Studies on Degradation of Pulp and Paper Mill Industrial Dye Fast Red by Indirect Electrochemical Method

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ABSTRACT

The indirect electrochemical degradation of industrial effluents has become an attractive method in recent years. This paper deals with the electrochemical degradation of pulp and paper mill industrial dye, Fast Red from aqueous solution using graphite carbon electrodes. The experimental results indicated that initial pH, supporting electrolyte and current density played an 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 maximum colour removal efficiency of 96% could be achieved for dye at 2.5 g.L⁻¹ of NaCl concentration. The results revealed the suitability of the present process for the effective degradation of dye effluents.

INTRODUCTION

The pulp and paper industry ranks the sixth largest polluter after oil, cement, leather, textile and steel industries discharging a variety of gaseous, liquid and solid waste into the environment (Choudhary et al. 2011). The effluents generated during the processing of pulp and paper are highly coloured. The dark colour in untreated effluent is a major environmental concern as its discharge into waters inhibits the photosynthetic activity of aquatic biota by reducing sunlight, besides exhibiting the toxic effects on biota (Deilek et al. 2001, Singh et al. 2002, Merilainen et al. 2009). The treatment of dye effluent is difficult and ineffective with conventional biological processes (Guven et al. 2009) 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 (Sarala et al. 2012). In this context, electrochemical techniques are considered to be a powerful means for the treatment of dye wastewater (Szpyrkowicz et al. 2000). Electrochemical method has certain significant advantages such as simple equipment, easy operation and lower operating cost (Kariyajjanavar et al. 2010). To improve electrochemical treatment efficiency, many researchers have focused on the development of various types of electrodes, such as graphite (Kariyajjanavar et al. 2013), activated carbon filter (Fan et al. 2006, Yi et al. 2008), platinum electrodes (Jovic et al. 2013) and boron-doped diamond electrodes (Chen et al. 2003, Zhang et al. 2014, Del Rio et al. 2009). Graphite electrodes were used as anode and cathode by many researchers for the application in organic oxidation (Kariyajjanavar et al. 2012, Cameselle et al. 2005, Sanroman et al. 2005). In the past, graphite was frequently used as an anode for the electrochemical degradation of textile wastewater as it is relatively cheaper and gives satisfactory results (Vlyssides et al. 2000, Kariyajjanavar et al. 2011). The purpose of this study was to investigate the degradation of dye, Fast Red by electrochemical method using graphite carbon electrode (GCE).

MATERIALS AND METHODS

Materials: The industrial Fast Red dye was obtained from Mysore Paper Mill Industry, Bhadravathi, India. Chemicals used for the experiment were of analytical grade. Cylindrical carbon electrodes (chemical composition: graphite carbon+coke: 85% and ash 15%) 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.

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.

**UV-vis studies:** A UV-vis spectrophotometer (UV-2600) was employed to measure the optical density of dye solution ($\lambda_{\text{max}}$: 530 nm) before and after electrolysis. The degradation efficiency was calculated using the relation:

$$\% E = \left( \frac{A_i - A_f}{A_i} \right) \times 100 \quad \ldots(1)$$

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

**pH and conductivity measurement:** A water analyser (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 analysed by LC-MS studies (LC-MS-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 the dye was 5 L. 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 spectrometer (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.

**RESULTS AND DISCUSSION**

**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 5 g.L$^{-1}$. The initial pH of the solution (3-11) was adjusted using 1M H$_2$SO$_4$ or NaOH (Hasnain et al. 2007, Basiri et al. 2009). The electrolysis was carried out at the current density of 85 A.m$^{-2}$ for 20 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 (Fatiha et al. 2006). However, the hypochlorite can lead to partial mineralization of dyes (Yi et al. 2008) and degradation efficiency of Fast Red was found 94% in acidic pH 3, and at initial pH 11 the degradation efficiency was found to be 79% (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.

**Effect of supporting electrolytes:** Fig. 2 shows the effect of supporting electrolyte NaCl on decolourization efficiency with twenty minutes of electrolysis time keeping the pH at 3 and the current density at 85 A.m$^{-2}$. It can be seen that in the presence of NaCl, the decolourisation efficiency was increased with a subsequent decrease in the applied voltage. From this observation, it was concluded that the introduction of Cl$^-$ containing electrolytes can enhance the degradation efficiency and shorten the electrolysis time, which may be attributed to the reaction between the generated chlorine/hypochlorite and the dye molecule.

Based on these studies, the optimum concentration of NaCl was found to be 2.5 g.L$^{-1}$. With an increase in the concentration of NaCl (>2.5 g.L$^{-1}$) there was a slight improvement in the decolourization efficiency (Fig. 2) with a decrease in the operating voltage (Fig. 3).

**Effect of current density:** Current density is an 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 degradation of Fast Red keeping NaCl concentration at 2.5 g.L$^{-1}$, dye concentration at 50 ppm (w/v), pH 3 and room temperature. It can be found that degradation and COD removal efficiencies increased (Fig. 4) with increasing the applied current density. This is because of the increased oxidants such as: chlorine/hypochlorite, hydroxyl radicals at higher current densities. Up to a current of 340 A.m$^{-2}$, the decolourization efficiency of both the dyes was increased almost linearly.

**Analysis of COD & TOC:** In the present study it can be seen that the degradation of Fast Red from their aqueous solutions may proceed by indirect electrochemical oxidation rather than direct electrochemical process. The maximum COD of 85% and TOC of 96% 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 Fast Red, respectively. The electrolysis was carried out at a current density of 340 A.m$^{-2}$. At this current density, Cl$^-$ generated in the solution drives the oxidation process. The Cl$^-$ 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 (Narayana et al. 2015). The percent removal of COD and TOC was 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.

Liquid chromatography-mass spectrometry studies (LC-MS): LC-MS studies were employed to monitor the diminution in mass of the fragments of Fast Red dye before and after electrolysis. MS spectrum of the dye Fast Red recorded before electrolysis shows more number of peaks at higher m/z values due to the presence of dye and other impurities (Fig. 5a). The MS spectrum of the filtrate solution after complete electrolysis shows the absence of majority of the peaks (Fig 5b). This clearly indicated that almost all the 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.

FT-IR: FT-IR spectra of dye Fast Red obtained before electrochemical treatment showed several bands at finger-
print region. After the electrochemical treatment a significant reduction of bands was observed in fingerprint region (Fig. 6). This indicated the disappearance of functional groups during electrolys.

**Energy consumption:** The major operating cost is associated with the electrical energy consumption during electrochemical degradation process. The electrical energy consumption (E) required to decompose 50 mg.L⁻¹ Fast Red dye solution at various current densities was calculated using the relation:

$$E = \left(\frac{VI_{E}}{V_s}\right) \times 10^{-3}$$

Where, E is the electrical energy consumption (kW.h.m⁻³), V is the applied voltage (V), I is the applied current (A), tₘ is the electrolysis time (h) and Vₘ is the volume of dye solution or wastewater (m³). As per the results, the minimum electrical energy consumption was 9.63 kW.h.m⁻³ at 340 A.m⁻² current density. At higher current densities, the energy consumption was found to be increased and it may be attributed to the increased hydrogen and oxygen evolution reaction (Table 1).
CONCLUSIONS

In the present work, the electrochemical degradation of Fast Red was carried out using graphite carbon as anode and cathode, in the optimal operating conditions (current density 340 A.m\(^{-2}\), NaCl concentration 2.5 g.L\(^{-1}\) and at room temperature). Increasing the initial pH will lead to corresponding decrease in the degradation efficiency of Fast Red dye. The effect of the hypochlorite at pH 3 can lead to the degradation efficiency of the dye. UV-vis and FT-IR studies confirmed that the proposed electrochemical degradation process is an effective method for the degradation of Fast.
Table 1: The electrical energy consumed during electrochemical degradation of Fast Red dye solutions (50 mg.L⁻¹) at various current densities.

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Current density (A.m⁻²)</th>
<th>Required time (min)</th>
<th>Energy Consumption (kW.h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0. 1</td>
<td>85</td>
<td>20</td>
<td>0.98</td>
</tr>
<tr>
<td>0. 2</td>
<td>170</td>
<td>20</td>
<td>2.89</td>
</tr>
<tr>
<td>0. 3</td>
<td>255</td>
<td>20</td>
<td>5.77</td>
</tr>
<tr>
<td>0. 4</td>
<td>340</td>
<td>20</td>
<td>9.63</td>
</tr>
<tr>
<td>0. 5</td>
<td>425</td>
<td>20</td>
<td>13.62</td>
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Red dye is used in paper industries.

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