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Electrochemical Degradation Of Dye Basic Violet 10 On Graphite Carbon Electrode

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ABSTRACT

The indirect electrochemical degradation of Basic Violet 10 has been studied on graphite carbon electrodes. The decolourisation and degradation of the dye was followed using UV-Vis spectroscopy, COD and TOC measurements. The destruction of aromatic rings was characterized by UV-Vis techniques and chemical oxygen demand levels were monitored during degradation process to evaluate the degradation efficiency. The maximum colour removal efficiency of 94%, chemical oxygen demand (COD) 77% and total organic compound (TOC) 89% could be achieved for dye, at pH 3, current density 340 A m⁻², NaCl 2 g L⁻¹. The effect of initial pH, supporting electrolyte and current density on the degradation of dye was discussed. The results revealed the suitability of the present process for the effective degradation of dye effluents.

KEY WORDS: Carbon electrodes; electrochemical degradation; electrolyte; TOC; industrial dye

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INTRODUCTION

Pulp and paper mills are considered one of the most polluting industries worldwide. Paper making process demands large amount of fresh water and produces enormous quantities of wastewater. Wastewater from pulp and paper mills constitutes a major source of aquatic pollution since it contains high organic substances causing high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), chlorinated organic suspended solids, metals, fatty acids, tannins, lignin and its derivatives, etc¹⁻⁵.

The electrochemical treatment of wastewater is considered as one of the advanced oxidation processes, potentially a powerful method of pollution control, offering high removal efficiencies⁶. To improve electrochemical treatment efficiency, many researchers have been focused on electrode development, various types of electrode such as graphite^{7,8}. Activated Carbon Filter⁹⁻¹¹, Platinum electrodes¹²⁻¹³ and Boron Doped Diamond electrodes¹⁴⁻¹⁸ has been studied. In the past, graphite was frequently used as anode for the electrochemical degradation of textile wastewater as it is relatively cheaper and gives satisfactory results¹⁹. The aim of the present work is to study electrochemical degradation of dye using graphite carbon electrodes.

EXPERIMENTAL

Materials

The industrial basic dye Basic Violet 10 (CAS No. 81-88-9) and was obtained from Mysore Paper Mill Industry, Bhadravathi, India. All other 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} : 516 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.

RESULT AND DISCUSSION

Influence of electrolysis conditions on dye degradation

Effect of supporting electrolytes:

Figure 1 shows the effect of supporting electrolytes NaCl on decolouration efficiency with thirty 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 decolouration 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 shortens the electrolysis time, which may be attributed to the reaction between the generated chlorine/hypochlorite and the dye molecule.

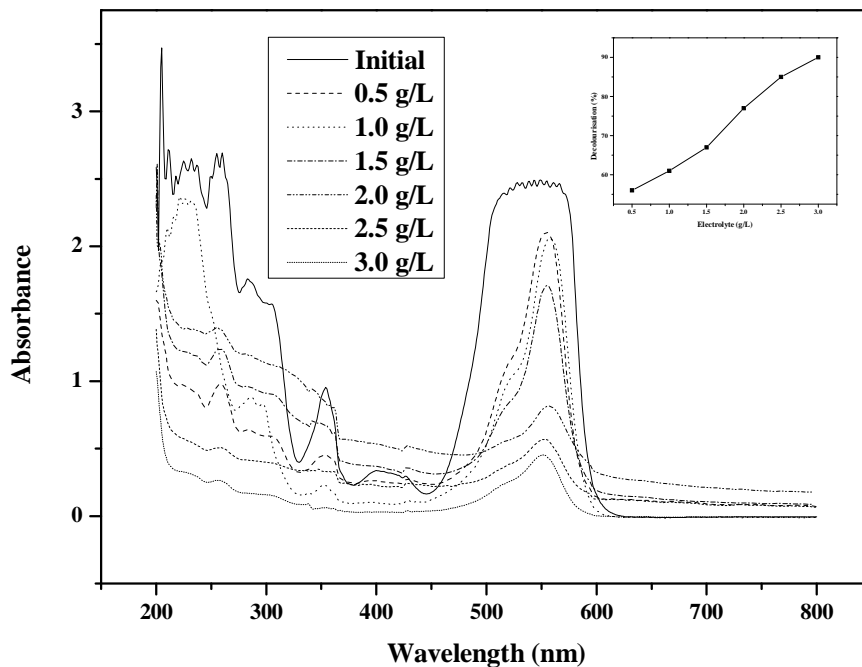


Figure 1: Absorption spectra for Basic Violet 10 dye solution before and after electrolysis for different concentration of NaCl. Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, current density 85 A m⁻², time: 30 min. Inset plot effect of NaCl concentration on colour removal of dye solution

Based on these studies, the optimum concentration of NaCl was found to be 2 g L⁻¹. With increase in the concentration of NaCl (>2 g L⁻¹) there was a slight improvement in the decolouration efficiency (Fig. 1) with a decrease in the operating voltage (Fig. 2).

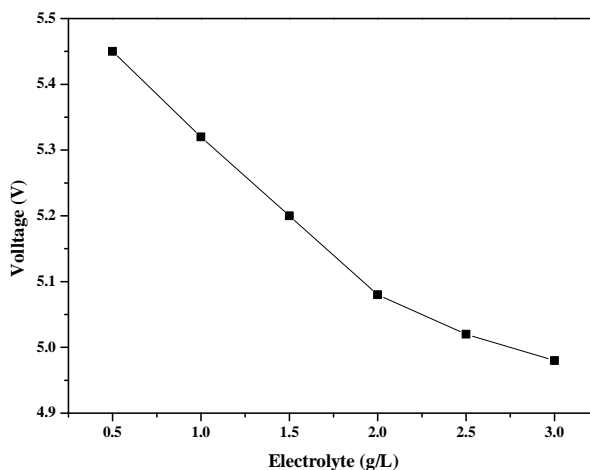


Figure 2: Influence of supporting electrolytes concentration on applied voltage during electrolysis dye solution. Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, current density 85 A m⁻²

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. 3). The higher decolourisation efficiency in presence of NaCl is attributed to the generation of more powerful oxidizing agents such as Cl_2 , HOCl , and OCl^- ²⁰.

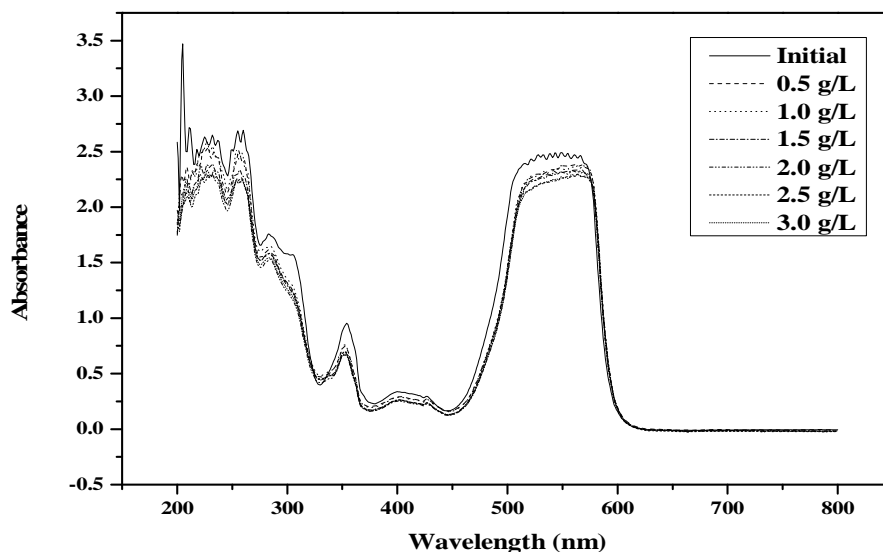


Figure 3: Absorption spectra for Basic Violet 10 dye solution before and after electrolysis for different concentration of Na_2SO_4 . Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, current density 85 A m^{-2} , time: 30 min.

Effect of initial pH

Solution pH is one of the important factors that affect the performance of electrochemical process. Hence experiments were conducted to study the effect of pH on the degradation efficiency of Basic Violet 10. A significant difference in the extent of decolourisation was noted when concentration of NaCl was at 3 g L^{-1} . The initial pH of the solution (3-11) was adjusted using 1N H_2SO_4 or NaOH ²¹. The electrolysis was carried out at the current density of 85 Am^{-2} for 30 min with a dye concentration of 50 ppm (w/v) at room temperature. After electrolysis the results were indicated that final pH was remained almost same in acidic and neutral conditions and decreased at basic condition.

The decolouration efficiency of dye was found 90% in acidic pH 3 and at initial pH 11 the decolouration efficiency was found to be 48% (Fig 4). It indicated that the degradation of dye in acidic solution is higher than that of in the basic media. Therefore the optimum pH: 3 were maintained in subsequent experiments.

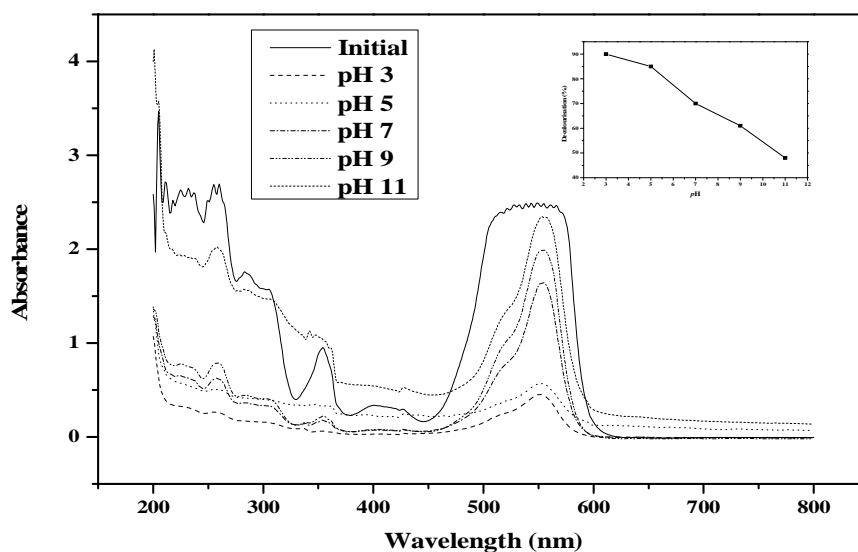


Figure 4: Absorption spectra for Basic Violet 10 dye solution before after electrolysis at different pH Electrolysis condition: concentration of dye solution: 50 ppm (w/v), pH: 3, NaCl: 3 g L⁻¹, current density: 85 A m⁻² Inset plots: effect of pH on colour removal of dye solution.

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 Violet 10 keeping NaCl concentration at 2 g L⁻¹, dye concentration at 50 ppm (w/v), pH 3. It can be found that decolouration efficiencies increased (Fig. 5) with increasing the applied current density²². 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.

At higher densities (>340A 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 electrodes²³.

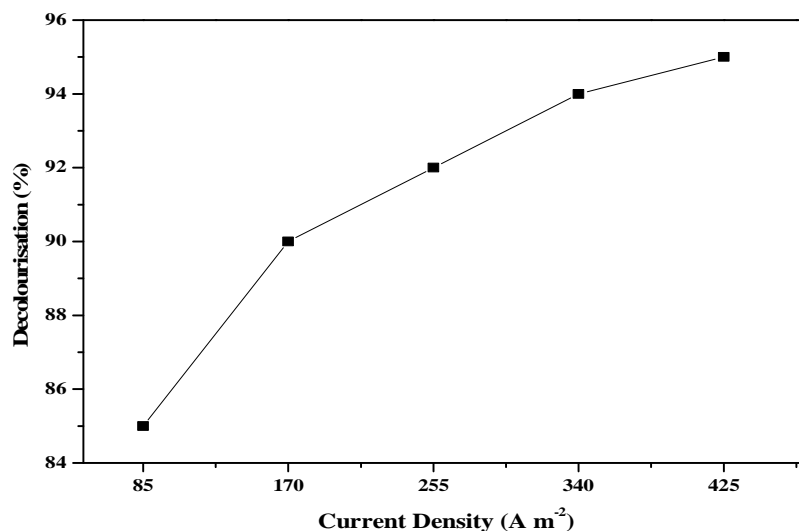


Figure 5: Effect of current densities on colour removal efficiencies of dye Basic Orange 10. Electrolysis condition: concentration of the dye solution: 50 ppm (w/v), pH: 3, NaCl: 2 g L⁻¹.

Analysis of COD & TOC

In the present study it can be seen that the degradation of Basic Violet 10 from their aqueous solutions may proceed by indirect electrochemical oxidation rather than direct electrochemical process. The maximum COD of 77% and TOC of 89% could be achieved for the dyes at 2 g L⁻¹ of NaCl concentration, current density 340 A m⁻² at pH 3 for Basic Violet 10, 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. The percent removal of COD and 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.

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 6.24 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.

Table No. 1: The electric energy consumed during degradation of 50ppm (w/v) Basic Violet 10 dye solution at various current densities

Current (A)	Current density A m ⁻²	Required time (min)	Energy Consumption (k Wh m ⁻³)
0.1	85	30	1.36
0.2	170	28	2.93
0.3	255	25	4.50
0.4	340	22	6.24
0.5	425	20	8.14

CONCLUSIONS

In the present work graphite carbon electrodes used as anode and cathode for the electrochemical degradation of Basic Violet 10 in aqueous solution at different parameters including initial pH, supporting electrolyte and current density. The optimal operating conditions are pH 3, NaCl concentration 2 g L⁻¹ current density 340 A m⁻², time 22 min. Increasing the initial pH will lead to corresponding decrease in the degradation efficiency of Basic Violet 10. In this method the experimental results were obtained, nearly 100% decolourisation of dyes with less time consuming and low power consumption. UV-vis studies confirmed that the proposed electrochemical degradation process is an effective method for the degradation of Basic Violet 10 is used in Paper industries.

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