



## Treatment of Industrial Azo Dye Effluents by Electrochemical Technique And Its COD Measurement

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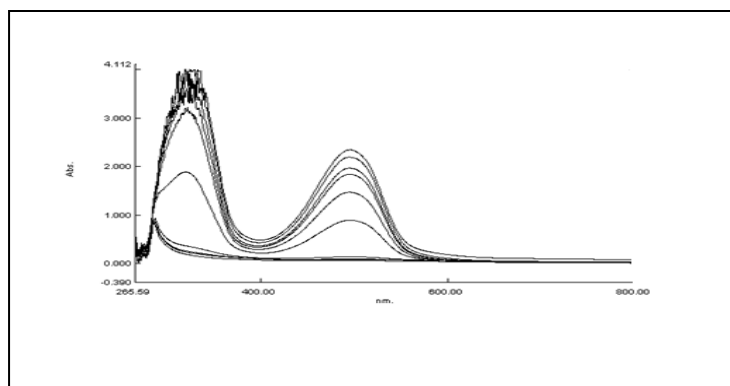
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### ABSTRACT

Electrochemical reductive degradation of azo dye such as diazoaminobenzene (DAB) was carried out in dilute sulphuric acid solution on different cathodes such as Lead, Copper and Graphite by galvanostatic technique. The result of the electrolysis of the dyestuff solutions were expressed in terms of chemical oxygen demand (COD) values and the values of absorption intensity of dye solution. The different operating conditions of the treatment process were studied and optimized. The optimum operating conditions for the degradation of dye were determined, where good results for complete removal of the dye and COD were achieved. COD removal efficiency was reached 71%, the value of absorption maxima in both UV and visible region was decreased from 3.982 to 0.179 and 2.341 to 0.065. The % decolorization was 97.2 on lead electrode. Maximum degradation efficiency was observed in 5% acid solution, at  $0.15\text{Acm}^{-2}$  current density (1080C) on lead electrode at room temperature.

### Graphical Abstract



UV-VIS spectrum of reaction mixture

**Keywords:** Azo dyes, COD, Diazoaminobenzene, Electrochemical degradation, UV-VIS spectral studies.

## INTRODUCTION

Dyes are organic colorants used in textile, pharmaceutical, cosmetic, food and other industries for imparting shades of colors [1-2]. Azo dyes are probably released into the environment, particularly into water and soil. Azo dyes may, for example, be discharged into water in relation to the production of azo pigments or when the dyes are used in production. They may also be discharged into soil via sludge from local water treatment plants spread on farmland. About 1,200 tones of dyes are placed in landfills each year. About 300,000 tons of different dyestuffs are used per year for textile dyeing operations, thus dye houses belong to the big consumers of synthetic dyes. Dyeing almost always takes place from aqueous solution. As a result a considerable volume of colored wasted water has to be treated in a dye house. Dye manufacturers and users, particularly the textile industries, release wastewaters in massive quantities containing dyes to the extent of 0.001-0.7% (w/v) often with dissolved inorganic salts, dispersing agents, surfactants and organic washed out from the materials [2-5]. Reports also suggest that dye house effluent contain 0.1% to 2% (w/v) dye resulting in 2-9% of total global annual dye production, which is nearly 50000 tons [5-9]. The deleterious aspects of dye effluent are their unacceptable color and high COD, Further the dye components are largely degradable by physicochemical or biological methods and degradation becomes highly difficult as the textile dyes are constantly being replaced with modern dyes which are resistant to chemical, photochemical and biological degradation [3,7]. Once released these untreated discharges may deteriorate soil resources and the environments.

Dyestuffs such as sulphur, vat dyes and azo dyes play an important role in today's dyeing industry. However, the generation of non-regenerable oxidation products causes various problems in the disposal of the dyeing bath and the washing water. Thus sulphite, sulphate, thiosulphate and toxic sulphides heavily contaminate wastewater from dyeing plants. In addition, as a result of the considerable excess of reducing agent necessary to stabilize the oxidation-sensitive dyeing baths, the wastewater may contain excess dithionite, which affects aerobic processes in wastewater treatment [10]. Recently many attempts have been made to replace the environmentally unfavorable sodium dithionite by ecologically more attractive alternatives. Investigations were focused on the replacement of sodium dithionite by an organic reducing agent (i.e.  $\alpha$ -hydroxyketones) of which the oxidation products are biodegradable or the use of ultrasound to accelerate the vating procedure and increase the conversion.

Conventional biochemical oxidative treatment of waste water containing azo dyes are often result in colored water unfit for reuse, while other methods such as coagulation, absorption, chemical oxidation, reverse osmosis, ultra filtration, photodecomposition etc., alone or in combination are found to be ineffectual due to their cost, regeneration or reusability and secondary pollution [1]. Chemicals such as hypochlorite, ozone and hydrogen peroxide in the absence and in the presence of UV light and hydrogen peroxide with ferrous ions, have been used for pretreatment of dye-bearing waste water [1,11-15]. Traditional methods [14-17] for dealing with textile wastewater effluents involve various combinations of biological, physical and chemical methods. These are becoming, troublesome because of the large variability of the composition of the textile wastewaters. The treatment of textile wastewater from a large dyeing and finishing mill by a continuous process of combined chemical coagulation, electrochemical oxidation, and activated sludge treatment has been investigated [18-20].

Electrochemistry would be an elegant way to reduce dye molecules, because it minimizes the consumption of chemicals [10]. The removal of undesirable organic or dyestuff impurities through electrochemical processes is based on the selection of suitable electrodes and potential/current conditions. The wastewater treatment by indirect electrochemical reduction has also been investigated [18].

In recent years, electrochemical reduction/oxidation has been shown to be a promising technique for wastewater treatment due to its promising technique and its effectiveness and also ease of operation. Electrolysis can be used for partial or total degradation of toxic and refractory organic substances. Many organic compounds in aqueous solution can be cathodically reduced by direct electron action or by hydrogen atom transfer. The reduction process can lead ultimately to carbon dioxide, nitrogen and water

through successive reactions, each of which has several steps, mass transport and direct or indirect adsorption at the electrode surface [19-20].

Textile wastewater from a reactive azo dyeing and finishing process for cellulose fibers was treated by an electrochemical oxidation method using Ti/Pt as the anode and stainless steel 304 as cathode [16,21]. The strong oxidizing potential of the chemicals produced when the wastewater was passed through the electro catalytic cell resulted in the oxidation of organic pollutants to carbon dioxide and water.

In the present paper, as a simple case the electrochemical decolorization and COD reduction of a DAB was carried out by using graphite, tin and lead as cathode and platinum as anode. The percent decolorization based on the absorption spectral data, and the percent COD removal by analytical methods have been studied at various possible current densities, concentration of sulphuric acid, dye concentration on different electrodes. A commensurate mechanism for the decomposition of the dye has been discussed.

### MATERIALS AND METHODS

The azo dye DAB was prepared by the procedure given elsewhere [22].  $K_2Cr_2O_7$ ,  $HgCl_2$ ,  $AgSO_4$ , and  $H_2SO_4$  were of analytical grade and procured from s.d. fine chemicals Mumbai, India and were used as such for the experiments. The solutions were prepared with doubly distilled water. The effluent was dilute sulphuric acid with known amount of DAB (0.005g to 0.03 g 100 mL). The strength of sulphuric acid for the electrolysis was ranging from 1 to 10% (v/v). The electrolysis was carried out in an H type cell of 150ml capacity. The anode and cathode electrodes were in the respective compartments. The electrodes were separated by placing a porcelain frit at the mid point of H cell. The platinum metal having an exposed area of  $1\text{ cm}^2$  was used as auxiliary electrode i.e. anode. Sulphuric acid of 1 to 10% (v/v) is used as anodic electrolyte. The working electrode was either lead, copper or graphite and was placed in cathode compartment. The exposed area of the cathode was  $1\text{ cm}^2$  and the surface was abraded with different grades of emery papers. The polished coupons were degreased with trichloroethylene vapors followed by water wash before each use. The SCE was used as reference electrode and kept in the cathode compartment such that the tip of the bend portion was close to the exposed area of working electrode.

The macroscale electrolytic degradation was performed under galvanostatic condition with Galvanostat PS-618, Chemi link system, Mumbai, India. The orange red coloured solution was gradually disappeared during electrolysis and the progress of degradation was confirmed by recording the UV-VIS spectrum of the reaction mixture for different interval of time. The decrease in dye concentration of the reaction mixture was also confirmed by the decrease of COD value with time of electrolysis.

The UV-VIS spectrum of reaction mixture was recorded with Shimadzu UV-1650PC spectrophotometer. The COD values were determined by standard methods given elsewhere [1].

The percent decolorization (eq.1) and percent COD reduction (eq.2) are presented in Table 1.

$$\% \text{ Decolorization} = \frac{[(OD)_B - (OD)_A]}{(OD)_B} \times 100 \quad (1)$$

$$\% \text{ COD reduction} = \frac{[(COD)_B - (COD)_A]}{(COD)_B} \times 100 \quad (2)$$

where  $(OD)_B$  and  $(OD)_A$  are the absorbance at 495 nm, and  $(COD)_B$  and  $(COD)_A$  are the chemical oxygen demand of the pre-and post- treated effluent respectively.

**Table 1.** UV-VIS spectral data of representative electrolytic reactions

Time (min)	Absorbance (320nm)	Absorbance (495nm)
0	3.982	2.341
30	3.836	2.194
60	3.787	1.967
90	3.511	1.837
120	3.170	1.463
150	1.869	0.894
180	0.358	0.130
210	0.244	0.098
240	0.179	0.065

## RESULTS AND DISCUSSION

To investigate the effects of current density, electrical energy consumption, acid strength, nature of cathode material, initial dye concentration, the COD removal efficiencies of refractory pollutants in electrolysis were compared. The parameter at which maximum COD removal efficiency achieved was taken as optimum.

**Decolorization pathway:** Azo dyes are synthetic organic colorants, they consist of a functional group possessing two doubly bonded nitrogens (-N=N-) attached to a trivalent ( $sp^2$ ) carbon atom of aromatic or heterocyclic nucleus on one side and an unsaturated molecule of the carbocyclic, heterocyclic or aliphatic type on the other side. The chromophoric nature of these dye effluent is due to the electronic transition between the nonbonding electrons of N atom of the azo group and the  $\pi$  molecular orbital energy levels of conjugated systems attached to it. Partial or complete cleavage of -N=N- bond forming simple amines results in the decolorization of the effluent, which on prolonged electrolysis degraded to molecular  $N_2$ . Quite essentially the chemical oxygen demand (COD) of a dye effluent is the requirement of total oxidizing power able to annihilate the dye molecule and the organics. In the process of COD reduction, the effluent may also be reduced in color and hence these methods are preferred. The % decolorization of DAB with time of electrolysis is given in Table 2.

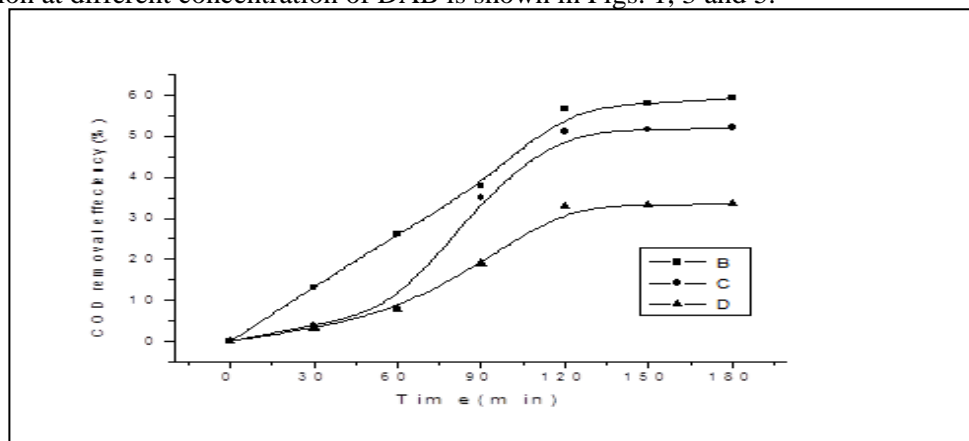
**Table 2 .** (%) Decolorization of DAB with time of electrolysis

Cathode = Lead,  $cd = 0.15Acm^{-2}$ (1080C), Temp = 303K, Dye concn = 0.01%, Acid conc.=5%

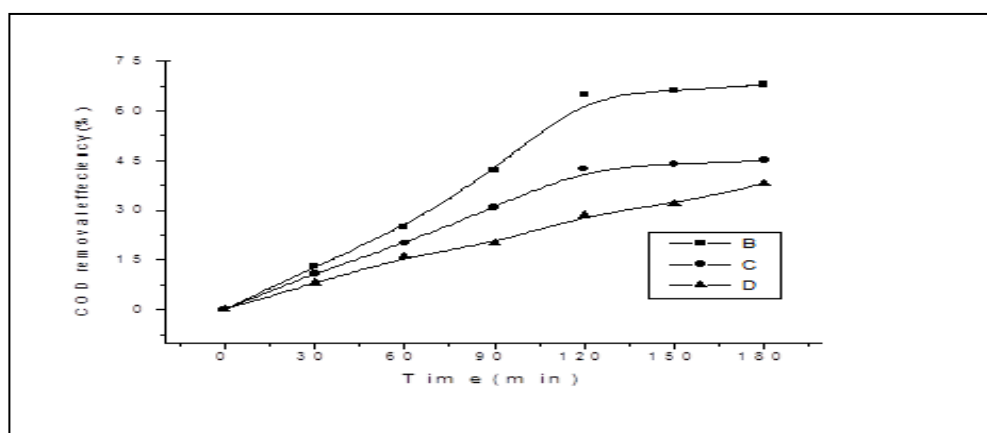
Time of Electrolysis (min)	% Decolorization
30	6
60	15
90	21
120	37
150	61
180	94
210	95
240	97.2

**Effect of cathode material:** Electro reductive degradation was carried out on Pb, Cu and graphite electrodes. Electrolysis was carried out in 1% sulphuric acid containing 0.01% of DAB by applying a constant current density of  $0.15Acm^{-2}$  (1080C). The decolorization of the effluent and COD removal efficiency was determined on each electrode at different time of electrolysis. The decolorization was found to be more effective on lead cathode in which COD removal efficiency was 71% and it was 67 on copper

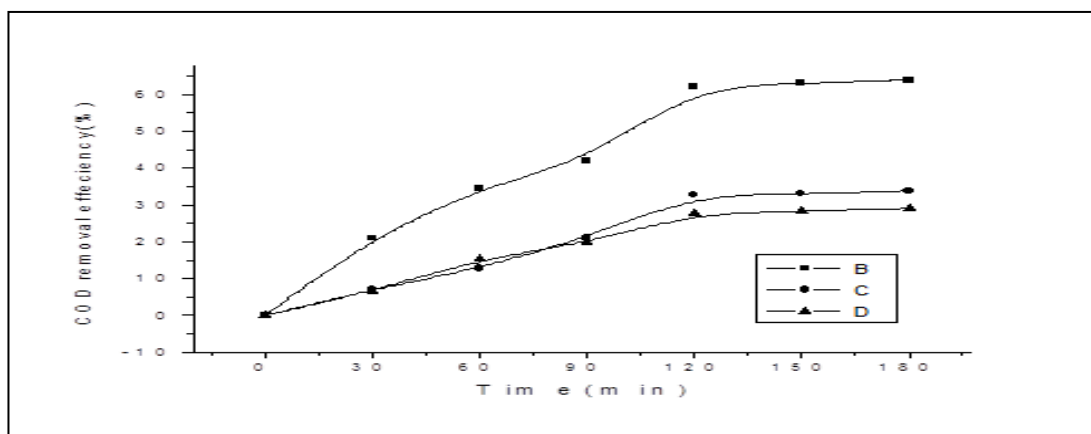
and 68 on graphite electrode. COD removal efficiency was found to be almost constant after 2 h of electrolysis on all the three electrodes so that the optimum time of electrolysis was fixed at 2 h. The variation of COD removal efficiency on each electrode at a constant current density of  $0.15 \text{ Acm}^{-2}$  (1080C) in 1% acid solution at different concentration of DAB is shown in Figs. 1, 3 and 5.



**Figure 1:** Variation of COD removal efficiency values with time of electrolysis  
Cathode = Lead, Acid concentration = 1% (v/v), Temperature= 303K, B= 0.01%, C=0.02%, D=0.03%



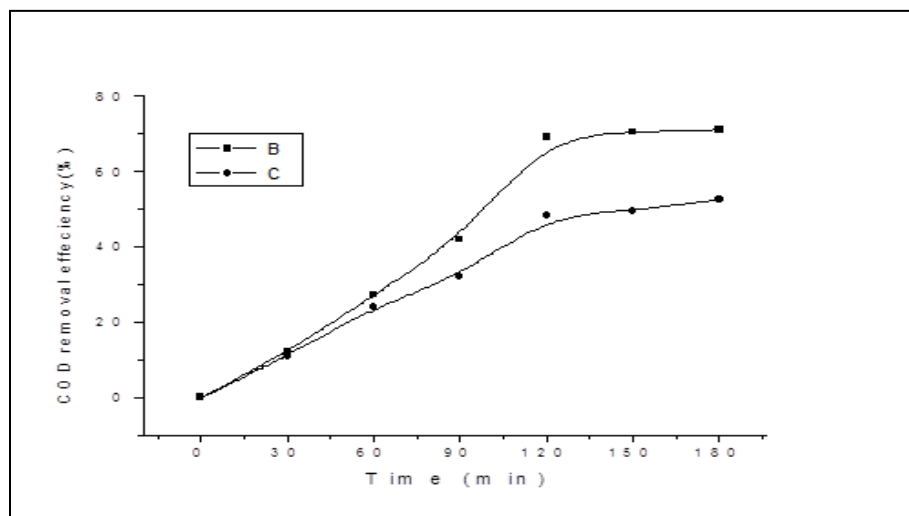
**Figure 3:** Variation of COD removal efficiency values with time of electrolysis  
Cathode = Graphite, Acid concentration = 1% (v/v), Temperature= 303K, B= 0.01 %, C=0.02 %, D=0.03%



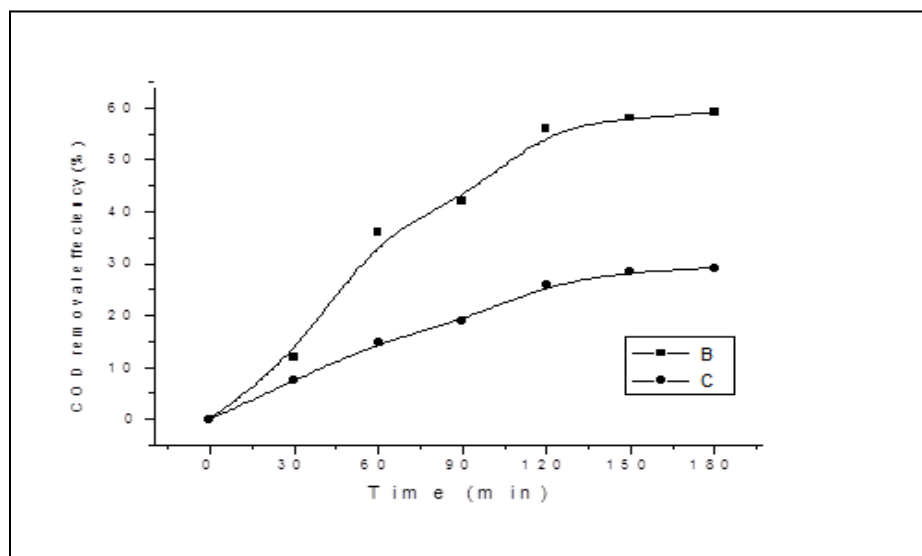
**Figure 5:** Variation of COD removal efficiency values with time of electrolysis  
Cathode = Copper, Acid concentration = 1% (v/v), Temperature= 303K, B= 0.01 %, C=0.02 %, D=0.03%

The higher value of COD removal efficiency on lead cathode was due to high hydrogen overvoltage in which active form of hydrogen is easily available for the reductive cleavage of  $-N=N-$  bond.

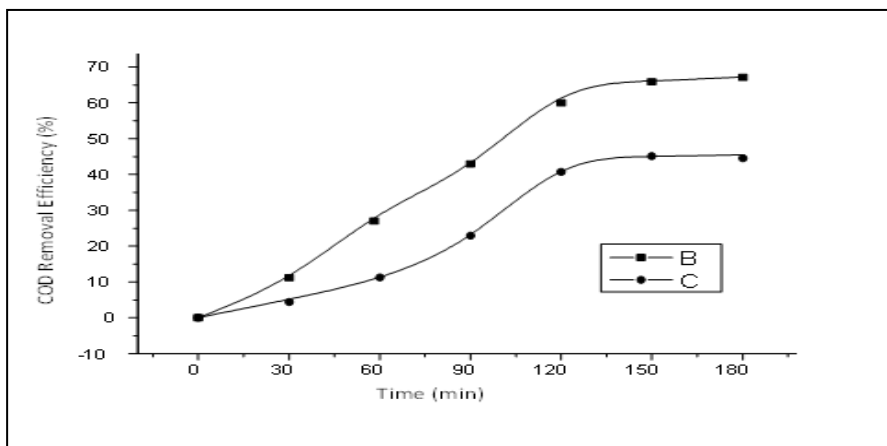
**Effect of acid strength:** To study the effect of acid concentration on the cathodic degradation of  $-N=N-$  bond, electrolysis was carried out in different concentration of sulphuric acid varying from 1% to 10% on all the three electrodes at a constant current density of  $0.15 \text{ Acm}^{-2}$  (1080C). COD removal efficiency was found to be high at 5% of acid strength on all the three electrodes. The value of COD removal efficiency was decreased with increasing acid strength above 5% which may be attributed to increase of hydrogen evolution which hinders the reduction of  $-N=N-$  bond. So that the optimum concentration of sulphuric acid in the reaction mixture was fixed at 5% (v/v). Variation of COD removal efficiency with acid strength on all the three electrodes at a constant current density of  $0.15 \text{ Acm}^{-2}$  (1080C) and at 0.01% of DAB concentration is shown in Fig. 2, 4 and 6.



**Figure 2:** Variation of COD removal efficiency values with time of electrolysis Cathode=Lead, Dye concentration = 0.01 %, B= 5% H<sub>2</sub>SO<sub>4</sub>, C=10% H<sub>2</sub>SO<sub>4</sub>



**Figure 4:** Variation of COD removal efficiency values with time of electrolysis Cathode=Graphite, Dye concentration = 0.01 %, B= 5% H<sub>2</sub>SO<sub>4</sub>, C=10% H<sub>2</sub>SO<sub>4</sub>



**Figure 6:** Variation of COD removal efficiency values with time of electrolysis  
Cathode=Copper, Dye concentration = 0.01 %, B= 5% H<sub>2</sub>SO<sub>4</sub>, C=10% H<sub>2</sub>SO<sub>4</sub>

**Effect of Dye concentration:** To study the effect of dye concentration on the % COD removal efficiency, electrolysis was carried out at different concentration of dye (0.005 to 0.03% w/v) at an acid concentration of 1% and a current density of 0.15 A cm<sup>-2</sup> (1080C). The % COD removal efficiency was high up to a concentration of 0.01%. Above this concentration the removal efficiency was decreased indicating the incomplete removal of dye at the given set of conditions. To achieve complete COD removal efficiency it requires high current density and prolonged time of electrolysis. Variation of % COD removal efficiency with dye concentration on each electrode is shown in figs. 1,3 and 5.

**Effect of Current Density and Electrical Energy Consumption:** To study the effect of Current density and the major operating cost in the electrochemical degradation, electrical energy consumption was calculated. The electrical energy consumption (E) required for decomposition of DAB of 0.01% (w/v) concentration at various current density was calculated interms of kWhm<sup>-3</sup> according to the relation, [23].

$$E = \frac{VI t_E}{V_S} \times 10^{-3}$$

Where V is the voltage applied, I is the current density, t<sub>E</sub> is the time of electrolysis and V<sub>S</sub> is the volume of the solution taken. According to the above relation, the electrical energy consumption for the above set of condition was found to be 2.592 kWhm<sup>-3</sup>, at current density of 0.15Acm<sup>-2</sup> and at higher current density, the energy consumption was increased so the optimum current density of 0.15Acm<sup>-2</sup> (1080C) was fixed.

## APPLICATIONS

The method developed in the present work gives an idea that how effluents containing azo dyes can be treated by electrochemical method. The work focused on the influence of various electrochemical parameters on treatment efficiency. Also, the measurement of COD, with respect to time of electrolysis shows how the effluents concentration is decreasing with respect to time. So overall work open ups a new methodology to treat the azo dye effluents in industry very effectively.

## CONCLUSIONS

Electrochemical reduction gave good efficiency values for the destruction of azo dye DAB. The COD of DAB was decreased significantly by an electrochemical reduction process. It was found that increase in the concentration of DAB in the effluent decreases the COD removal efficiency. COD removal efficiency was high at 5% of acid strength on all the three electrodes. The value of COD removal efficiency was high on

lead cathode and it reached 71%, whereas on copper it was 67 and on graphite it was 68. The % decolorization was 97.2% on lead cathode.

The UV-VIS spectroscopic studies of DAB in dilute sulphuric acid reveal the complete cleavage of  $-N=N-$  bond in the DAB molecule and the spectrum is shown in Fig 7.

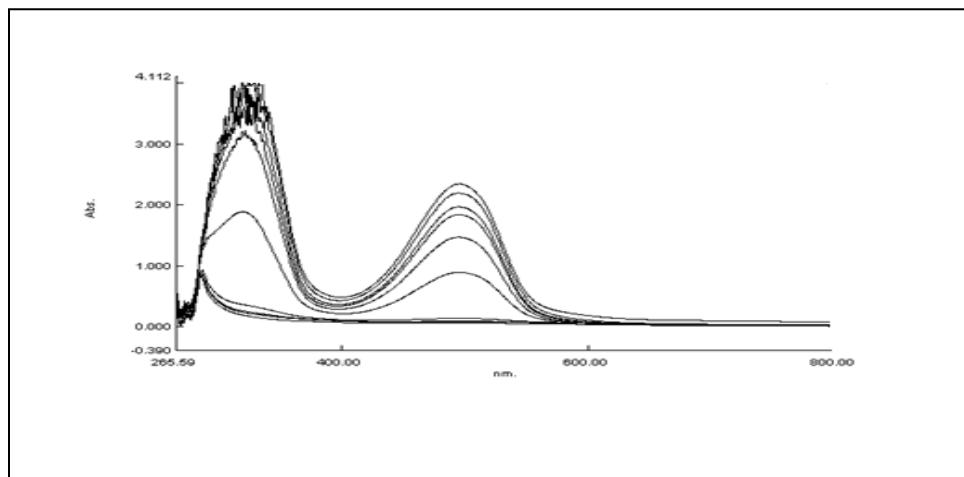


Figure 7: UV-VIS spectrum of reaction mixture

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