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Electrochemical degradation of p-aminobenzoic acid β-naphthol azo dye in alkaline solution

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The potentiostatic as well as galvanostatic electrochemical degradation with copper (Cu) as working electrode for p-aminobenzoic acid β-naphthol azo dye in alkaline solution was examined. The electrolysis was carried out in undivided cell containing Cu as cathode, platinum (Pt) as anode and calomel as reference electrode. The UV-Visible absorbance and chemical oxygen demand (COD) values were used to monitor the electrochemical treatment process. Normalized absorbancy values were calculated. The electrochemical behavior of the dye was studied using cyclic voltammetry. The degradation mechanism was explained.

Key words: Galvanostatic, potentiostatic, copper, degradation, normalized absorbancy.

INTRODUCTION

The azo dyes find extensive applications and it is estimated roughly that 70% (Edgar et al., 2011) of the existing commercial dyes are azo class of compounds and they usually impart intense colour to water. The main user of these dyes is the textile industry, which generates large volumes of wastewater containing not only dyes of appreciable concentration, but also possesses surfactants, suspended solids and organic matter. Furthermore, the azo dyes are resistant to oxidation and reduction conditions, light exposure as well as biodegradation, and hence, they are stable in the environment. Some of the commercial azo dyes contain chromium (Cr) atoms which are highly toxic and carcinogenic; therefore, they pose greater threat to the environment (Peiqiang et al., 2012). In addition, the presence of small amount of dye in water produces highly visible colour which affects the water transparency and finally the gas solubility of water bodies.

Many treatment methods, such as biological treatment (Chatezisymeon et al., 2009), chemical precipitation, adsorption by activated carbon (Konstantinos, 2010), photo catalytic oxidation (Yousuf et al., 2010), ozonation (Ahmed et al., 2010), Fenton's reaction and electrochemical methods (Yan yang chu et al., 2010) are cited in the literature to degrade the dyes of effluents.

The electrochemical method is simple and it requires significantly less area than conventional biological treatment processes (Zainal et al., 2008) and is successfully applied in the treatment of coloured effluents. Electrochemical methods, such as electro oxidation, electro coagulation and electro flotation have been widely used in wastewater treatment, and several applications have been reviewed elsewhere. Anodes made of oxides of titanium (Ti), Ir and lead (Pb), graphite, platinum (Pt), several Ti-based alloys and more recently, boron doped diamond electrodes in the presence of a supporting electrolyte have been employed for the decontamination of various industrial effluents (Chatzisymeon, 2006; Chen, 2004). Textile wastewater, containing a high concentration of Cl⁻ ions was treated by an electrochemical method using Ti/RuO_2, Ti/Pt and Ti/Pt/Ir electrodes and was proved to be very effective in direct or indirect oxidation of textile wastewater (Abu Ghalwa and Abdel-Latif, 2005). Vlyssides et al. (1999) used Ti/Pt as anode and stainless steel 304 as cathode for the treatment of reactive azo dye. Chen et al. (2003) studied Orange II and 16 reactive dye mineralization with Ti/B-Diamond and found out that the electrode is much

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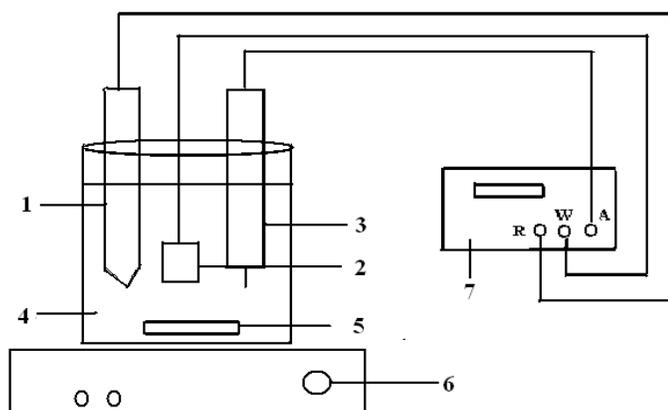
Figure 1. Schematic representation of electrochemical set up. (1) Saturated calomel electrode (reference electrode), (2) Copper electrode (working electrode), (3) Platinum electrode (auxiliary electrode), (4) Dye solution, (5) Magnetic bit, (6) Magnetic stirrer and (7) Potentiostat/Galvanostat.

better than $Ti/Sb_2O_5/SnO_2$. In all the aforementioned work, a galvanostatic technique was employed for electrochemical degradation.

Fan et al. (2008, 2004) investigated electrochemical degradation of aqueous solution of amaranth azo dye under potentiostatic condition. Three different electrode materials: aluminium-, copper- and iron-zinc alloy were tested in the potential range -1.0 to -2.5 V by Ceron-Rivera et al. (2004) taking basic yellow 28 and reactive black 5 as the model dyes.

The main significance of this study is that in earlier degradation studies, majority of the researchers used galvanostatic condition, and no work was done on degradation studies using potentiostatic condition. In the present investigation, both conditions are employed and degradation efficiency is compared. The study gives the superior of galvanostatic method over potentiostatic condition in the degradation process. In the present work, the degradation of dye using copper foil as cathode in alkaline solution was investigated. The potentiostatic as well as galvanostatic techniques were adopted. The degradation mechanism was given.

MATERIALS AND METHODS

Alkaline solution of p-amino benzoic acid β-naphthol azo dye was used as a model compound and was synthesized by diazotization reaction (compound number-MolPort-001-969-144) in the laboratory using analytical grade reagents and chemicals. The surface of Cu and Pt electrodes were activated by immersing the in 5% HNO_3 for few seconds and washing them thoroughly with double distilled water, and they were used for the experiments.

Experimental facility

A conventional three electrode cell with copper (Cu) plate as

working electrode (area, 6.02 cm^2), platinum (Pt) foil as counter electrode and saturated calomel electrode (SCE) as reference electrode was used in this study. The experimental set up is as shown in Figure 1. All experiments were conducted under stirred condition using magnetic stirrer. A potentiostat/galvanostat (Model PS-618 Chemilink Systems, India) was used as direct current (DC) source for electrolysis. The rate of decolourization was monitored through measured values of absorbance of dye solution by UV-Vis spectrophotometer (UV-1650 PC SHIMADZU). The cyclic voltammetry measurements were done at room temperature with a conventional three electrode cell using a computer controlled electrochemical work station (CH Instruments 660C, USA).

Determination of chemical oxygen demand (COD)

The degradation was monitored by COD measurement (Open reflux method) (Clesceri et al., 1998), based on Formula 1:

$$COD(O_2mg/L) = \frac{V_0 - V_1 \times N \times 8 \times 1000}{V_2}$$

(1)

where N is the concentration and V_1 is the volume of $(NH_4)_2Fe(SO_4)_2$ titrant, V_0 is the volume of $(NH_4)_2Fe(SO_4)_2$ titrant used in the blank and V_2 is the volume of water sample. Test samples were collected at every 30 min time interval and COD was measured using Open reflux method. The calculated COD values decrease continuously during the process of degradation. Finally, the percentage of COD removal is calculated using the Formula 3.

Experimental conditions

The initial concentration of dye solution in each experiment was 50 mg/L in 0.05 M NaOH solution. The initial pH of the dye solution was 12. The electrolysis was carried out under potentiostatic and galvanostatic conditions. Cu plate was used as cathode. For potentiostatic condition, the potential range of -0.8 to -2.5 V was used. Similarly, in galvanostatic condition, the range of the current density used was 16.6 to 67.0 mA cm^{-2}. The electrolysis was carried out at 27 ± 2°C under stirred condition with electrolysis time of 1.5 h.

The percentage of colour removal was calculated using the Equation 2:

$$X_{Colour} = \frac{A_o - A_t}{A_o} \times 100$$

(2)

where A_t and A_o are the absorbency values at 455 nm at time t and 0, respectively.

The percentage of COD removal ratio was calculated using Equation 3:

$$X_{COD} = \frac{COD_o - COD_t}{COD_o} \times 100$$

(3)

where COD_o and COD_t are the COD values before and after treatment, respectively.

The ratios of normalized absorbency values (Fan et al., 2008) were calculated with Equation 4:

Table 1. The normalized absorbency for decolourization of dye under potentiostatic and galvanostatic conditions.

Potentiostatic condition [Potential (V)]	Normalized absorbency at 280 nm $Z\left(\frac{455}{280}\right)$	Normalized absorbency at 340 nm $Z\left(\frac{455}{340}\right)$	Galvanostatic condition [Current density (mA/cm2)]	Normalized absorbency at 280 nm $Z\left(\frac{455}{280}\right)$	Normalized absorbency at 340 nm $Z\left(\frac{455}{340}\right)$
-0.8	1.0000	1.0000	16	1.0000	1.0000
-2.0	0.3375	0.5200	17	0.3375	0.5000
-2.2	0.4086	0.5600	25	0.5184	0.8000
-2.3	0.2625	0.6250	33	0.3780	0.5000
-2.4	0.4440	0.7700	42	0.3960	0.6100
-2.5	0.0000	0.0000	50	0.0000	0.0000
-	-	-	67	0.0000	0.0000

$$Z\left(\frac{455}{X}\right) = \frac{\frac{A^{I}_{455}}{A_{455}}}{\frac{A^{I}_{X}}{A_{X}}} \qquad (4)$$

where Z (455/X) is the ratio of normalized absorbency values, x is 340 or 280 nm. A_{455}, A_x and A^{I}_{455}, A^{I}_x are the absorbency values of dye solution before and after treatment, respectively.

RESULTS

Normalized absorbency values

Based on the ratios of the normalized absorbency values, the mechanisms of the decolourization can be estimated. If the ratios of the normalized absorbency values were equal to 1.0, then the dye structure was kept intact. Otherwise the dye structure was destroyed and the electrochemical reaction took place (Fan et al., 2008). Table 1 shows the results of the normalized absorbency values for decolourization of dye under potentiostatic and galvanostatic conditions. The ratio was equal to 1.0 at -0.8V and at 16 mA/cm^2 implying no chemical reaction under these conditions. The electrolysis in the potential range of -2.0 to -2.5V and the current above 16 mA/cm^2, results in the Z values which were lower than 1.0 and hence the electrochemical reaction occurs leading to decolourization. This help to select suitable potential and current range for degradation experiments.

Cyclic voltammetric (CV) studies

To understand the electrochemical behavior of dye, the CV studies were carried out using solution with and without dye taking Cu wire as working electrode (Figure 2). The potential scan used for the study was –1.1 to -0.40 V. The blank and dye solutions, both showed single anodic peak approximately at -0.91 Volts and also both solutions showed two cathodic peaks, respectively at approximately -0.3 and -0.8 V. That is, the CV of both solutions was similar. This indicates that the dye is electrochemically inactive and its decolourization is due to indirect electrochemical reactions.

Electrochemical degradation under potentiostatic condition

The electrolysis of dye solution was carried out for 120 min at room temperature. The decolourization was monitored by recording UV-Visible spectra of solution at every 30 min during electrolysis. In order to see the effect of cell voltage on decolourization process, the electrolysis was performed under cell potentials of -2.0, -2.2, -2.3, -2.4 and -2.5 V. The plot of the colour removal efficiency with time under each applied voltage is as shown in Figure 3. Initially, the colour removal efficiency was 22.0% at -2.0 V. But the decolourization of dye increases with increase in voltage and reaches 100% at -2.5 V.

COD removal

The effect of applied potentials on COD removal ratio is as shown in Figure 3. The COD removal ratio of 19.2% was noticed at cell potential of -2.0 V. This COD removal efficiency gradually increased to 55% (maximum) as electrolysis cell potential rises from -2.0 to -2.5 V. Further rise in cell potential after -2.5 V results in no improvement on COD removal efficiency. Also, at this cell potential, the colour removal efficiency was 100% inferring that the chromophoric group of the dye gets destroyed to give colourless solution, but the COD results indicated partial mineralization. This is due to the over potential that exist at anode which may be equal to the decomposition potential of the dye which finally results in maximum COD removal efficiency and 100% colour removal efficiency.

Electrochemical degradation under galvanostatic condition

The influence of electrolysis time on colour removal
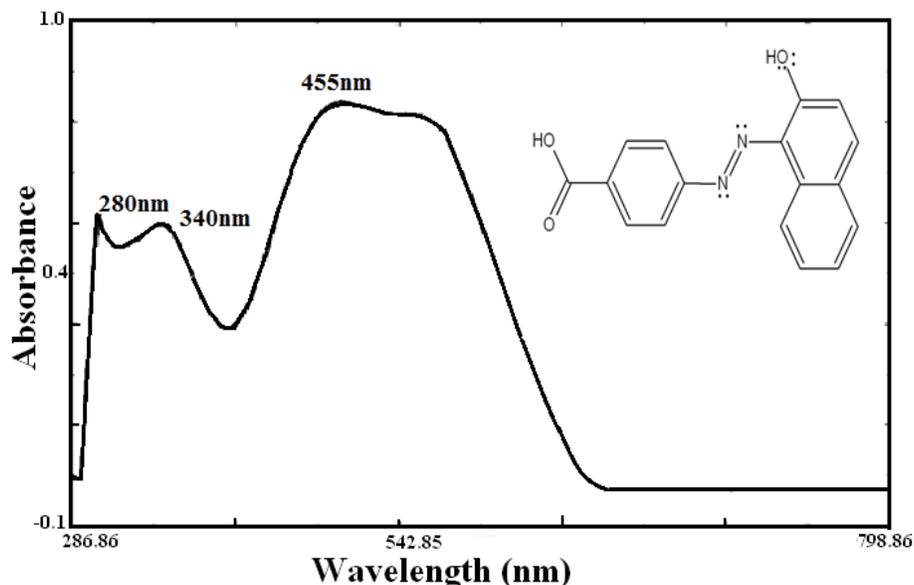
Figure 2. UV-Vis spectrum of initial dye solution and molecular structure of the dye. λ_{max} : 455, 340 and 280 nm.
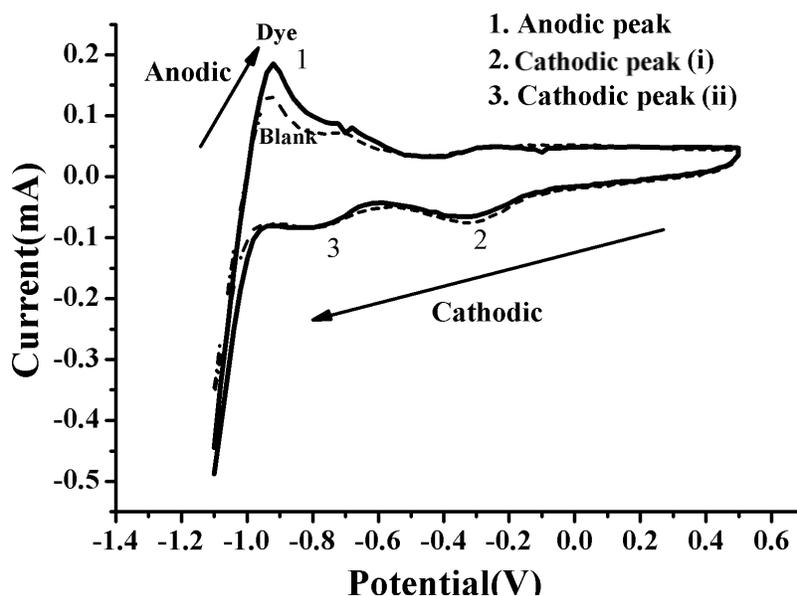
Figure 3. Cyclic voltammograms of p-amino benzoic acid β-naphthol azo dye on Cu wire electrode at scan rate of 20 m versus dye concentration of 50 mg/L and supporting electrolyte concentration of 0.05 M.

efficiency at different current densities (17, 25, 33, 42, 50 and 67 mA/cm^2) is as shown in Figure 4a. The colour removal efficiency increases with current densities and reaches 100% at 50 mA/cm^2, whereas COD removal efficiency was 90%. Further rise in current densities results in no change in COD removal efficiencies (Figure 4b).

DISCUSSION

The structure and UV spectrum are as shown in Figure 5a and b. The dye, before electrolysis under galvanostatic condition shows the absorption with higher intensity in the range 455 to 506 nm. The intensity in this range decreases on electrolysis and reaches zero
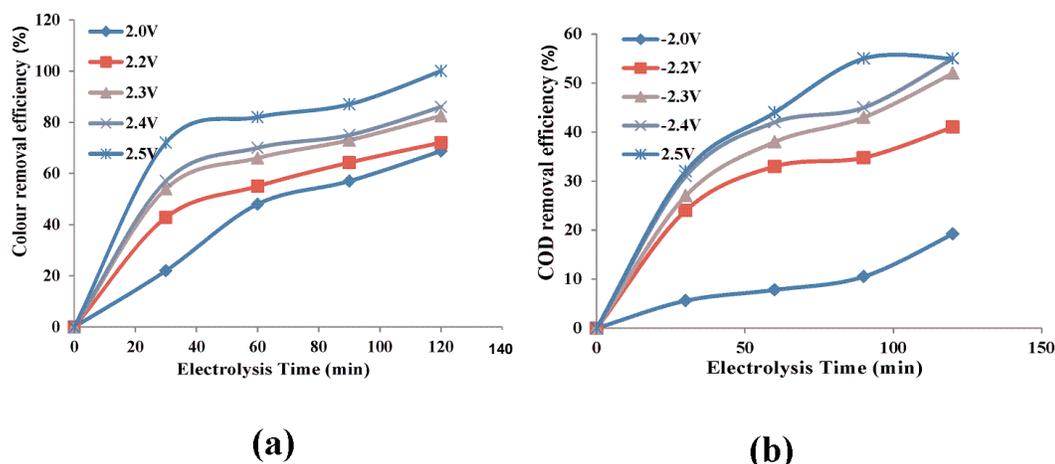
Figure 4. (a) Variation of colour removal efficiency with electrolysis time at different potentials. (b) Plot of COD removal efficiency versus electrolysis time at different potentials.
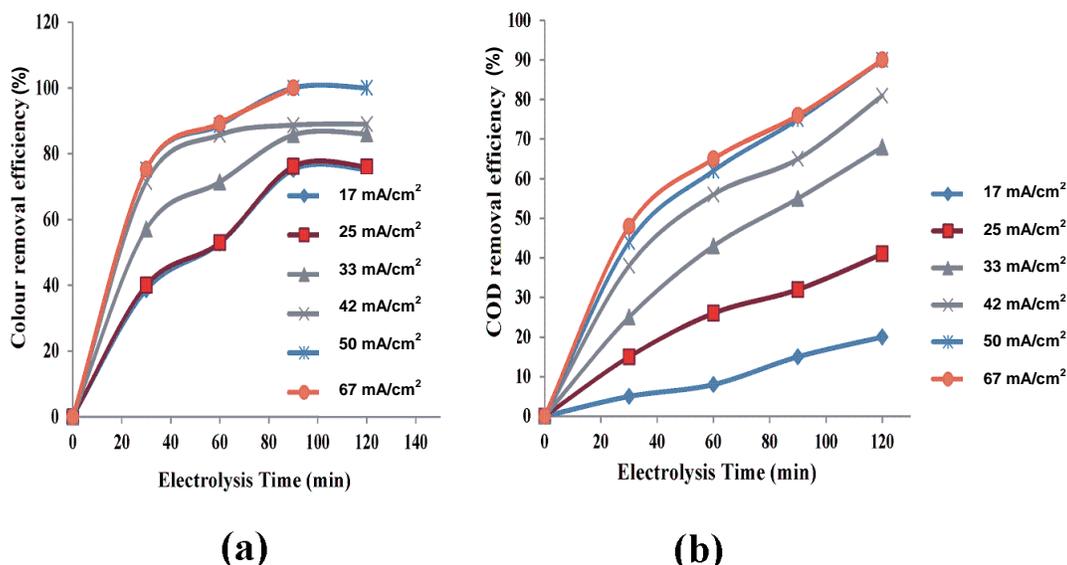
Figure 5. (a) Variation of colour removal efficiency with electrolysis time at different current densities. (b) Plot of COD removal efficiency versus electrolysis time at different current densities.

indicating complete destruction of -N=N- group which is responsible for imparting colour to the dye (Figure 6). Hence, zero intensity of absorbance of dye contaminated water after electrolysis in the UV-Vis spectra indicates 100% colour removal efficiency.

The peak at 340 nm corresponds to naphthalene ring of the dye. The gradual decrease of intensity at this peak, during electrolysis indicates the degradation of naphthalene ring (Hanna et al., 2010). This is also evidenced by COD removal efficiency of 90%. The UV spectra show the slight intensity at this wavelength even after electrolysis indicating the existence of small amount of few organic compounds. Furthermore, the peaks in

UV-Visible spectra recorded for electrolyzed solution at different current densities indicated that higher percentage of degradation (80%) was achieved at lower current densities. Whereas, experiments at higher current densities contributes only 10% to the total COD removal efficiency of 90%.

The dye solution after electrolysis under potentiostatic condition showed UV-Vis absorbance (455 to 506 nm) (Figure 7) which is similar to the results obtained in galvanostatic condition. Here also, the complete decolourization was noticed, whereas the peak intensity at 340 nm gradually reduced and reaches a limiting value which is higher as compared to galvanostatic condition.
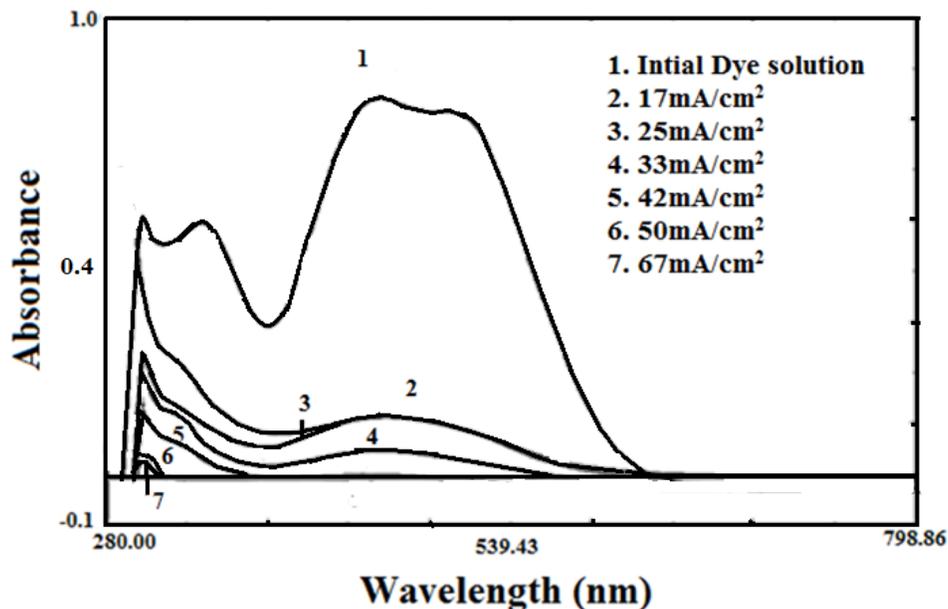
Figure 6. UV-Visible spectra of dye solution at different potentials.
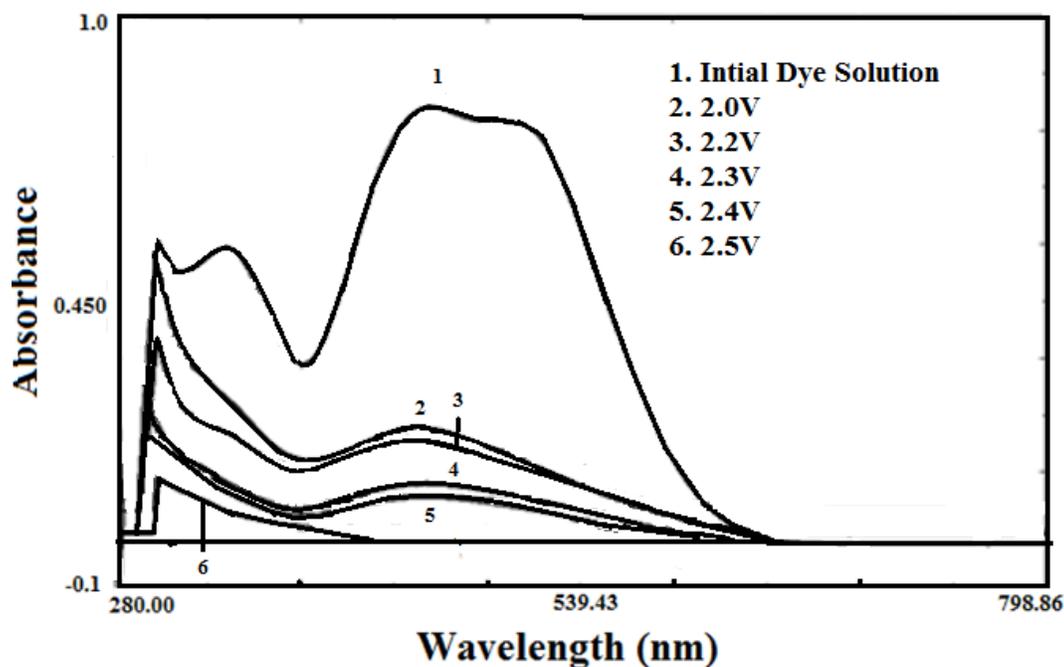
Figure 7. UV-Vis spectra for dye solution at different current densities.

This implies considerable amount of organic compounds present in the electrolyzed solution. In addition, the COD removal efficiency is 55% and further supports the presence of considerable amount of organic compounds. The results of treatment under galvanostatic and potentiostatic conditions revealed that the former gives higher   COD removal efficiency than the latter. The

reason is obvious that under galvanostatic condition, the current kept constant and the potential of the electrode varies resulting in different electrochemical reactions. The various organic products formed during electrolysis may possess different decomposition potentials. When the electrode reaches that particular potential, the corresponding organic compound undergo electrochemical

reaction and hence breakage of the molecule. During this, the concentration of the organic molecule reduced causing rise in the potential of the electrode. As a result, the other compound having corresponding potential undergoes electrode reaction. Also, the compounds which are inert in case, to electrochemical reaction, formed during treatment process undergo decomposition or breakage from the radicals which are generated at the anode (Henning and Hammerich, 2000).

In the potentiostatic condition, the potential remains constant which makes the alteration in the amount of current flow, that is, generally decreases. In electrochemical kinetics, the magnitude of current gives the rate of reaction at the electrode, hence decrease of current in potentiostatic condition implies lower rate of degradation. As a result, the efficiency of the process decreased. In the present case, the efficiency is lower as compared to galvanostatic condition. This study reveals that the galvanostatic condition is superior for the degradation of dyes.

In both conditions, the slopes of the plots percentage colour, COD removal versus time increase with current density as well as potential. But, the value of the slope is higher in galvanostatic condition. Hence, the rate of reaction is higher in the case of galvanostatic condition over potentiostatic condition.

To test the role of anode and the cathode during electro degradation process, the experiments were conducted in a divided cell. Both anode and cathode compartments solutions were visually observed, and also, the COD removal efficiency was calculated. It was noticed that only anode compartment solution which was intense coloured get decolourized, whereas in the cathode compartment, there was no change in the intensity of the colour. Also, the COD removal efficiency values indicated its change in solution of anodic comportment and no change in cathodic compartment. The same experimental observations were noticed even after changing the counter electrode Pt (anode) as working electrode.

This suggests that the reactions occurring at the anode are responsible for decolourization as well as degradation of organic compounds. Furthermore, the cyclic voltammetric studies of dye solution indicated that the dye is electrochemically inactive. This implies that degradation occurs through indirect means of oxidation. This oxidation of organic compounds could occur through a mechanism where the first step is the oxidation of water molecules at the electrode surface [M]. There is formation of M [OH$^\cdot$] radicals according to the fallowing equation (Awad and Abo Galwa, 2005).

$$M+H_2O \rightarrow M[OH^\cdot]+H^++e^- \tag{5}$$
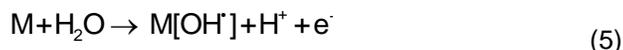
Thus, in situ electro generated hydroxyl radicals on metal surface oxidize the organic compound to CO_2 and H_2O:

$$M[OH^\cdot]+R(Dye) \rightarrow M+mCO_2+nH_2O+H^++e^- \tag{6}$$
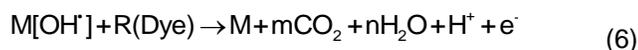
Also, there may be indirect oxidation in the liquid bulk which is mediated by the OH$^\cdot$ radicals generated during electrolysis.

$$H_2O+M \rightarrow M[OH^\cdot]+H^++e^- \tag{7}$$

$$M[OH^\cdot] \rightarrow M+OH^\cdot \tag{8}$$

$$OH^\cdot +R(Dye) \rightarrow RO+H^++e^- \tag{9}$$

$$RO+OH^\cdot \rightarrow CO_2+H_2O \tag{10}$$
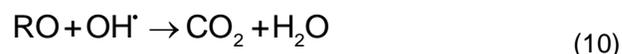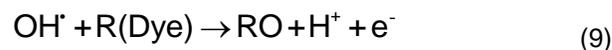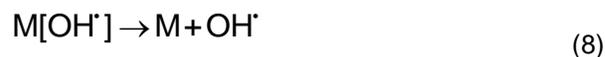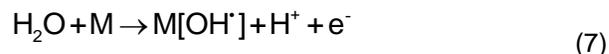
Therefore, oxidation of dye occurs through any one of the aforementioned reactions proposed or through the oxidation reactions.

Conclusions

The dye p-aminobenzoic acid β-naphthol was degraded successfully by two electrochemical conditions. The workable potential range, -2.0 to -2.5 V, and the current density greater than 16 mA/cm^2 were suitable for the degradation of dye. The cyclic voltammogram shows the electrochemical inactiveness of the dye. Both conditions gave 100% colour removal efficiency, whereas COD removal efficiency of 90% was achieved under galvanostatic condition. The degradation occurs at the anode through the generation of hydroxyl radicals. The degradation by galvanostatic condition was superior to potentiostatic condition for the p-aminobenzoic acid β-naphthol azo dye.

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