International Journal of Research in Engineering, Science and Management
Volume-1, Issue-9, September-2018
www.ijresm.com | ISSN (Online): 2581-5782

268

Degradation and Removal of Paper Mill Dye Basic Orange 2 by Electrochemical Treatment Method

Spoorthi[1], J. Narayana[2]

[1]Research Scholar, Dept. of P.G. Stu. & Res. in Environmental Sci., Kuvempu University, Shankaraghatta, India
[2]Professor, Dept. of P.G. Stu. & Res. in Environmental Sci., Kuvempu University, Shankaraghatta, India

Abstract—**This study deals with the treatment of Paper Mill dye Basic Orange 2, by electrochemical degradation. The graphite carbon electrodes were used as anode and cathode. During electrochemical degradation, the chromoporic groups and aromatic rings were destroyed. The experimental results indicated that initial *p*H, current density and supporting electrolytes such as NaCl and Na₂SO₄ were played an important role in degradation of dye. The maximum colour removal efficiency of 85% and total organic compound (TOC) 93% could be achieved for dye, at *p*H 3, current density 340 A m⁻², NaCl 2.5 g L⁻¹. The results revealed the suitability of the present process for the effective degradation of dye effluents.**

Index Terms—**carbon electrodes, electrochemical degradation, electrolyte, TOC, industrial dye**

I. INTRODUCTION

The pulp and paper industry is one of the oldest industries in our country. Varieties of papers and similar products are now manufactured in different mills through the country Paper is made by pulping wood, bleaching this pulp and then spreading it out into sheets to make it into paper. At various stages of the process, chemicals are used to give the paper particular properties, such as the bleaching chemicals that make paper white. This wastewater generally large quantities of suspended solids, it also, it also contains considerable amount of COD and BOD. The generated wastewaters can be very dangerous they should be treated before being discharged into environment. [1-5]. The treatment of dye effluent is difficult and ineffective with conventional biological processes [6] and several physic-chemical methods because many synthetic dyes are very stable to light, temperature and non-biodegradable nature of most dyes [7]. In this context, electrochemical techniques are considered to be powerful means for the treatment of dyeing of wastewater [8-10]. Electrochemical method is most eco-friendly, easy operated method for effective dye removal [11]. Graphite electrodes were used as anode and cathode by many researchers for the application in organic oxidation [12-13]. In the past, graphite was frequently used as anode for the electrochemical degradation of wastewater as it is relatively cheaper and gives satisfactory results [14]. The aim of this work was to test

feasibility of electrochemical method for the degradation of Basic dye, Brilliant Green using graphite carbon electrode.

II. MATERIALS AND METHODS

A. Experimental Part

1) Materials

The industrial dye Basic Orange 2 (CAS No. 532-82-1) was obtained from Mysore Paper Mill Industry, Bhadravathi, India. Chemicals used for the experiments were of analytical grade reagents obtained from s d fine chem-limited, Mumbai, India. Cylindrical carbon electrodes (chemical composition: graphite carbon+-coke: 85% and ash15%) were obtained from Power Cell Battery India Limited. A digital DC power supply (AESC: 30 V, 2A) was used as an electrical source. Double distilled water was used to prepare the desired concentration of dye solutions and the reagents.

B. Instrumentation

1) Electrochemical degradation studies

Graphite carbon electrodes of 4.6 cm length and 0.8 cm diameter were used as anode and cathode for electrochemical degradation studies. The effective electrode area was 11.97 cm². The supporting electrolyte such as NaCl was added to the electrolysis time. The solution was kept under agitation using magnetic stirrer.

2) UV-vis studies

A UV-vis spectrophotometer (UV-2602) was employed to measure the optical density of dye solution (λ_{max}: 498 nm) before and after electrolysis. The degradation efficiency was calculated using the relation:

$$\%E = ((A_i - A_f) / A_i) \times 100 \qquad (1)$$

Where A_i and A_f are absorbance values of dyes solutions before and after treatment with respect to their λ_{max} respectively or A_i and A_f are initial and final COD values of the dyes solutions, respectively.

3) pH and conductivity measurement

A water analyzer (Systronics, Model-371) was used to measure the pH and conductivity of the dye solution before and

International Journal of Research in Engineering, Science and Management
Volume-1, Issue-9, September-2018
www.ijresm.com | ISSN (Online): 2581-5782

269

after electrolysis under different electrolysis conditions.

III. RESULTS AND DISCUSSION

A. Influence of Electrolysis Conditions on Dye Degradation

1) Effect of initial pH

A significant difference in the extent of degradation was noted when the concentration of NaCl was at 3 g L^{-1}. The initial pH of the solution (3-11) was adjusted using 1M H_2SO_4 or NaOH [15]. The electrolysis was carried out at the current density of 85 A m^{-2} for 60 min with a dye concentration of 50 mg L^{-1} at room temperature. From the absorption spectral studies it was confirmed that, the larger dye molecules were degraded into simple substituted aromatic compounds. However, the hypochlorite can lead to partial mineralization of dyes [16] and degradation efficiency of Basic Orange 2 was found 75% in acidic pH 3 and at initial pH 11 the degradation efficiency was found to be 56% (Fig. 1). It indicated that the degradation of dye in acidic solution is higher than that of in the basic media. Therefore the optimum pH 3 was maintained in subsequent experiments.
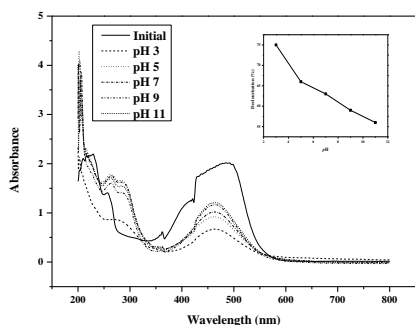

Fig. 1. Absorption spectra for Basic Orange 2dye solution before after electrolysis at different pH Electrolysis condition: concentration of dye solution: 50ppm (w/v), pH: 3, NaCl: 3 g L^{-1}, current density: 85 A m^{-2} Inset plots: effect of pH on colour removal of dye solution.

2) Effect of supporting electrolytes

From Fig. 2, it can be observed that, the addition of NaCl to the dye solution during electrolysis increases the decolourisation efficiency of Basic Orange 2. From this observation it was concluded that the introduction of NaCl as an electrolyte can enhance the degradation efficiency and shortens electrolysis time, which may be attributed to the reaction between the electro generated chlorine and dye molecule. The possible mechanism of electrochemical degradation is given bellow,
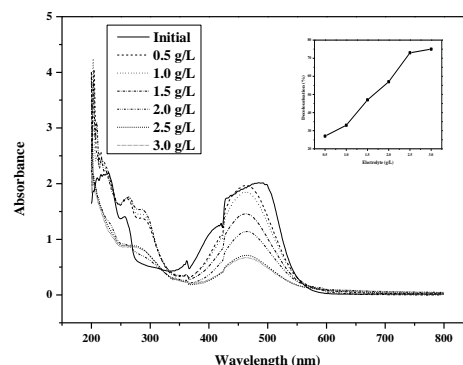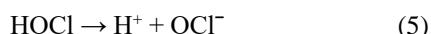
Anode reaction: $\quad 2Cl^- \rightarrow Cl_2 + 2e^-$ $\qquad$ (2)

Cathode reaction: $\quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $\qquad$ (3)

Bulk solution reaction: $Cl_2 + H_2O \rightarrow HOCl + HCl$ $\qquad$ (4)

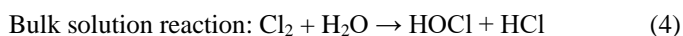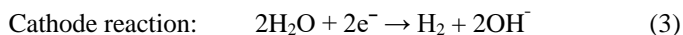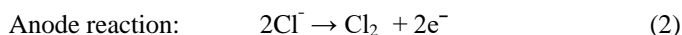$\qquad\qquad HOCl \rightarrow H^+ + OCl^-$ $\qquad$ (5)

Fig. 2. Absorption spectra for Basic Orange 2 dye solution before and after electrolysis for different concentration of NaCl. Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, current density 85 A m^{-2}, time: 60 min. Inset plot effect of NaCl concentration on colour removal of dye solution.

The above mechanism was classified as indirect electro-oxidation of pollutant. Increase in the concentration of NaCl up to 2.5g L^{-1} accelerated the decolouration rate, enabling degradation of dye to the extent of 58% decolourisation efficiency of Basic Orange 2 (Fig. 2).

Further increase in NaCl concentration (> 0.5g/L) there was a slight improvement in decolourisation efficiency, and therefore the optimal concentration of NaCl in successive degradation studied was fixed at 2.5g L^{-1}. Moreover, the increased optimal concentration of NaCl results in a decrease in operating voltage at the given current density 85 A m^{-2} (Fig. 3) [16].
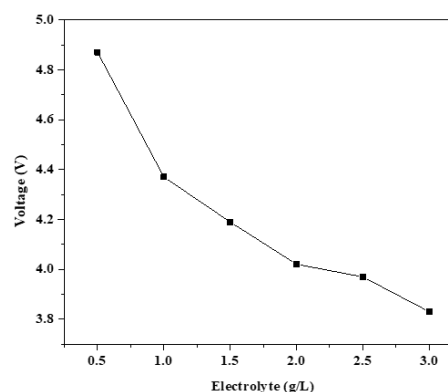

Fig. 3. Influence of supporting electrolytes concentration on applied voltage during electrolysis dye solution. Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, current density 85 A m^{-2}

Demonstrates the effect of Na_2SO_4 on the degradation of dyes. The decolourisation efficiency was found to be lower than that of NaCl (Fig. 4). The higher decolourisation efficiency in presence of NaCl is attributed to the generation of more powerfull to oxidizing agents such as Cl_2, HOCl, and OCl^-. The decolourisation on presence of Na_2SO_4 is attributed to the

International Journal of Research in Engineering, Science and Management
Volume-1, Issue-9, September-2018
www.ijresm.com | ISSN (Online): 2581-5782

270

generation of persulphate ions that can oxidize organic dyes [16].
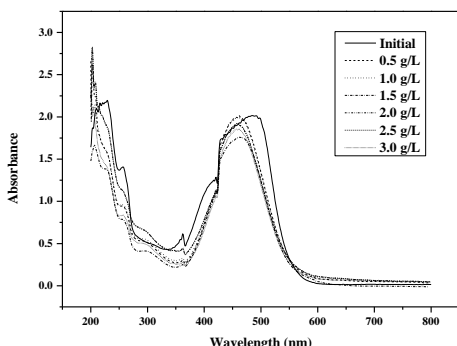

Fig. 4. Absorption spectra for Basic Orange 2 dye solution before and after electrolysis for different concentration of Na_2SO_4. Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, current density 85 A m^{-2}, time: 60 min.

3) Effect of current density

Current density is a very important variable in electrochemical process. Different current densities (85, 170, 255, 340 and 425 A m^{-2}) were applied to the cell to investigate the influence of current density on the electrochemical decolouration of Basic Orange 2 keeping NaCl concentration at 2.5g L^{-1}, dye concentration at 50 ppm (w/v), pH 3. It can be found that decolouration and efficiencies increased (Fig. 5) with increasing the applied current density [17]. This is because of the increased oxidant such as: chlorine/hypochlorite, hydroxyl radicals at higher current densities. Up to a current of 340 A m^{-2}, the decolouration efficiency of both the dyes was increased almost linearly.
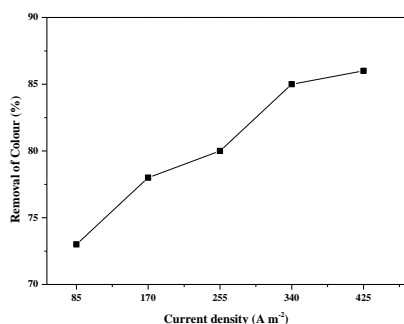

Fig. 5. Effect of current densities on decolourisation and Colour removal efficiencies of dye Basic Orange 2. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v), pH: 3, NaCl: 2.5 g L^{-1}.

At higher densities (>340 A m^{-2}) the decolouration efficiency was attained almost constant. Also the energy consumption was found to be more at higher current densities with a subsequent stripping of electrodes [18].

B. Analysis of COD & TOC

In the present study it can be seen that the degradation of Basic Orange 2 from their aqueous solutions may proceed by indirect

TABLE I
ENERGY CONSUMPTION

Current (A)	Current density Am^{-2}	Required time (min)	Energy Consumption (k Wh m^{-3})
0.1	85	60	2.56
0. 2	170	50	4.36
0. 3	255	45	6.23
0. 4	340	40	7.72
0. 5	425	40	10.26

electrochemical oxidation rather than direct electrochemical process. The maximum TOC of 93% could be achieved for the dyes at 2.5 g L^{-1} of NaCl concentration, current density 340 A m^{-2} at pH 3 for Basic Orange 2, respectively. The electrolysis was carried out at a current density of 340 A m^{-2}. At this current density, Cl_2 generated in the solution drives the oxidation process. The Cl_2 species is a powerful oxidizing agent capable of oxidizing the dyestuffs. In the absence of chloride containing electrolytes, the TOC removal and dye degradation efficiency was very low. The percent removal of TOC found to be increased with increase in the concentration of NaCl. This confirmed that the electro generated chlorine/hypochlorite will play an important role in the electrochemical degradation process of the dyestuffs.

C. Electric Energy Consumption

The major operating cost is associated with the electrical energy consumption during electrochemical degradation process. As per the results the minimum electrical energy consumption was 7.72 k W h m^{-3} for dye at 340 A m^{-2} current density. At higher current densities, the energy consumption was found to be increased, which may be attributed to the increased hydrogen and oxygen evolution reactions.

IV. CONCLUSION

In the present study the decolourisation of the pulp and paper mill dyes selected for the study namely, Basic Orange 2 was treated to find out the electrochemical decolourisation methods. In this method the experimental results were obtained, nearly 100% decolourisation of dyes with less time consuming and low power consumption. In the optimal operational electrolytic conditions current density 340 A m^{-2}, NaCl concentration 2.5 g L^{-1}, pH 3 for Basic Orange 2 influences the degradation of dyeing intermediates.

REFERENCES

[1] S. Mahesh,S., I. D. Prasad, Mall and I. M. Mishra, "Electrochemical Degradation of Pulp and Paper Mill Wastewater. Part 1. COD and Color Removal," *Ind. Eng. Chem. Res.,* 2006, *45*: 2830-2839.

International Journal of Research in Engineering, Science and Management
Volume-1, Issue-9, September-2018
www.ijresm.com | ISSN (Online): 2581-5782

271

[2] V. Saravanan and T. R. Sreekrishnan, "Bio-physico-chemical treatment for removal of colour from pulp and paper mill effluents," *J. Sci. Ind. Res.*, 2005, 64: 61-64.

[3] D.V. Savant, R. Abdul-Rahman, D. R. Ranade, "Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater," *Bioresour. Technol.*, 2006, 97: 1092-1104.

[4] O. Ashrafi, L. Yerushalmi, F. Haghighat, "Wastewater treatment in the pulp-and-paper industry: A review of treatment processes and the associated greenhouse gas emission," *Journal of Environmental Management,* 2015, 158: 146-157.

[5] M. Rahaman, K.B. Kabir, "Waste water treatment options for paper mill using waste paper/ imported pulps as Raw materials: Bangladesh perspective," *Chemical Engineering Research Bulletin*, 2010, 14: 65-68.

[6] J. Narayana, Spoorthi and P. Kariyajjanavar, "Degradation of Pulp and Paper Mill Industrial Dyes by Indirect Electrochemical Method Using Carbon Electrodes," *International Journal of Environmental Sciences*, 2015, 4: 144-149.

[7] P. Kariyajjanavar, J. Narayana, Y.A. Nayaka, "Degradation of Simulated Dye Wastewater by Electrochemical Method on Carbon Electrodes," *Indian Journal of Natural Sciences*, 2012, 10: 976-997.

[8] G.O. El-Sayed, M.S. Awad, Z.A. Ayad, "Electrochemical decolourization of Maxilon Red GRL textile dye," *International Research Journal of Pure and Applied Chemistry*, 2014, 4: 402-416.

[9] M. S. El-Geundi, "Colour Removal from Textile Effluents by Absorption techniques," *Water Research*, 1991, 25: 271-273.

[10] P. Nigam, I. M. Banat, D. Singh and R. Marchant, "Microbialm process for the Decolourisation of Textile Effluent containing Azo, Diazo and Reactive Dyes," *Process biochemistry*, 1995, 31: 435-442.

[11] N. Mohan and N. Balasubramanian, "In situ Electrocatalitic Oxidation of Acid Violet 12 dye Effluent," *Journal of Hazardous materials*, 2006, 136: 239-243.

[12] C. Ketaki, B. Vaidehi, B. Arpit, S. Seshadri, "Combinational System for the treatment of textile wastewater: A future perspective", *Assian Journal of Water and Environmental Pollution*, 2010.

[13] P. Kariyajjanavar, J. Narayana, Y.A. Nayaka, "Studies on degradation of reactive textile dyes solution by electrochemical method," *J. Hazard. Mater.*, 2011, 190: 952-961.

[14] P. Kariyajjanavar, J. Narayana, Y.A. Nayaka, "Degradation of textile dye C.I. Vat Black 27 by electrochemical method," *Journal of Environmental Chemical Engineering*, 2013 1: 975-980.

[15] I. M. Hasnain, L.S Lang, F.A.H. Asaari, H.A., Aziz, N.A. Ramli and J.P.A. Dhas, "Low cost removal of disperse dyes from aqueous solutions using plan ash," *Dyes and Pigments*, 2007, 74: 446-453.

[16] F. Yi, S. Chen and Yuan, "Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater," *Journal of Hazardous Materials*, 2008, 157: 79-87.

[17] N.M. Abu Ghalwa and L.M.S. Abdel, "Electrochemical degradation of acid green dye in aqueous wastewater dyestuff solutions using a lead oxide coated Titanium electrode," *Journal of the Iranian Chemical Society*, 2005, 2: 238-243.

[18] D. Rajkumar, B.J. Song and J.G. Kim, "Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds," *Dyes and Pigments*, 2007, 72: 1-7.