



PULP AND PAPER MILL DYE EFFLUENT TREATMENT BY ELECTROCHEMICAL DEGRADATION

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Abstract– Untreated pulp and paper mill dye effluents are very toxic to most aquatic life. This paper deals with the electrochemical degradation of pulp and paper mill dye, Basic Brown 1 from aqueous solution using graphite carbon electrodes. The experimental results indicated that initial pH, supporting electrolyte and current density were played important role in the degradation of dye. During electrochemical degradation, the chromophoric groups and aromatic rings were destroyed. The decolourisation and degradation of the dye was followed using UV-Vis spectroscopy, FT-IR, LCMS, TOC and COD measurements. The results revealed the experimental method followed for the study found to be effective degradation of dye effluents.

Key words: Untreated pulp and paper mill dye effluents, carbon electrodes; electrochemical degradation; FTIR; LC-MS

INTRODUCTION

The pulp and paper mill effluent is one of the high polluting effluents amongst the effluents obtained from polluting industries [1]. Production of paper requires huge amount of water and chemicals other than the raw materials. As a result, such production facilities produce substantial amount of liquid effluent [2]. The generated effluent is characterized by dark colour, foul odour, high organic content and extreme quantities of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and pH [3]. The colouring body present in the wastewater from pulp and paper mill is organic in nature and is comprised of wood extractives, tannin resins, synthetic dyes, lignin and its degradation products formed by the action of chlorine on lignin [4]. The presence of dyes in water is most undesirable, so a very small amount of these colouring agents are highly visible and may be toxic to the aquatic environment [5]. The treatment of dye effluent is difficult and ineffective with conventional biological process [6] and several physical and chemical methods because dyes are resistant to oxidation and reduction conditions, light exposure as well as biodegradation process. Hence, they are stable in the environment [7]. In this context, electrochemical techniques are considered to be powerful means for the treatment of dyeing of wastewater [8].

Electrochemical method has certain significant advantages such as simple equipment, easy operation and lower operating cost [9]. Graphite electrodes were used as anode and cathode by many researchers for the application in organic oxidation [10-12]. In the past, graphite was frequently used as anode for the electrochemical degradation of textile wastewater as it is relatively cheaper and gives satisfactory results [13]. The aim of this work was to test feasibility of electrochemical method for the degradation of Basic dye, Basic Brown 1 using graphite carbon electrode

Materials

The industrial basic dye Bismarck Brown Y (C.I. Basic Brown 1, CAS No. 10114-58-6) was obtained from Mysore Paper Mill Industry, Bhadravathi, India. The chemicals used for the experiments were of analytical grade reagents and obtained from s d fine chem-limited, Mumbai, India. Cylindrical carbon electrodes (chemical composition: graphite carbon+coke: 85%andash15%) were obtained from Power Cell Battery India Limited. A digital DC power supply (AESC: 30V, 2A) was used as an electrical source. Double distilled water was used to prepare the desired concentration of dye solutions and the reagents.

Instrumentation

Electrochemical degradation studies: Graphite carbon electrodes of 5.6cm length and 0.8cm diameter were used as anode and cathode for electrochemical degradation studies. The effective electrode area was 14.56 cm². The supporting electrolyte such as NaCl and Na₂SO₄ were added to the electrolysis time. The solution was kept under agitation using magnetic stirrer.

UV-vis studies: A UV-vis spectrophotometer (UV-2602) was employed to measure the optical density of dye solution (λ_{max} : 484 nm) before and after electrolysis. The degradation efficiency was calculated using the relation:

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

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.

pH and conductivity measurement: A water analyzer (Systronics, Model-371) was used to measure the pH and conductivity of the dye solution before and after electrolysis under different electrolysis conditions.

Liquid chromatography–mass spectrometry studies (LC–MS): The extent of degradation of dye samples were analyzed by LCMS studies (LCMS-2010A, Shimadzu, Japan). The LC-MS was fitted with column C18. The mobile phase was methanol: water (90:10). The flow rate was 0.2 mL min^{-1} and the injection volume of dye was 5 μL . The dye solutions were injected into LC column before and after electrolysis. Analyses using ESI (electron spray ionization) interface were done under the same chromatographic conditions as described for the APCI (atmospheric pressure chemical ionization) analysis, except the guard column, which was not used in the ESI analysis.

FTIR studies: To study the structural changes of dye before and after electrolysis the dye samples were characterized by using Fourier transform Infrared Spectrometry (FTIR) spectrometer (model 3010 Jasco, Japan). The scan range of the wave number was set from 400 to 4600 cm^{-1} . The dye samples (freeze dried) were kept in the sample holder and scanned to obtain the FTIR spectra.

RESULT AND DISCUSSION

The C.I. Basic Brown 1 is an industrial papermill dye

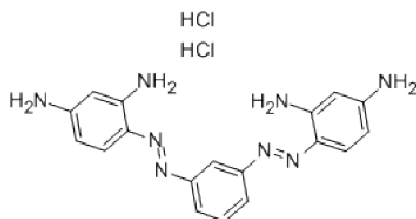


Figure 1: Molecular structures of the basic dye, Basic Brown 1

Influence of electrolysis conditions on dye degradation

Effect of initial pH

A significant difference in the extent of degradation was noted when the concentration of NaCl was at 3 g/L. The initial pH of the solution (3-11) was adjusted using 1M H_2SO_4 or NaOH [14-15]. The electrolysis was carried out at the current density of 85 Am^{-2} for

40 min with a dye concentration of 50 mg/L at room temperature. From the absorption spectral studies it was confirmed that, the larger dye molecules were degraded into simple substituted aromatic compounds [16]. However, the hypochlorite can lead to partial mineralization of dyes [17] and degradation efficiency of Basic Brown 1 was found higher in both acidic and neutral pH and slightly lower in acidic pH. After electrolysis the final pH was found to be slightly basic.

The decolouration efficiency of dye was found only 80% in acidic pH 3 and the final pH 11 decolouration efficiency was found to be 89% (Fig. 2). It indicated that the degradation of dye in basic solution is higher than that of in the acidic media. At pH 9 the decolouration efficiency was found 90% (Fig 2). Therefore the optimum pH: 9 were maintained in subsequent experiments.

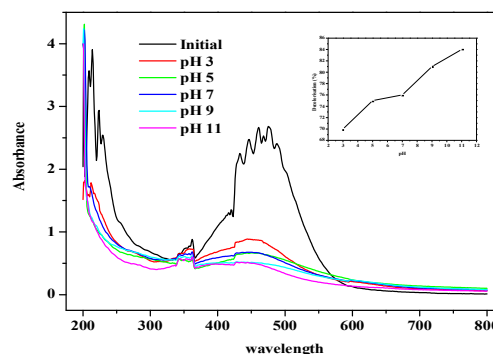
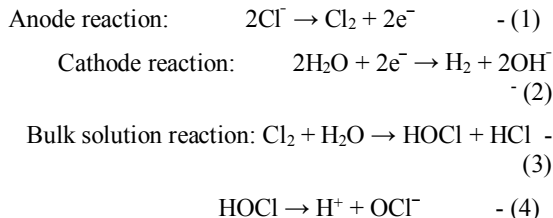


Figure 2: Absorption spectra for Basic brown 1 dye solution before and after electrolysis at different pH Electrolysis condition: concentration of dye solution: 50ppm (w/v), pH: 9, NaCl: 3g/L, current density: 85 Am^{-2} , time: 40 min. Inset plots: effect of pH on colour removal of dye solution.

Effect of supporting electrolytes:

Figure 3 show the effect of supporting electrolytes (NaCl and Na_2SO_4) and their concentration of on decolourisation efficiency. As can be seen from the Figure when Na_2SO_4 was substituted by NaCl , the decolourisation efficiency increased with a subsequent decrease

in the applied voltage. From this observation it concluded that the introduction of NaCl as electrolyte can enhance the degradation efficiency and shortens electrolysis time, which may be attributed due to the reaction between the electro generated chlorine/hypochlorite and the dye molecule present in the effluent. The possible mechanism of electrochemical degradation is given below:



The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation [18] and were classified as indirect electrooxidation of pollutant. Moreover, the increased NaCl results in a decrease in the operating voltage at constant current density (Figure 4). Increase in the concentration of NaCl up to 1.5 g/L accelerated the degradation rate, enabling degradation of dye effluent (Figure 6b) to the extent of 70.7% decolourisation efficiency in 40 min. A further increase in NaCl concentration (> 1.5 g/L) there was slight improvement indecolourisation efficiency, so the optimal concentration of NaCl used in the successive experiments was 1.5 g/L.

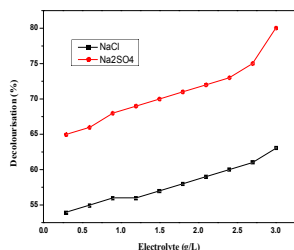


Figure 3: Effect of different supporting electrolyte and their concentration on decolourisation of dye effluent.

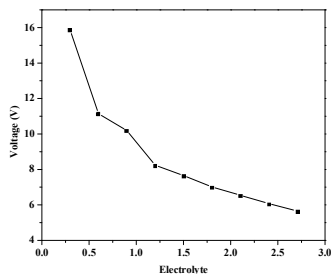


Figure 4: Influence of supporting electrolytes concentration on applied voltage during electrolysis dye solution. Electrolysis condition: concentration of dye solution: 50ppm (w/v), pH: 9, current density 85Am⁻²

Effect of current density

Current density is a very important variable in electrochemical process. Different current densities (85, 170, 255, 340 and 425 Am⁻²) were applied to the

cell to investigate the influence of current density on the electrochemical decolouration of Basic brown 1 keeping NaCl concentration at 1.5g L⁻¹, dye concentration at 50ppm (w/v), pH at 9. It can be found that decolouration and COD removal efficiencies increased (Figure 5) with increasing the applied current density [19]. This is because of the increased oxidant such as: chlorine/hypochlorite, hydroxyl radicals at higher current densities. Up to a current of 340Am⁻², the decolouration efficiency of both the dyes was increased almost linearly.

At higher densities (>340Am⁻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.

Analysis of COD & TOC

In the present study it can be seen that the degradation of Basic Brown 1 from their aqueous solutions may proceed by indirect electrochemical oxidation rather than direct electrochemical process. The maximum COD of 80% and TOC of 95.83% could be achieved for the dyes at 1.5 g L⁻¹ of NaCl concentration, current density 340 A m⁻² at pH 9 for Basic Brown 1, respectively. The electrolysis was carried out at a current density of 340 A m⁻². At this current density, Cl₂ generated in the solution drives the oxidation process. The Cl₂ species is a powerful oxidizing agent capable of oxidizing the dyestuffs. In the absence of chloride containing electrolytes, the COD, TOC removal and dye degradation efficiency was very low [25]. The percent removal of COD and TOC found to be increased with increase in the concentration of NaCl. This confirmed that the electrogenerated chlorine/hypochlorite will play an important role in the electrochemical degradation process of the dyestuffs.

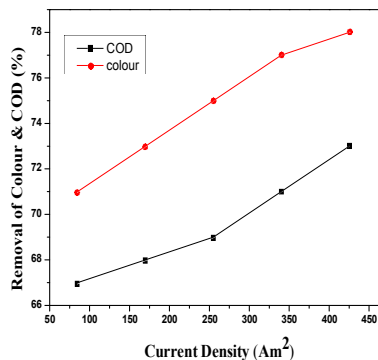


Figure 5: Effect of current densities on colour and COD removal of Basic Brown 1 dye. Electrolysis condition: concentration of the dye solution: 50ppm (w/v), pH: 9, NaCl: 1.5gL⁻¹, time: 40 min.

Liquid chromatography- mass spectrometry studies (LC-MS)

LC-MS studies were employed to monitor the diminution in mass of the fragments of dye Basic Brown 1 before and after electrolysis. MS spectrum of the dye Basic Brown 1 recorded before electrolysis shows more number of peaks at higher m/z values due to the presence of dye and other

impurities (Fig 6a). The MS spectrum of the filtrate solution after complete electrolysis shows the absence of majority of the peaks (Fig 6b). This clearly indicated that almost all dye was coagulated and removed in the form of sludge. The remaining peaks at low m/z values in the mass spectra may be due to the presence of substituted simple aromatic compounds.

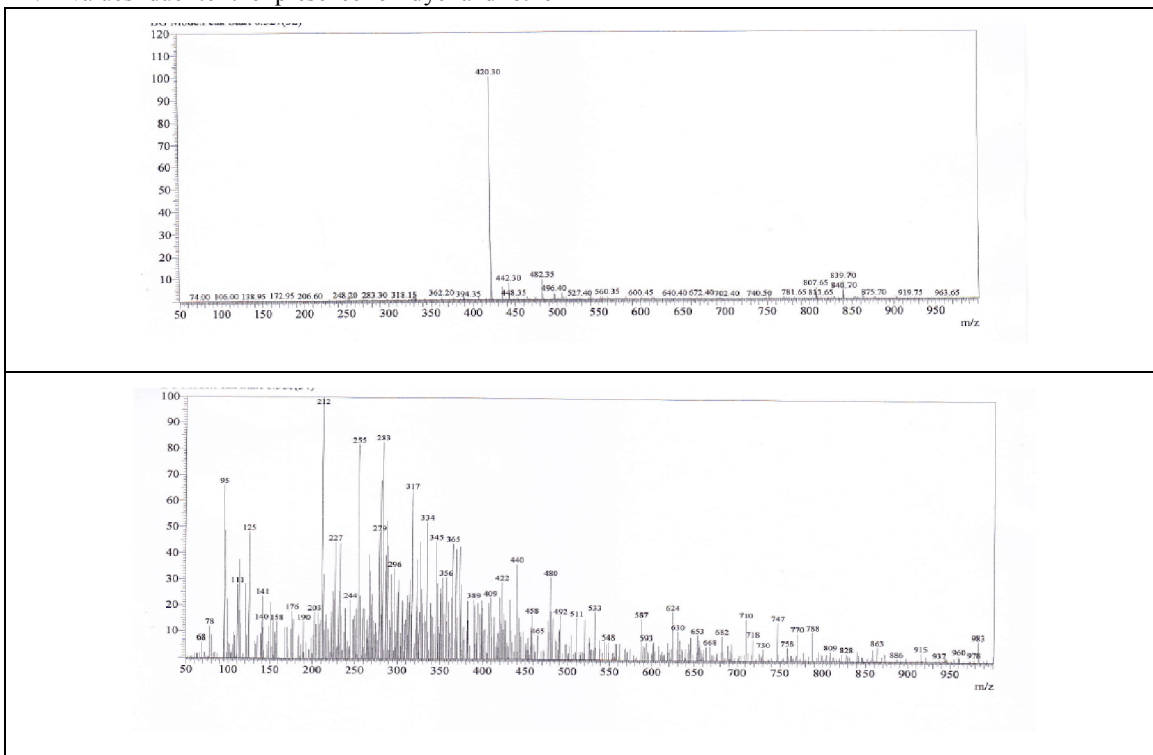


Fig 6: MS spectrum

FT-IR

FT-IR spectra of dye Basic Brown 1 was obtained before electrochemical treatment showed several bands at fingerprint region. After the electrochemical treatment a significant reduction of bands were observed in fingerprint region (Fig 7). This indicated the disappearance of functional groups during electrolysis. of functional groups during electrolysis.

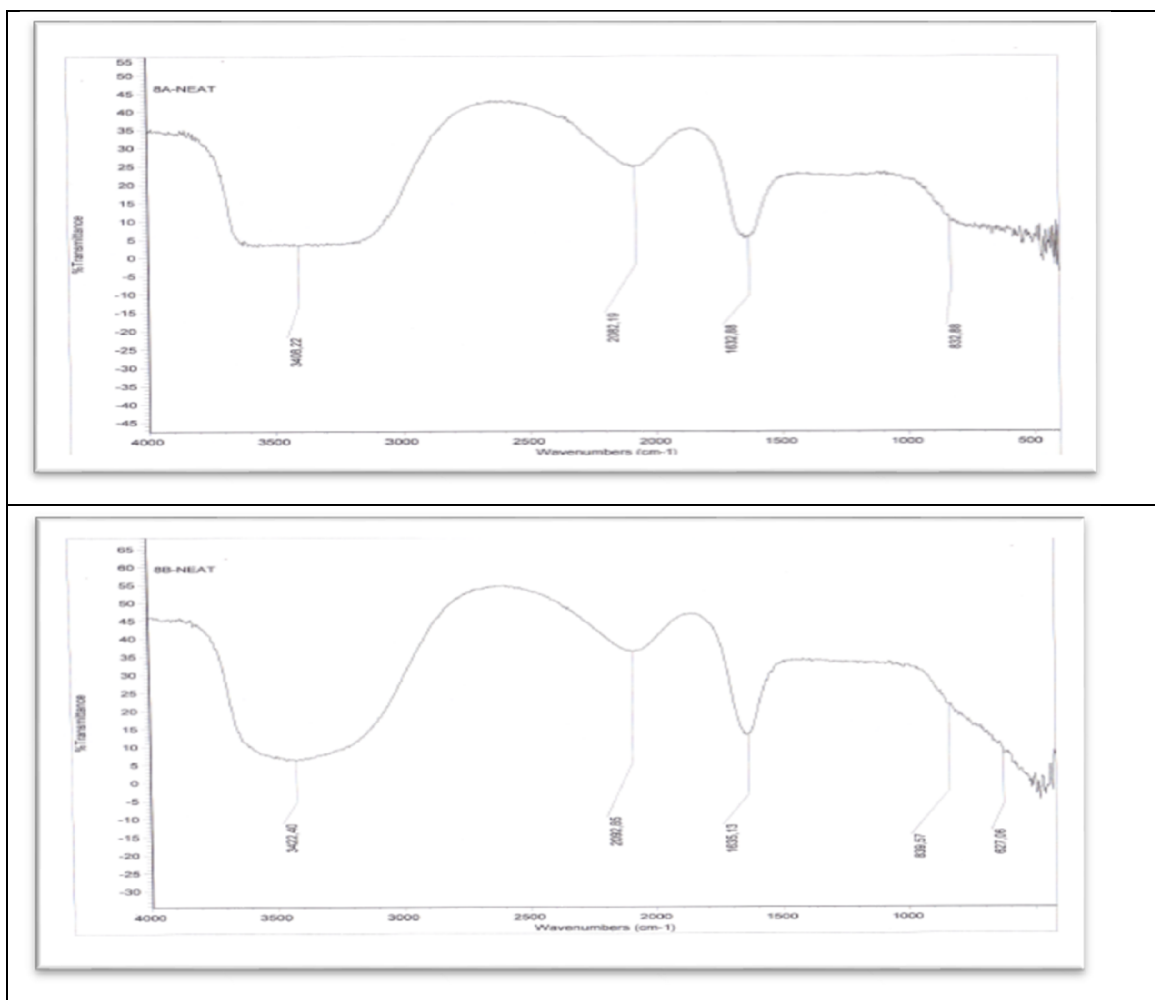


Figure 7: FT-IR spectrum of Basic Brown 1: (a) before electrolysis and (b) after electrolysis, Electrolysis condition: concentration of the dye solution: 50mg/L, electrodes: graphite carbon, pH: 9, NaCl: 1.5g/L, time: 40 min.

Electric energy consumption

The major operating cost is associated with the electrical energy consumption during electrochemical degradation process. The electrical energy consumption (E) is required to decompose 50 mgL^{-1} Fast Red dye solution at various current densities was calculated using the relation:

$$E = (It_E / V_s) \times 10^{-3} \quad - (6)$$

where, E is the electrical energy consumption (kWh m^{-3}), V is the applied voltage (V), I is the applied current (A), t_E is the electrolysis time (h) and V_s is the volume dye solution or wastewater (m^3). As per the results the minimum electrical energy consumption was 0.96 kWh m^{-3} for dye at 255 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.

CONCLUSIONS

The result obtained during the study concludes that electrochemical treatment technology can be used to treat dye effluent for discharges into water bodies without any harmful contents. In this method the experimental results were obtained, nearly 90% decolourisation and 80% COD removal of dyes with less consuming and low power consumption. UV spectral studies, LCMS, FTIR confirmed that the proposed electrochemical degradation process could be effective method for the degradation of paper mill dye effluent.



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