

Role of electrode materials in the Electrochemical Oxidation of Malachite Green dye

Rajvir Kaur, Harpreet Kaur*

Department of Chemistry, Punjabi University, Patiala- 147002, Punjab, India.

Abstract

The aim of the present study is to degrade Malachite green (MG) dye electrochemically, which is become an alternative attractive method in recent years. The degradation of dye was studied in KCl as supporting electrolyte medium at graphite anode and platinum cathode under amperostatic condition. The variation of the dye concentration was accessed by UV-Visible measurements and Chemical oxygen demand (COD) reductions were also performed. The results clearly shown that at the optimum conditions (current density = 1.805 mA cm^{-2} , initial dye concentration = 100 mgL^{-1} , KCl concentration = 5 gL^{-1} , Temperature = $25 \pm 2 \text{ }^{\circ}\text{C}$, pH = 4, electrode gap = 1 cm), 99% MG degradation and 82% of reduction in COD was achieved within 120 min during electrolysis with maximum energy resource management, i.e., $21.212 \text{ KWh kg}^{-1}$. The reaction mechanism of electrocatalytic MG degradation was characterized with mass spectrum and Fourier transform infrared spectroscopy (FT-IR). Kinetic studies showed that at different initial dye concentration degradation takes place through a first order diffusion controlled reaction. The study showed that electrochemical oxidation is a superior technology for treatment of Malachite green with maximum power management after 120 min of electrolysis treatment.

* Corresponding author:

preetjudge@yahoo.co.in
preetjudge@yahoo.co.in

Received 03 April 2016,

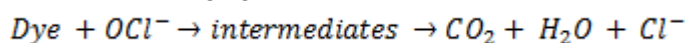
Revised 12 Feb 2017,

Accepted 16 Feb 2017

Keywords: Electrochemical degradation, Malachite green, Graphite-Platinum electrode, Environment friendly, Energy management

1. Introduction

4-[[4-(dimethylamino)phenyl](phenyl)methylidene]-*N,N*-dimethylcyclohexa-2,5-dien-1-iminium chloride dye commonly known as Malachite green is a cationic dye and used for silk, leather, plastic and paper industries [1-3]. It is highly cytotoxic to mammalian cells and also acts as a liver tumor enhancing agent [4-5]. As most of the dyes occur at low concentrations in effluent. Due to their complex structure it is presumed that removing these from effluent is difficult. A number of methods have been reported for the removal of dyes from the effluents such as; physical and chemical methods, which include adsorption [6-8], photocatalytic decolourization [9] and Fenton oxidation process [10]. These have disadvantages like high operation cost and production of other waste products that require further disposal. Electrochemical treatment method for the dye removal is found to be an effective, environment friendly and cost effective method [11]. During electrochemical degradation of dye in the effluent generated hypochlorite ions act as main oxidizing agents. The overall reaction can be written as [12].



Thus the aim of the present work is to use electrochemical oxidation method for the degradation of hazardous Malachite green dye.

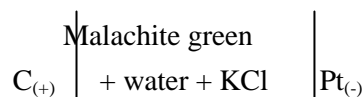
2. Materials and methods

2.1. Reagents

Malachite green (Basic green 4), cationic dye (CAS No. 573-58-0, M.W. 364.911 gmol⁻¹) was obtained from sd fine-chem limited, Mumbai. All the chemicals used were of analytical grade. Water was purified by adding potassium permanganate and a pellet of potassium hydroxide and then was fractionally distilled.

2.2. Apparatus

The electrochemical experiments were carried in electrochemical cell, which consists of an undivided cell with two monopolar electrodes, i.e., Graphite was used as anode and platinum as a cathode. The electrodes were placed vertical and parallel to each other with total effective graphite electrode area of 16.623 cm² and connected to terminals of DC power supply (0 - 100 mA, 1 - 300 V) equipped with amperostatic operational conditions. The potential across the electrodes was adjusted so that a current of 30 mA was passed through the cell. Potassium chloride was used as supporting electrolyte. The electrolytic solution was stirred thoroughly with the help of magnetic stirrer. The electrolytic cell can be represented as:



Where, C₍₊₎ and Pt₍₋₎ represent sacrificial graphite anode and inert platinum cathode respectively.

2.3. Analysis

The electrolysis of 100 mL solution of definite concentration of dye containing 5 gL⁻¹ of supporting electrolyte KCl was carried out at graphite anode and platinum cathode. 2 mL of solution was withdrawn at preset intervals of time and the amount of dye decomposed was measured with the help of Shimadzu-1800 UV-Visible Spectrophotometer at 618 nm. In order to study the effect of different parameters the electrolysis was carried out by varying the current density, initial dye concentration, electrolysis time, amount of supporting electrolyte, pH, cathode and anode materials. All the reagents were prepared and analyzed as per standard methods. All the experiments were performed at room temperature. The percentage of degradation of dye was calculated by using the following relation:

$$\% \text{ dye degradation} = \frac{C_o - C_t}{C_o} \times 100$$

Where, C_o and C_t are the initial dye concentration and concentration of dye at time t in solution (mgL^{-1}), respectively. Electrochemical oxidation degrades the organic pollutants in the wastewater and thereby causes the reduction in COD and decrease in the colour. The chemical oxygen demand (COD) was measured by volumetric analytical method as reported in literature [13].

3. Results and Discussions

3.1. Optimization of current density

In order to study the influence of current density and electrolysis time, electrolysis was conducted at different current densities (0.602, 1.203, 1.805, 2.406 and 3.008 mA cm^{-2}) as shown in Fig. 1. with the increase of current density, rate of production of hypochlorite ions increases at constant pH, which result in increase in H_2 evolution as per Faraday's law [14].

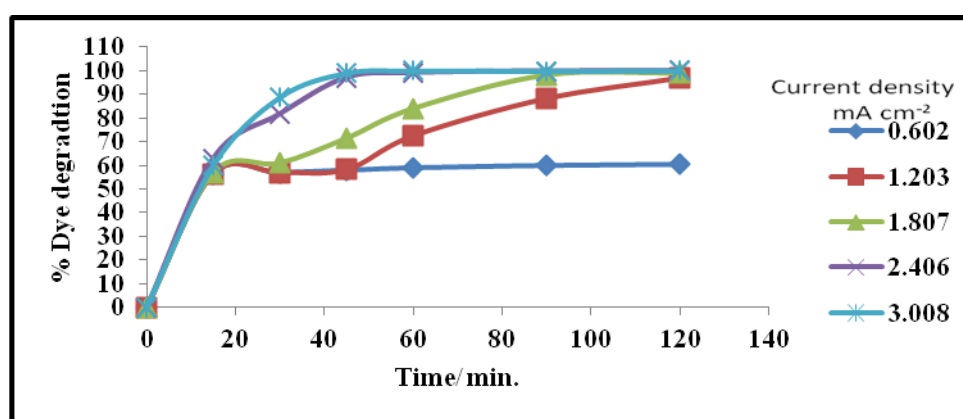


Figure 1. Effect of current density on percentage dye degradation ($C_o = 100 \text{ mgL}^{-1}$, $\text{KCl} = 5 \text{ gL}^{-1}$, $\text{pH} = 4.00$, Temperature = $25 \pm 2 \text{ }^\circ\text{C}$)

3.2. Optimization of initial dye concentration

Electrolysis of Malachite green of different initial dye concentrations (50, 75, 100, 125 and 150 mgL^{-1}) were conducting at current density of 1.805 mA cm^{-2} . It was observed that degradation efficiency decreases with increasing initial dye concentration as shown in Fig. 2. This may be due to reason that during electrolysis, the ratio Cl_2/OCl^- to the initial dye concentration decreases at a given current density [15].

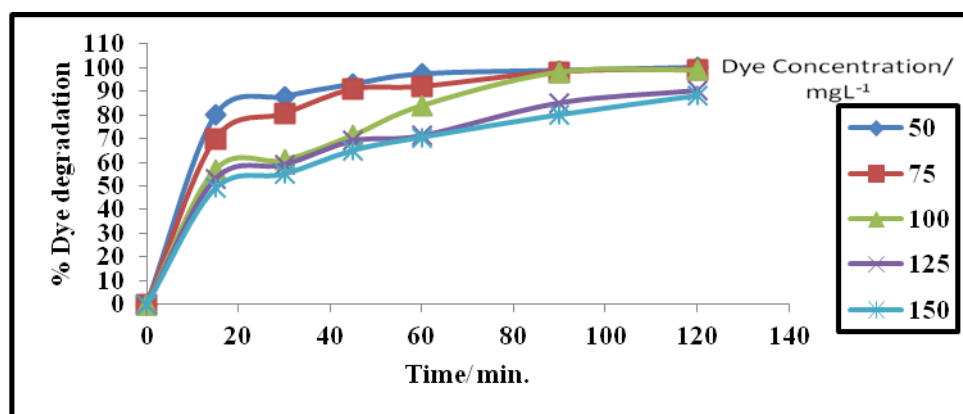


Figure 2. Effect of initial dye concentration on percentage dye degradation (Current density = 1.805 mA cm^{-2} , $\text{KCl} = 5 \text{ gL}^{-1}$, $\text{pH} = 4.00$, Temperature = $25 \pm 2 \text{ }^\circ\text{C}$)

3.3. Optimization of supporting electrolytes

It is evident from Fig. 3 that the removal efficiencies increases with increase of amount of supporting electrolyte. This may be ascribed to the fact that as the concentration of supporting electrolyte increases, more Cl_2 are formed which increases the dye oxidation. But at very high concentration the percentage removal of dye become nearly constant, which may be due to complete evolution of oxygen at high concentration [16]. Fig. 4 depicted that KCl in comparison to NaCl increase the percentage degradation of dye.

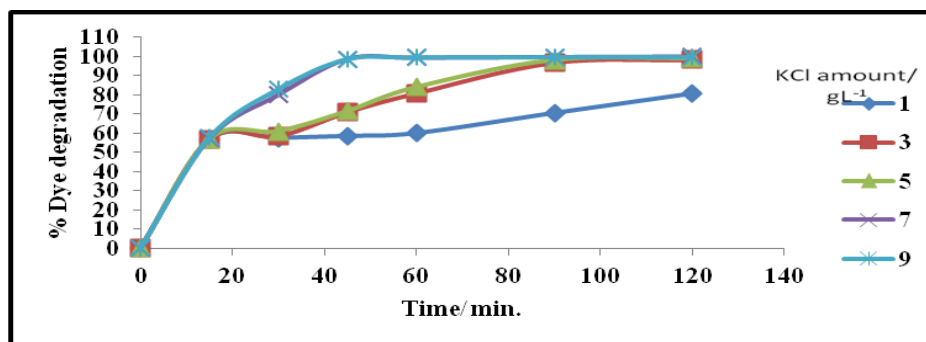


Figure 3. Effect of amount of supporting electrolyte KCl on percentage dye degradation (Current density = 1.805 mA cm^{-2} , $C_o = 100 \text{ mgL}^{-1}$, pH = 4.00, Temperature = $25 \pm 2^\circ \text{C}$)

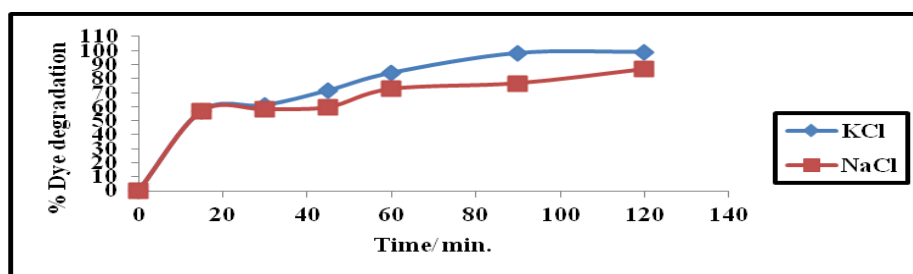


Figure 4. Comparison of amount of supporting electrolyte KCl with NaCl on percentage dye degradation (Current density = 1.805 mA cm^{-2} , $C_o = 100 \text{ mgL}^{-1}$, pH = 4.00, Temperature = $25 \pm 2^\circ \text{C}$)

3.4. Optimization of pH

A series of experiments were conducted by adjusting the pH of the solution to the desired level (2, 4, 6 and 7). It is cleared from Fig. 5 that pH of solution affect the rate of dye degradation much at initial stages, but effect at later stage is low.

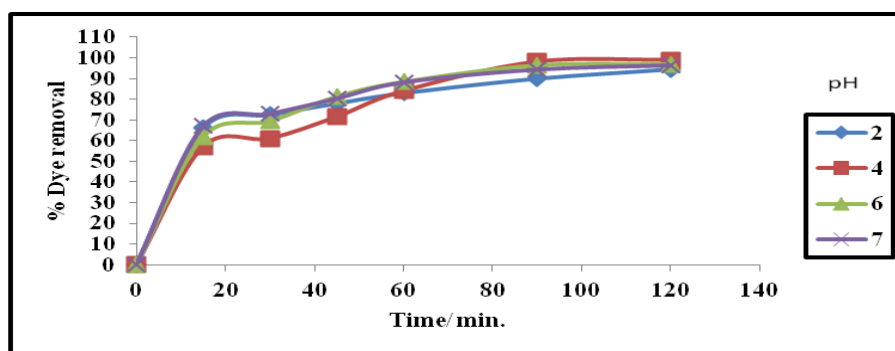


Figure 5. Effect of pH on percentage dye degradation (Current density = 1.805 mA cm^{-2} , $C_o = 100 \text{ mgL}^{-1}$, KCl = 5 gL^{-1} , Temperature = $25 \pm 2^\circ \text{C}$)

3.5. Effect of cathodic and anodic material

In order to evaluate the comparative behaviour of cathodic and anodic materials, the electrochemical oxidation of Malachite green dye from aqueous solution studies were carried by varying the electrode material. When Pt electrode has been employed as cathode as well as anode then the percentage of colour removal is very high, i.e., approximately 100 % as shown in Fig. 6, but when cathode material is replaced with graphite then there is slight decrease in dye degradation at final stage and when anode is replaced with graphite then there is decrease in percentage of dye degradation at initial as well as at final stage. When both the electrodes were replaced with graphite then again the difference is more at initial stages. It can be concluded that for electrochemical removal of dye graphite can be used as an alternative electrode.

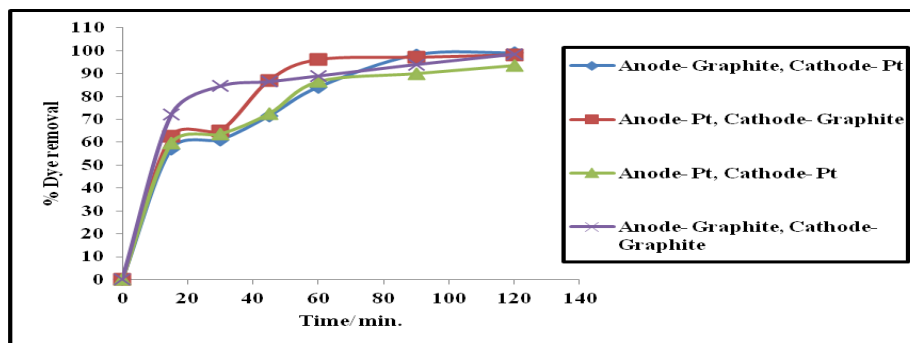


Figure 6. Comparison study of various electrodes on percentage dye degradation (Current density = 1.805 mA cm^{-2} , $C_0 = 100 \text{ mgL}^{-1}$, $\text{KCl} = 5 \text{ gL}^{-1}$, Temperature = $25 \pm 2 \text{ }^\circ\text{C}$)

3.6. Kinetic studies

In order to investigate the mechanism of electrolysis of Congo red dye, the following kinetic models were considered. In an attempt to correlate the present data with a kinetic first-order rate equation is as follows:

$$\ln \left[\frac{C_0}{C_t} \right] = K_1 t$$

where, C_0 and C_t are the initial dye concentration and concentration of dye at time t in solution (mgL^{-1}), respectively and K_1 is the first-order rate constant (min^{-1}). Kinetic First-order reaction plot at different dye concentration is shown in Fig. 7. Values of rate constant K_1 for first-order kinetic rate equation at different initial dye concentration are listed in Table 1.

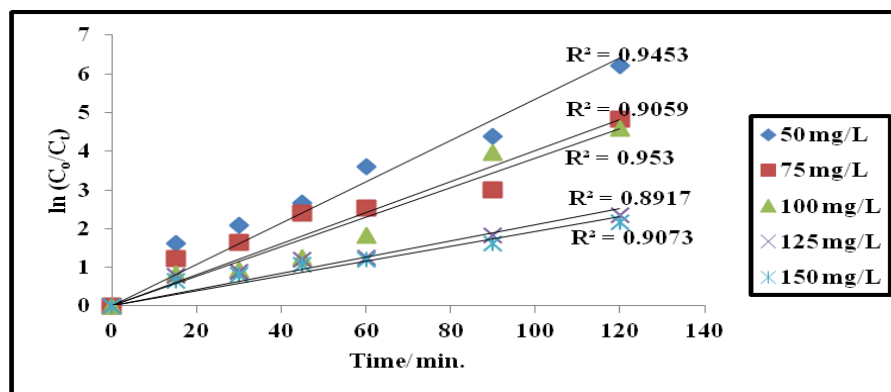


Figure 7. Kinetic First-order reaction plot at different dye concentration.

Table 1: Values of rate constant K1 for first-order kinetic rate equation at different initial dye concentration

Initial dye concentration, mgL ⁻¹	50	75	100	125	150
Rate constant, min ⁻¹	0.0471	0.0348	0.0397	0.0174	0.0162

3.7. Analysis of COD

Chemical oxygen demand was taken as an effective parameter to measure the amount of organic matter degraded from aqueous solution. Volumetric method was applied for the COD measurement in different experimental conditions. Table 2 shows that the COD reduction percentage increases with the increase in current density, amount of potassium chloride and pH of dye solution. This may be due to reason that the electrochemically produced chlorine/hypochlorite play an important role in the electrocatalytic degradation process for the removal of dye [11,17]. But the reduction percentage in COD value is low for higher initial dye concentration as the dye molecules tend to associate to large molecules of low diffusivity, which may lowers the dye diffusion to the anode.

Table 2. Analysis of COD at different operating conditions for electrochemical degradation

	c.d,					KCl amount,					pH				Initial dye concentration,				
	mA cm ⁻²					gL ⁻¹									mgL ⁻¹				
COD	0.602	1.203	1.805	2.406	3.008	1	3	5	7	9	2.0	4.0	6.0	8.0	50	75	100	125	150
reduction %	50	75.5	82	83	84	68.7	80	82	88.7	92	72	82	80	77	84	83	82	78	70

3.8. Electric Energy consumption

The electric energy consumption values during electrochemical degradation of dye were calculated in terms of kWh kg⁻¹ using the following equation [15].

$$\text{Energy consumption} = \frac{VIt \times 10^3}{60 (C_0 - C_t) \times \text{treated volume (L)}}$$

Where, V is the cell voltage (V), I is the current (A), t is the time of electrolysis (min), C₀ and C_t are the initial dye concentration and concentration of dye at time t in solution (mgL⁻¹). Table 3 indicate that the energy consumption increases with increasing current density and decreases with increasing KCl amount. With very small electrical energy consumption, almost complete degradation of dyes was achieved after 60 min of electrolysis. In India ~6.43 rupees are required to remove one kilogram of dye from wastewater during this process.

Table 3. Electric energy consumption values at various parameters during electrochemical process

Energy	consumption,	c.d,	KCl amount,					pH					Initial dye concentration,				
kWh	kg ⁻¹	colour	0.602	1.203	1.805	2.406	3.008	1	3	5	7	9	50	75	100	125	150
removed			8.265	12.387	21.212	32.019	45.000	33.449	24.395	21.212	18.002	15.018					

3.9. Fourier Transform Infrared Spectroscopy (FT-IR) analysis

FT-IR spectra of electrochemical degradation of Malachite green dye before and after electrolysis at optimum condition was recorded in the region of 4000 - 400 cm⁻¹. Fig 8(a), FT-IR spectrum of Malachite green before degradation show peaks at 3407 cm⁻¹, 2921 cm⁻¹, 1612 cm⁻¹, 1446 cm⁻¹ and 1585 cm⁻¹ for N-H the tertiary amine

group, CH₃ stretching vibrations, C=O stretching, C–H bending vibrations and N=N stretching vibrations respectively. The FTIR spectrum obtained after electrolysis of dye consist very weak peaks (Fig.8(b)). Thereby indicating that most of dye is degraded.

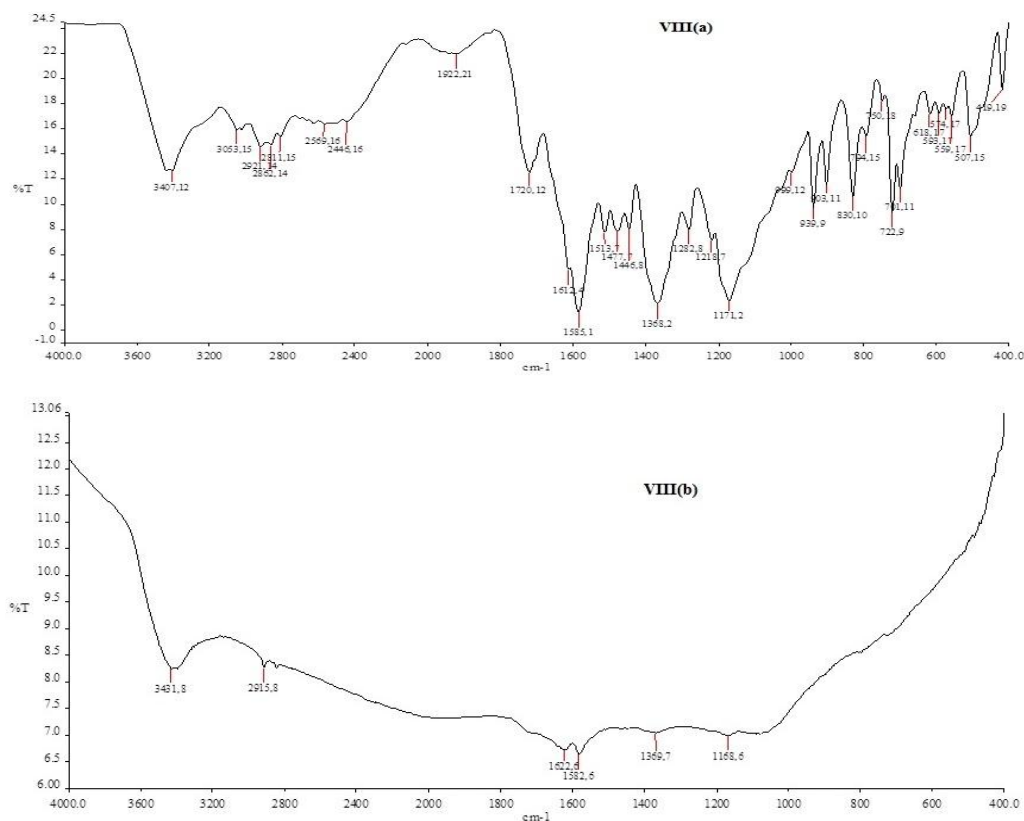


Figure 8. FTIR spectrum of Amido black 10B dye VIII(a) before electrolysis, VIII(b) after electrolysis

3.10. Liquid chromatography–mass spectrometry studies (LC-MS)

In electrochemical degradation of Malachite green dye the intermediate compounds was identified by LC-MS. The sample was collected after 60 minutes of electrolysis. Based on the identification of mass fragmentation, the following pathway (Fig. 9) is proposed for the electrochemical degradation of dye.

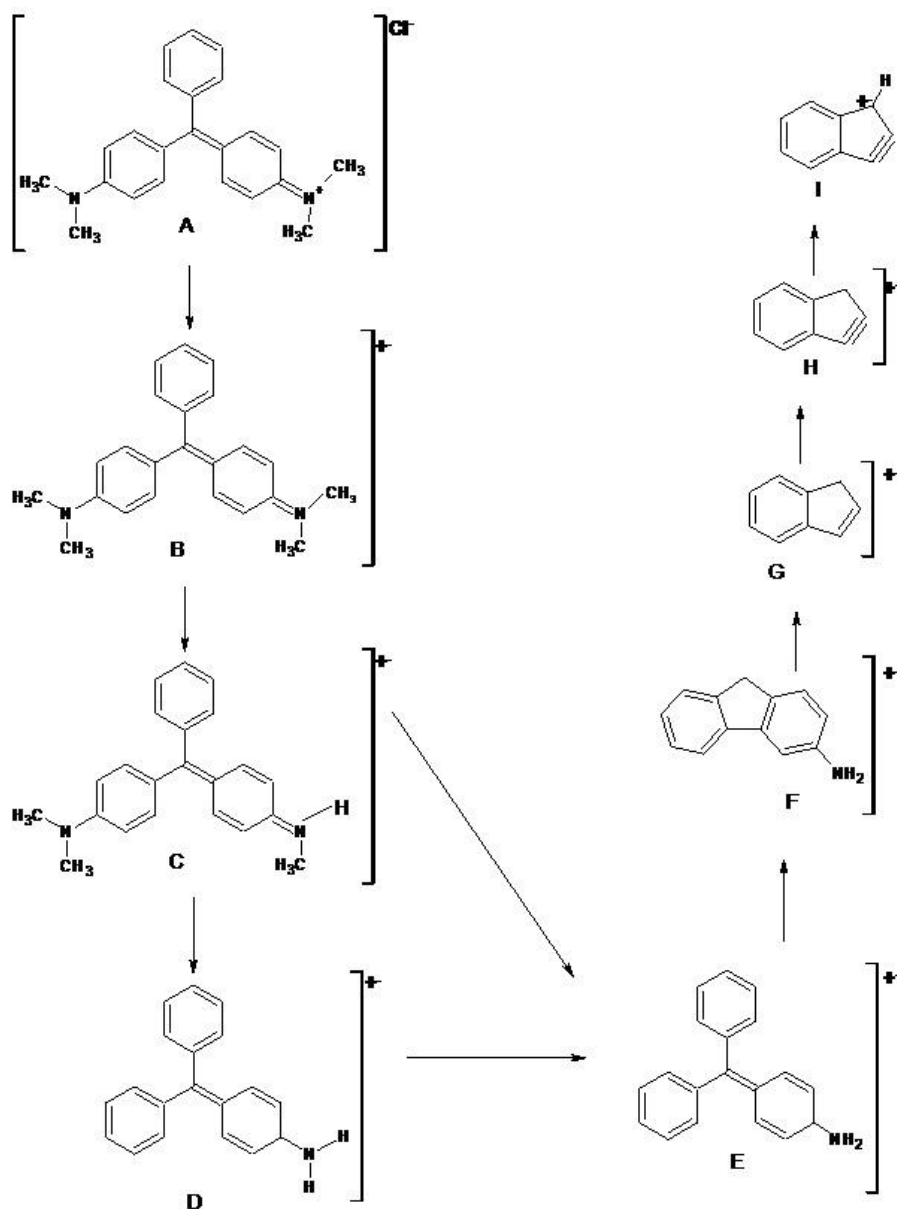


Figure 9. Proposed pathways of electrochemical degradation of Malachite green dye

4. Conclusion

Thus it can be concluded from the present study that electrochemical oxidation method for the degradation of Malachite green using platinum cathode and graphite anode under amperostatic condition is an effective method. It was observed that degradation depends on parameters such as current density, initial dye concentration, KCl concentrations, pH and electrode materials. Its kinetics was successfully fitted to first order kinetic model. The intermediates formed during electrolysis were identified with LC-MS and FT-IR spectral studies.

Acknowledgements

Authors acknowledge sincere thanks to UGC, New Delhi for awarding the UGC-BSR Fellowship (to Ms. Rajvir Kaur) for carrying out the research work successfully.

References

- [1] S. Singh, V. C. Srivastava, I. D. Mall, J. Phys. Chem. C., 117 (2013) 15229–15240.
- [2] G. Crini, H. N. Peindy, F. Gimbert, C. Robert, Sep. Purif. Technol., 53 (2007) 97–110.
- [3] L. Liu, F. Zhao, F. Xiao, B. Zeng, Int. J. Electrochem., Sci., 4 (2009) 525 – 534.
- [4] S. Srivastava, R. Sinha, D. Roy, Aquatic Toxicol., 66 (2004) 319-329.
- [5] E. Sudova, J. Machova, Z. Svobodova, T. Vesely, Veterinarni Medicina. 52(2007)527-539.
- [6] H. Kaur, R. Kaur, J. Mater. Environ. Sci., 5(6) (2013) 1830-1838.
- [7] H. Kaur, Swati, R. Kaur, Chem Sci Trans., 3(4) (2014) 1300-1309.
- [8] H. Kaur, A. Thakur, Chem Sci Rev Lett., 3(11S) (2014) 159-169.
- [9] R. Katwal, H. Kaur, G. Sharma, M. Naushad, D. Pathania, J. Ind. Eng. Chem. 31 (2015) 173-184.
- [10] J. H. Sun, S. P. Sun, G. L. Wang, L. P. Qiao, Dyes Pigments, 74 (2007) 647-652.
- [11] A. Kaur, R. Kaur, H. Kaur, Mor. J. Chem. 4(1) (2016) 93-100.
- [12] N. Mohan, Balasubramanian, J. Hazard. Mater. B136 (2006) 239-243.
- [13] L. S. Clesceri, A. E. Greenberg, R. R. Trussell (Eds.), “Standard methods for the examination of water and wastewater,” 17th edition, 1989.
- [14] C. T. Wang, W. L. Chou, Y. M. Kuo, F. L. Chang, J. Hazard Mater. 169 (2009) 16-22.
- [15] E. S. Z. El-Ashtouky, Int. J. Electrochem. Sci., 8 (2013) 846-858
- [16] J. O’ M. Bockris, B. E. Conway, E. Yeager, R. E. White (eds), Comprehensive Treatise of Electrochemistry, 2, Plenum Press, N.Y (1981).
- [17] P. Kariyajjanavar, J. Narayana, Y. A. Nayaka, M. Umanaik, Portugaliae Electrochimica Acta 28(4) (2010) 265-277.