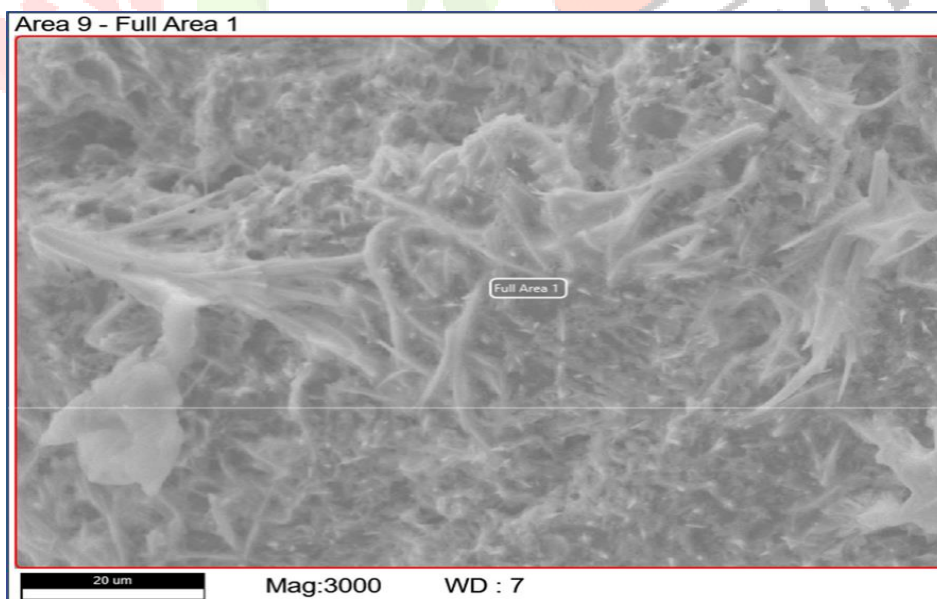


Fig. 12(A): SEM micrographs of stannous graphite modified electrode

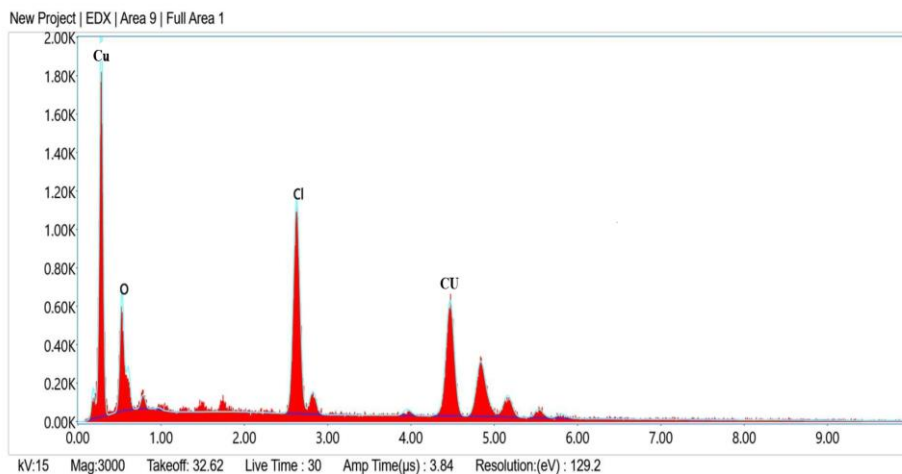


Fig. 12(B): EDAX spectra of Cu/GME

Fig 12(A) & (B) shows the SEM and EDAX profile of copper encapsulated in graphite rod. The SEM image of copper encapsulated graphite rod can clearly distinguish from graphite rod. Further, the heterogeneous block dots were observed on the surface, which indicates the copper 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 copper peaks in different oxidation states along with graphite carbon peak.

Conclusion

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

Acknowledgements

One of the author, acknowledgements Department of Chemistry, Manasagangotri university of Mysore, UGC-BSR Programme, PES College of Engineering Mandya

Reference:

1. Electrochemical Degradation of Reactive Black 5 using twodiferent reactor configuration. Tamara Droguett et.al. Scientific Reports | (2020) 10:4482 | <https://doi.org/10.1038/s41598-020-61501-5>
2. Daneshvar, N., Oladegaragoze, A. & Djafarzadeh, N. Decolorization of basic dye solutions by electrocoagulation: An investigation of the efect of operational parameters. J. Hazard. Mater. 129, 116–122 (2006).
3. 2. Şengil, I. A. & Özacar, M. Te decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes. J. Hazard. Mater. 161, 1369–1376 (2009).
4. Bandala, E. R. et al. Photocatalytic decolourisation of synthetic and real textile wastewater containing benzidine-based azo dyes. Chem. Eng. Process. Process Intensif. 47, 169–176 (2008).
5. Ahmad, A. L. & Puasa, S. W. Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process. Chem. Eng. J. 132, 257–265 (2007).
6. Koyuncu, I. & Topacik, D. Efects of operating conditions on the salt rejection of nanofiltration membranes in reactive dye/salt mixtures. Sep. Purif. Technol. 33, 283–294 (2003).
7. Damodar, R. A., You, S. J. & Chou, H. H. Study the self cleaning, antibacterial and photocatalytic properties of TiO₂ entrapped PVDF membranes. J. Hazard. Mater. 172, 1321–1328 (2009).
8. Srivastava, H. P., Arthanareeswaran, G., Anantharaman, N. & Starov, V. M. Performance of modified poly(vinylidene fluoride) membrane for textile wastewater ultrafiltration. Desalination 282, 87–94 (2011).
9. M.R. Samarghandi et al .Electrochemical degradation of methylene blue dye using a graphite doped PbO₂ anode: Optimization of operational parameters, degradation pathway and improving the biodegradability of textile wastewater.. *Arabian Journal of Chemistry* Volume 13, Issue 8, August 2020, Pages 6847-686
10. Abu Ghalwa, N., Hamada, M., Abu Shawish, H.M., Shubair, O., 2016. Electrochemical degradation of linuron in aqueous solution using Pb/PbO₂ and C/PbO₂ electrodes. Arab. J. Chem. 9, S821–S828
11. Ansari, A., Nematollahi, D., 2018. A comprehensive study on the electrocatalytic degradation, electrochemical behavior and degra- dation mechanism of malachite green using electrodeposited nanostructured b-PbO₂ electrodes. Water Res. 144, 462–473. <https://doi.org/10.1016/j.watres.2018.07.056>.

12. Aquino, J.M., Rocha-Filho, R.C., Ruotolo, L.A.M., Bocchi, N., Biaggio, S.R., 2014. Electrochemical degradation of a real textile wastewater using b-PbO₂ and DSAO anodes. *Chem. Eng. J.* 251, 138–145. <https://doi.org/10.1016/j.cej.2014.04.032>
13. . Mateusz Łuba et al. .Electrochemical Degradation of Industrial Dyes in Wastewater through the Dissolution of Aluminum Sacrificial Anode of Cu/Al Macro-Corrosion Galvanic Cell. *Molecules* 2020, 25, 4108; doi:10.3390/molecules25184108
14. Vasudevan, S.; Lakshmi, J.; Sozhan, G. Effects of alternating and direct current in electrocoagulation process on the removal of cadmium from water. *J. Hazard. Mater.* 2011, 192, 26–34. [CrossRef] [PubMed]
15. Nguyen, Q.H.; Kawamura, Y.; Watari, T.; Niihara, K.; Yamaguchi, T.; Nakayama, T. Electrocoagulation with a nanosecond pulse power supply to remove COD from municipal wastewater using iron electrodes. *Int. J. Electrochem. Sci.* 2020, 15, 493–504. [CrossRef]
16. Chaplin, B.P. Advantages, Disadvantages, and Future Challenges of the Use of Electrochemical Technologies for Water and Wastewater Treatment. In *Electrochemical Water and Wastewater Treatment*, 1st ed.; Martínez-Huitle, C.A., Rodrigo, M.A., Scialdone, O., Eds.; Matthew Deans: Oxford, UK, 2018; Volume 17, pp. 451–494.
17. A. Pieczyńska et al. Electrochemical degradation of textile dyes in a flow reactor: effect of operating conditions and dyes chemical structure. *International Journal of Environmental Science and Technology* (2019) 16:929–942.
18. Balci B, Oturan N, Cherrier R, Oturan MA (2009) Degradation of atrazine in aqueous medium by electrocatalytically generated hydroxyl radicals. A kinetic and mechanistic study. *Water Res* 43:1924–1934. <https://doi.org/10.1016/j.watres.2009.01.021>.
19. Basha CA, Sendhil J, Selvakumar KV, Muniswaran PK, Lee CW (2012) Electrochemical degradation of textile dyeing industry effluent in batch and flow reactor systems. *Desalination* 285:188–197. <https://doi.org/10.1016/j.desal.2011.09.054>
20. P. A. Soloman et al. Electrochemical Degradation of Remazol Black B Dye Effluent. *Clean* 2009, 37 (11), 889 – 900.
21. G. McMullan et al., Microbial Decolorization and Degradation of Textile Dyes, *Appl. Microbiol. Biotechnol.* 2001, 56, 81.
22. C. I. Pearce, J. R. Lloyd, J. T. Guthrie, The Removal of Color From Textile Wastewater Using Whole Bacterial Cells: A Review, *Dyes Pigm.* 2003, 58, 179.
23. O. J. Hao, H. Kim, P. C. Chang, Decolorization of Wastewater, *Crit. Rev. Environ. Sci. Tech.* 2000, 30, 449.
24. J. H. Weisburger, Comments on the History and Importance of Aromatic and Heterocyclic Amines in Public Health, *Mutat. Res., Fundam. Mol. Mech. Mutagen.* 2002, 9, 506
25. S. Chinwetkitvanich, M. Tuntoolvest, T. Panswad, Anaerobic Decolorization of Reactive Dyebath Effluents by a Two-stage UASB System with Tapioca as a Co-substrate, *Water Res.* 2000, 34 (8), 2223
26. 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.
27. 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.
28. Sowbhagya, *S. Ananda and Rakesh "Electrochemical Degradation of Indigocarmine Dye at Ru-Doped Platinum Anode in Aqueous Solution" ISSN 0973-1792 Volume 8, Number 2 (2012) pp. 141-152