ISSN: 2347-7490 International Journal of Advanced Research and Technology (2016), Volume 4, Issue 2, pp. 108-113

Journal homepage: http://www.ijartjournal.com

RESEARCH ARTICLE

ELECTROCHEMICAL DECOLOURISATION OF DISPERSE-BLUE 26 DYE EFFLUENT

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Manuscript Info:

Manuscript History:

Received:

April 04, 2016

Final Accepted:

June 26, 2016

Published Online:

June, 2016 Issue

Abstract:

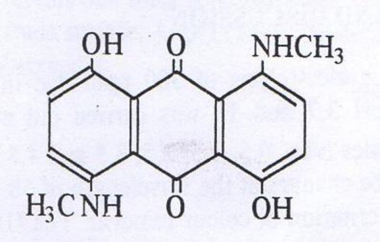
In dying industries the main environmental problem is the discharge of dyehouse effluents. An average sized mill discharges about one million litres of dye effluents daily. This spoils the ground water, well water and nearby river water. This effluent has to be treated to reduce pollutants within the prescribed limits before discharging. The primary treatment for these effluents is considered to be the removal of colour. Various technologies were tried for the colour removal, but complete decolouriation was found to be difficult. Anodic-oxidation technique was earlier tried for treating various effluents and maximum removal of the organics was observed. We have tried the complete decolourisation of Disperse blue 26 dye effluent using two types of anodes planar graphite and TSIA. Effect of pH, current density and time were studied. Current density is varied from 0.5A/dm^2 to 4.5A/dm^2. Sodium chloride 2gpl was used as supporting electrolyte. UV-VIS absorbance at 580nm wavelength , BOD and COD were monitored during electrolysis. Complete decolourisation, 96% absorbance reduction is achieved in neutral pH medium in the presence of TSIA anode.

INTRODUCTION:

Textile industries consume a large volume of water and discharge equal volume of wastewater containing a variety of dyes, salts, acids, alkali and organic materials like starch, oil, surfactants etc. The major problem with effluent is due to dark colour and high BOD, COD and TDS. Ecological aspects of these synthetic dyes used by dyeing industries are complex to evaluate. Some of the dyes are toxic, carcinogenic and mutagenic [1,2]. Decolourisation is very important before its disposal. The chemical oxidation [3] and biological action [4,5] have been used for treatment, the former pullets the atmosphere leaving toxic materials, which may reach ground water and the later needs much ground space and ultimately leaves toxic materials. Thus the need for new technology for the detoxification and removal of organics from aqueous effluents is widely recognized. Electrochemical oxidation offers one approach to developing such technology [6,7]. Anodic oxidation is found to be an alternative method for the destruction of dyestuffs present in the textile effluents [8,9]. Direct electrochemical oxidation anodic oxidation using metal oxide coated anodes have been proved successful for complete oxidation at a significant rate [10,11]. In presence of supporting electrolytes, the coated anodes were found to be very efficient in the treatment of dye effluent [12]. Lead dioxide is known to be most effective anode for the oxidation of organic compounds [13,14]. Most of the above studies are mainly for azo dyes. Anthraquinone dyes now a days widely employed. The present paper deals with the complete decolourisation of the dye effluent of a model compound in anthraquinone dyes, disperse blue-26 through electrochemical oxidation, using lead dioxide coated anode (TSAI - Titanium Substrate Insoluble Anode), since graphite anodes didn't decolourise the dye effluent.

EXPERIMENTAL

The model anthraquione dye taken is Disperse blue - 26 (C.I. 63305), whose structure is as follows



A stock solution of dye/l gpl was prepared and diluted with distilled water to get 300 ppm dye solution. This concentration was kept constant throughout the experiments. The characteristics of the above dye solution is given in table 1.

Table-1. Characteristics of the synthetic dye effluent of Disperse blue-26

Parameter	Before electrolysis	After continuous electrolysis
Colour	Dark blue	Colourless
pH	7.2 – 8.0	6.8- 8.5
Concentration	300ppm	-
λ_{max}	580nm	-
COD	1460 - 1475ppm	120ppm
TDS	2800ppm	2200ppm

Experiments were carried out under galvanostatic condition, varying current density from1.5 A/dm^2 to 4.5 A/dm^2. For electrolysis. Aplab regulated DC Power Supply L3230 was used. All the experiments were carried out under static batch mode treating 200ml of solution by passing a fixed quantity of electricity 3.6Ahr. Lead dioxide is coated on titanium bare substrate as per the procedure [15].PbO$_2$/Ti of 7cm length 4.5cm breath was used as anode and stainless steel of same dimension was used as counter electrode. NaCl (2gpl) was used as supporting electrolyte. Since the pH of the effluent from dyeing industries varied from time to time, studies were carried out at different pH viz. 3, 7 and 13 by the addition of either sulphuric acid or sodium hydroxide solution.

Cell voltage and electrode potentials were measured for every half an hour interval, using precision digital multimeter. During electrolysis samples were drawn for every one hour and COD estimation was carried out as per ASTM standards. The extension of decolourisation was estimated spectromatically at 580 nm, using Systronics Digital Spectrophotometer 166. The UV-Visible spectra were recorded before and after the electrolysis, using Jasco V 530 UV-VIS Spectrophotometer. The experiment results were recorded. Optimum current density condition is achieved for complete decolourisation and maximum removal of COD. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION:

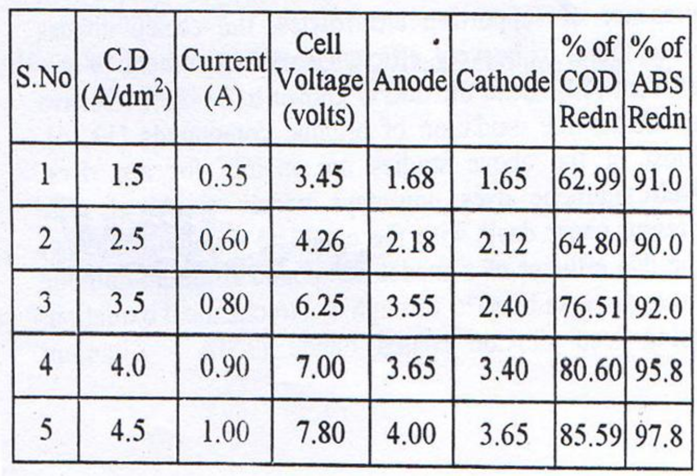
When the electrolysis of 300 ppm dye in aqueous medium at pH 3,7 and 13 was carried out at various current densities (viz., 0.5, 1.5, 2.5, 3.5 and 4.5 A/dm^2), the absorbance changes at the wavelength of 580 nm were taken as the criterion of colour removal. The UV-Visible spectra was recorded before and after the electrolysis and given in fig. 1. With an applied charge of 3.6 Ahr the absorbance at 580nm becomes almost zero (fig.2). Hence the quantity of electricity Q was kept constant at 3.6 Ahr for all experiments.

Effect of Current Density and pH on Chemical Oxygen Demand (COD)

The percentages of COD reduction values were calculated for the samples withdrawn periodically. Results obtained were given in Tables 2,3 & 4 for pH 3,7 and 13.0, respectively. From the tables it is clearly understood that the % COD reduction values in turn the amount of the destruction of dye depends upon the current densities, pH values and time of electrolysis also. At pH 7 and the current density of 4.5 A/dm^2, the % of COD reduction shows the maximum value. This indicates that the electrolysis is maximum at neutral pH and current density of 4.5 A/dm^2. A higher percentage of COD reduction, 85.59% is observed under these conditions.

Table2. Results observed from the treatment of Disperse blue-26 at different current density values(pH 3.0)

Table3. Results observed from the treatment of Disperse blue-26 at different current density values(pH 7.0)

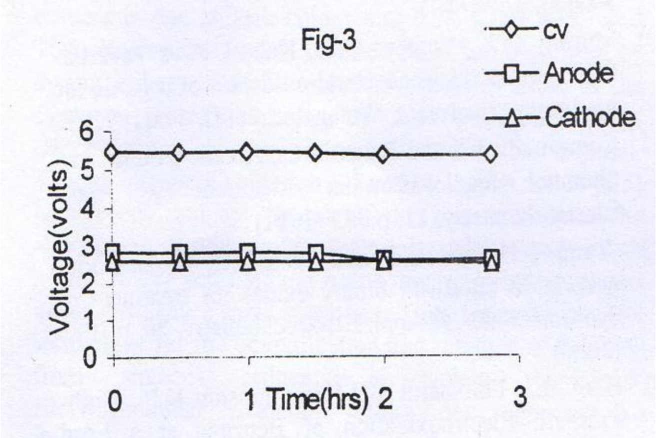


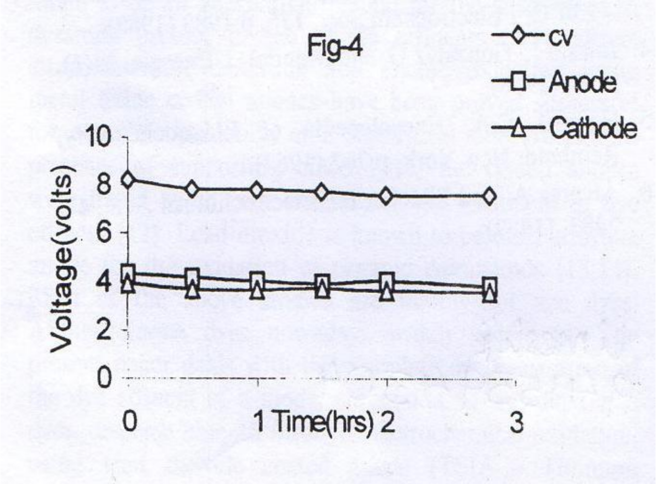
S.No	C.D (A/dm^2)	Current (A)	Cell Voltage (volts)	Anode	Cathode	% of COD Redn	% of ABS Redn
1	1.5	0.35	3.45	1.68	1.65	62.99	91.0
2	2.5	0.60	4.26	2.18	2.12	64.80	90.0
3	3.5	0.80	6.25	3.55	2.40	76.51	92.0
4	4.0	0.90	7.00	3.65	3.40	80.60	95.8
5	4.5	1.00	7.80	4.00	3.65	85.59	97.8

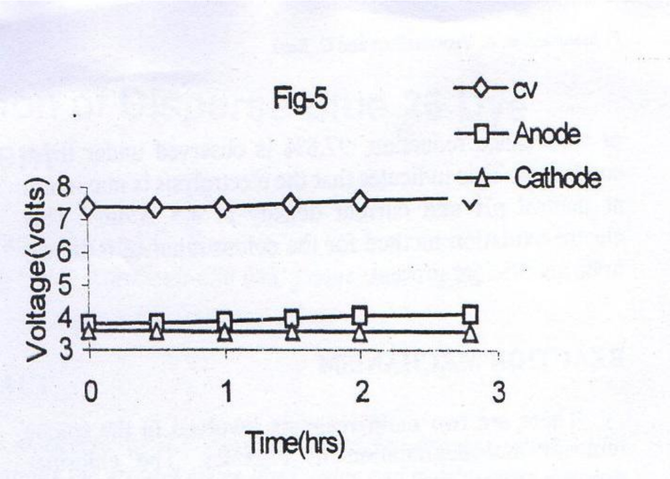
Table4. Results observed from the treatment of Disperse blue-26 at different current density values(pH 13.0)

Effects of Current Density and pH on Cell Voltage and Electrode Potentials

The variation of cell voltage with time at all current densities was studied. For pH 3 and 7 it remains more or less constant throughout the electrolysis with time. However in pH 13 slight increase in cell voltage and anode potential was observed. This may be due to film formation on the anodic surface at pH 13. Plots of cell voltage and electrode potentials vs time were given in Figures 3,4 and 5 for pH 3,7 and 13, respectively for the current density of 4.5 A/dm^2. Gradual increase in cell voltage with current density was observed.





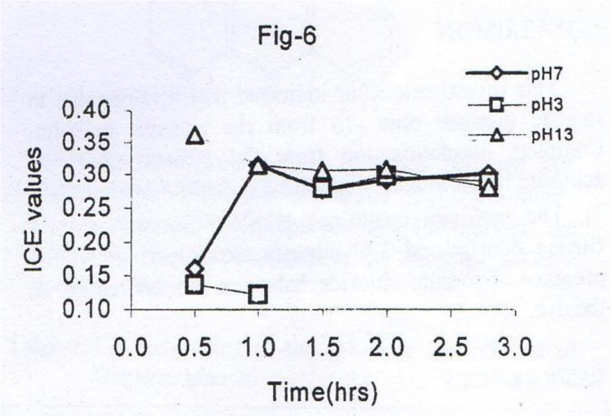


Determination of Instantaneous Current Efficiency (ICE)

ICE, Instantaneous current efficiency for the electro-oxidation of organics at given experimental conditions was calculated by two methods, Oxygen flow method and COD method. In our studies ICE values were calculated by COD method using the relation [16]

$$ICE = \frac{[(COD)_t - (COD)_{t+\Delta t}]\,F.V}{8\,I\,\Delta t}$$

where $(COD)_t$ and $(COD)_{t+\ \ t}$ are chemical oxygen demands at times t and t+ t (in g O_2 dm^{-3}) respectively, I is the current (A), F is the Faraday (96487C) and V is the volume of electrolyte (dm^3). Plot of ICE values vs time was given in fig. 6 at the current density 4.5A/dm^2. Absence of decrease in the ICE values for pH 3 and pH 7 with time reveals that there is no polymeric film formation in the electrode surface. At pH 13 a slight decrease in ICE values is observed.



SPECTRAL STUDIES

During electrolysis samples were withdrawn periodically, filtered and used for the spectral studies. Absorbance values were measured at λ_{max} 580nm and the % of absorbance reduction values were calculated for pH 3,7 and 13 and presented in tables 2,3 & 4 for comparison. At pH 7 and current density of 4.5 A/dm^2, the absorbance shows minimum value and a higher percentage of absorbance reduction, 97.8% is observed under these conditions. This indicates that the electrolysis is maximum at neutral pH and current density of 4.5 A/dm^2. This electro-oxidation method for the colour removal is shown to be an efficient process.

REACTION MECHANISM:

There are two main reagents involved in the colour removal and degradation of organics. The chlorine -generated insitu at anode and hypochlorite formed oxidize the organics present in the solution. The mechanism of such indirect electrochemical oxidation of organics in the treatment can be generally considered to take place through the formation of hypochlorite ion, when sodium chloride is used as the supporting electrolyte.

$$\begin{array}{ll} \text{Anode:} & 2Cl^- \rightarrow Cl_2 + 2e^- \\ & 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \\ \text{Cathode:} & 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ \text{Bulk:} & Cl_2 + H_2O \rightarrow HCl + HOCl \end{array}$$

In the cell in which anode and cathode products are not seperated, that is a process which can result in

$$Cl_2 + OH^- \rightarrow Cl^- + OCl^- + H_2O$$

Both the hypochlorite and the free chlorine can react as oxidizing agents and are also chemically reactive in their own right. Hence

$$C_{16}H_{14}N_2O_4 + 35[O] \rightarrow 16\ CO_2\uparrow + 7\ H_2O + N_2\uparrow$$

CONCLUSION:

This indication has indicated that it is possible to remove disperse blue-26 from theaqueous medium. Complete decolourisation from the effluent could be achieved by prolonged electrolysis in neutral medium (pH 7). The optimum conditions at pH 7 are 4.5A.dm^{-2} current density and 220 minutes electrolysis . The presence of sodium chloride enhances the destruction of the dye.

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