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DEGRADATION OF ORGANIC POLLUTANTS BY INDIRECT ELECTROCHEMICAL OXIDATION PROCESS USING COMPOSITE ELECTRODE

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ABSTRACT

The aim of this research work is to investigate the efficiency of electrochemical oxidation of industrial polluted water which contains Fast Blue B salt. A novel composite electrode was fabricated by pressing together Co_3O_4 *and graphite and it was used as the cathode and a platinum foil as the anode. The experiments were carried out in a glass beaker containing 100 ml of dye solution. The colour removal process was studied at different conditions of pH, treatment time, electrolyte concentration, current density, potential difference between electrodes and initial dye concentration. During the electrolysis, the organic pollutants are oxidized to carbon dioxide and water. The removal of chemical oxygen demand (COD) and dye colour were 85% and 95% respectively. The results revealed the suitability of the present process for the effective degradation of dye effluents.*

KeyWords: Co_3O_4 *electrodes, reactive azo dye, electrochemical degradation*

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1. INTRODUCTION

Textile and leather industrial waste water has a high content of pollutants due to the usage of dyed water in huge quantity. The sources of this pollution are processing chemicals and dyes. The discharge of this huge amount of waste water to the environment causes aesthetic problems due to the colour and also damages the quality of the river water and underground water. This is due to variety of dyes used in the industries and released to environment. Their breakdown products are toxic, carcinogenic or mutagenic to living being [1]. Azo dyes are the largest group of dyes used in the textile industry [2], constituting 30-40% of the dyes used for dyeing cotton, rayon, silk, wool, nylon and leather [3,4]. They have one or more azo groups (R_1–N=N–R_2) having aromatic rings mostly substituted by sulfonate groups. These complex aromatic conjugated structures are responsible for their intense colour.Recently, electrochemical technologies offers effective means to solve environmental problems related to industrial processes [5-10].The aim of this paper is to present electrochemical treatment of synthetic dye wastewaters using a novel composite electrode.

2. EXPERIMENTAL DETAILS

2.1. Materials and reagents

Fast Blue B salt, a reactive dye (CAS Number 14263-94 –M.W= 475.47 gmol-1, Color Index Number 37235) was obtained from sigma Aldrich. This azo dye contains $–NH_2$ as functional group and its chemical name is 3,3$^/$, dimethoxybenzidine (3,3$^/$ DMB) or o-Dianisidinebis(diazotized) zinc double salt. The chemical structure of 3, 3$^/$ DMB is shown in fig.1. Sodium chloride, dye, sulfuric acid and sodium hydroxide used were of analytical grade. Distilled water was used to prepare the desired concentration of dye stuff solution.

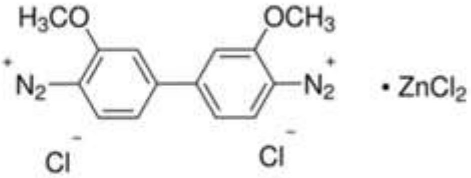

Figure.1: Structure of 3, 3$^/$, dimethoxybenzidine(3,3$^/$ DMB)

2.2 Instrumentation

a) Cyclic voltammetric studies

The electrochemical measurements were carried out using an Electroanalyser, model-201(ChemiLink, Mumbai, India) controlled by electrochemical software. A three electrodes system was used for the cyclic voltammetric experiments The Co_3O_4-graphite electrode was tested using cyclic voltammetry in a three-electrode system. The composite electrode was the working electrode with a Pt counter electrode and saturated calomel as the reference. The electrolyte was 10 g/L NaCl and the scanning rate was 50 mV/s. All the experiments were carried out at room temperature (25°C).

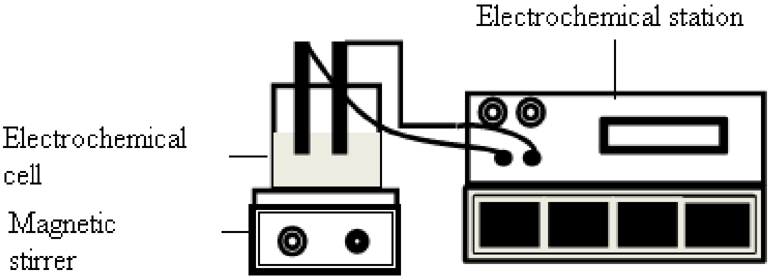

Figure. 2: Schematic diagram of the experimental setup

b) Electrochemical degradation studies

Fig. 2 show the experimental setup for the electrochemical oxidation studies. The Co_3O_4-graphite electrode was the cathode and the anode was a 1.0 cm^2 Pt. Different supporting electrolytes such as NaCl or Na_2SO_4 were added to the electrolytic cell to increase the conductivity of the solution and to decrease the electrolysis time. The solution was kept under agitation using a magnetic stirrer

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$$\%E = \frac{A_i - A_f}{A_i} \times 100$$

c) UV-Visible studies

A UV-Vis Spectrophotometer (Shimadzu, UV-256) was employed to measure the absorbance at maximum wavelength (α max=460) for dye solutions before and after electrolysis. The decolourisation efficiency was calculated using the relation:

Where, A_i is the initial absorbance value and A_f is the final absorbance value with respect to their maximum or A_i and A_f are initial and final COD values of the dye solution, respectively.

d) pH and conductivity measurement

Water analyzer (Systronics, Model-371) was used to measure the pH and conductivity of the dye solution before and after electrolysis under different electrolytic condition.

3. RESULTS AND DISCUSSION

The Co_3O_4-graphite composite cathode was prepared by loading Co_3O_4 on activate high purified graphite. The XRD diffraction pattern of the Co_3O_4-graphite composite is shown in Figure 3. The assignment was carried out by using the JCPDS database. All peaks in the XRD diffraction pattern was perfectly indexed to Co_3O_4(JCPDS 42-1467) with cubic crystal system.The sharp diffraction peak at 2θ =26.5° was corresponding to high purified graphite. All the remaining diffraction peaks were readily indexed to cubic phase $Co_3O_4$and have shown the high degree of crystallinity.

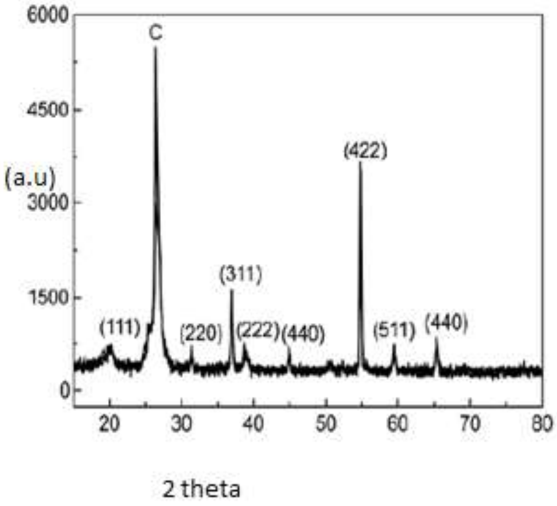

Figure 3. XRD diffraction pattern of the Co_3O_4-graphite composite

Nano-Co_3O_4 and graphite were mixed in an ethanol/PTFE emulsion, sonicated for 5 min to disperse the mixture evenly, and then dried at 50°C to form a dough-like paste. Two pieces of the paste were fixed on a stainless steel mesh current collector and pressed at 30 MPa for 2 min. The electrode was refluxed in acetone for 24 h to remove the ethanol and surface PTFE. The dimensions of the composite electrode were 1.0 cm^2. The dye contains two chlorine groups, which increase the water solubility of the dye, two amine groups, which are responsible for the relative stability of amine groups, and two $–OCH_3$ groups, which provide a strong adherence to the textile substrate.

Voltammograms of the Co_3O_4-graphite electrode under different pH are displayed in Figure 3. The cyclic voltammogram is not a regular rectangle, indicating that the capacitance of the Co_3O_4-graphite electrode is a pseudo-capacitance rather than a double layer capacitance. The electrode showed good electro-catalytic properties in the working voltage range. There were the two pairs of redox peaks in cyclic voltammogram. The figure 4 shows the response of the Co_3O_4-graphite electrode at different pH's, when the EFL system medium was acidic (pH = 3.0). The current peak at 0.18 V vs. SCE is produced by cathodic reduction of O_2 to H_2O_2 (Reaction (1a)) and the current peak at 0.25V vs. SCE is produced by the cathodic reduction of H^+ to H_2. Therefore, this EFL system could degrade POPs in a wide pH range.In the EFL system, the Co_3O_4-graphite electrode acts as the cathode and a Pt net as the anode. Two Co_3O_4-catalyzed cathodic reductions are of interest.

$$O_2 + 2H^+ + 2e \rightarrow \quad H_2O_2 \text{ (acidic)} \qquad (1)$$

$$O_2 + 2H_2O + 2e \rightarrow \quad H_2O_2 + 2OH^- \text{(basic)} \qquad (2)$$

$$H_2O_2 + 2e \longrightarrow \quad 2\ OH \qquad (3)$$

Degradation extent of $3,3^{/}$, dimethoxybenzidine ($3,3^{/}$ DMB) was monitored

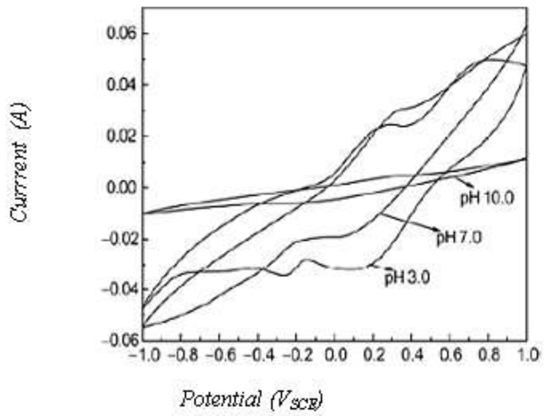

Figure 4 shows cyclic voltammogram of the Co_3O_4-graphite electrode at different pH's,

The absorption spectrum changes accompanying degradation of $3,3^{/}$ DMB in the electro-Fenton system are displayed in Figure 5. The spectrum of $3,3^{/}$ DMB is characterized by a maximum absorption peak at 460 nm in the visible region With increased electrolysis time, the broad absorption peak at 460 nm decreases, indicating degradation of $3,3^{/}$ DMB. This finding is significant in the search for new techniques to remove azo dyes with N–N bonds. The gradual decrease in intensity and then disappearance, indicates that the macromolecular structure of $3,3^{/}$DMB has been destroyed.

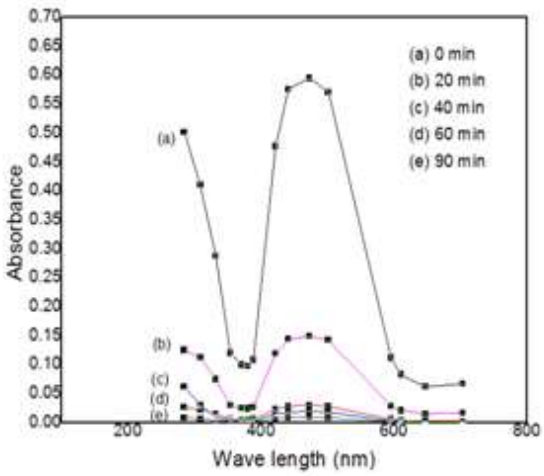

Figure.5UV-Vis absorption spectra of $3^{/}$ DMB during electrolysis at various time intervals

The effect of pH on decolorization of $3,3^{/}$ DMB during the electrochemical degradation is shown in figure 6. The result indicates that the color removal and decrease in COD with respect to the initial pH of the solution. Apart from the formation of H_2O_2formation, there may be the formation of hypochlorous acid in lower pH range. The liberated of chlorine reacts with water and form hypochlous acid which will oxidize the dye.

Bulk solution reaction :

$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^-$

$R + HOCl \longrightarrow P + Cl^-$ where R is dye pollutant, P is oxidised product

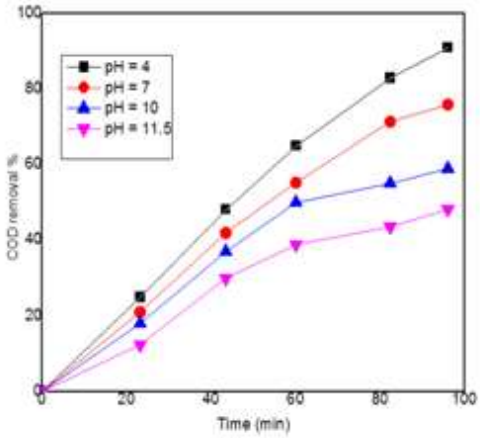

Figure.6 Effect of pH on the removal of COD

3. *CONCLUSION:*

In the present work the electrochemical method has been explored for the degradation of $3,3^{/}$ DMB using Co_3O_4- graphite carbon electrodes as anode and cathode. Optimum operational conditions for the effective degradation of $3,3^{/}$ DMB were: current density 100 Am^{-2}; NaCl concentration of 5 gL-1; and temperature 300.15K. Cyclic voltammograms indicated the quasi-reversible electrochemical nature of $3,3^{/}$ DMB. The effect of conducting salt clearlyshowed that, introduction of Cl^{-} containing electrolytes enhances the degradation efficiency of the dye. UV-Vis studies confirmed that the proposed electrochemical degradation process is an effective method for the degradation of $3,3^{/}$ DMB.

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