

Electrochemical treatment of pharmaceutical azo dye amaranth from waste water

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Abstract The electrochemical behavior of pharmaceutical azo dye amaranth has been investigated in distilled water and Britton–Robinson buffer. One well-defined irreversible cathodic peak is observed. This may be attributed to the reduction of the $-N=N-$ group. Calculation of the number of electrons transferred in the reduction process has been performed and a reduction mechanism proposed. Results indicate that the electrode process is diffusion controlled. The cathodic peak in the case of controlled potential electrolysis is found to reduce substantially with a decrease in color and absorbance. The reaction has first order kinetics with k value $5.75 \times 10^{-2} \text{ abs min}^{-1}$. The efficiency of different electrode materials (platinum and steel) for decolorisation is compared. Chemical oxygen demand (COD) decreases substantially from 2,680 to 96 ppm at platinum and to 142 ppm at steel. This translates to 97% COD removal at platinum and 95% at steel.

Keywords Electrochemical treatment · Amaranth · Azo dye · Industrial effluents · CV, COD

1 Introduction

Azo dyes continue to be a source of pollution from industrial processes which employ dyes to color paper,

plastics, foodstuffs, pharmaceutical products, and natural and artificial fibers [1, 2]. It is reported that approximately 5 tonnes of dye discharge from dye and coloration industries every year [3]. The release of such compounds into the environment is of great concern due to their toxicity, mutagenicity, carcinogenicity, and bio-transformation products [4–6]. Hence, much research has focused on methods of azo dye destruction. Many treatment processes have been investigated extensively to treat wastewaters such as chemical precipitation [7], adsorption [8], biological treatment [9], photocatalytic degradation [10, 11], electrocatalytic oxidation [12], ozonation [13], Fentons' reaction [14], and electrochemical methods [15–19]. Electrochemical techniques are an attractive methodology for the treatment of dye wastewaters. This technique has significant advantages viz., wide application, simple equipment, easy operation, lower temperature requirements, and no sludge formation [20–24].

Amaranth (Fig. 1) [trisodium salt of 1-(4-sulpho-1-naphthylazo)-2-naphthol-3, 6-disulphonic acid] is an acidic monoazo dye used as food and pharmaceutical colorant. Only a few analytical methods, such as square wave adsorptive stripping voltammetry (SWAdSV) and spectrophotometry are available for determination of amaranth in soft drink samples [25]. Degradation of amaranth from environmental samples has been studied on activated carbon fiber (ACF) electrodes [26, 27]. The amaranth azo dye has electroactive groups. However, its electrochemical behavior and treatment have not been investigated. Therefore, cyclic voltammetric and differential pulse polarographic studies have been undertaken in the present work for understanding the electrochemical behavior of amaranth. Results have been analyzed employing the criterion of complete decolorisation of the dye-containing solutions.

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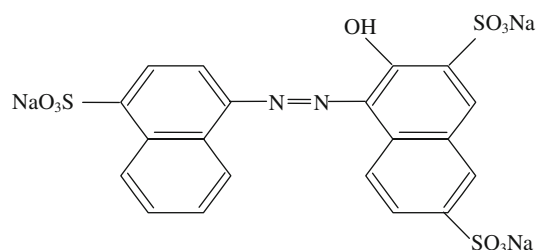


Fig. 1 Structure of amaranth

2 Experimental

2.1 Instrumentation

Cyclic voltammetric (CV) studies were carried out on an EG and G potentiostat (Princeton Applied Research) integrated with applied electrochemistry software. The working electrode potential was cycled between -1.2 and $+1.2$ V at different sweep rates (50 – $2,000$ mV s^{-1}). The electrochemical cell consisted of three electrodes (in close proximity) immersed in the solution to be electrolyzed. The voltammetric behavior was studied using platinum as working electrode, SCE as reference, and platinum wire as counter electrode. Controlled potential electrolysis was carried out using a BAS CV-27 cyclic voltammograph coupled to a digital electronic 2000 Omnigraph x–y/t recorder. The working electrodes used for controlled potential electrolysis (CPE) were platinum foil (3×3 cm^2) and steel foil (4.5×3.5 cm^2), Ag/AgCl as reference electrode and platinum wire as counter electrode.

Differential pulse polarographic (DPP) measurements were carried out on an Elico pulse polarograph model CL 90 connected with Polarocord recorder model LR-108. Triple distilled mercury was used for the DME. The capillary had a flow rate of 3.02 mg s^{-1} together with a drop time of 3 s. The pH measurements were made on a Hach digital EC-40 Benchtop pH/ISE meter. The absorption spectra of samples were recorded using an Elico SL I59 UV-Visible spectrophotometer. The chemical oxygen demand (COD) was determined using the open reflux method using COD digester apparatus (Spectralab 2015-S). The synthetic azo dye amaranth was obtained from Aldrich USA. All chemicals used were AR grade. Readymade silica gel G plate for TLC, having fine coating on alumina sheet, was obtained from E-Merck.

2.2 Reagents and materials

Stock solution of amaranth (2×10^{-3} M) was prepared in doubly distilled water. In order to evaluate the effect of varying pH, BR buffers in the pH range 2.5 – 12.0 were prepared as per a literature method [28]. The supporting

electrolyte was 1.0 M KCl. For the COD experiments reagents were prepared in accordance with standard methods (APHA, 1995) [29].

2.3 Procedure

The CV and DPP studies were carried out by mixing 1.0 mL of potassium chloride, 1.0 mL stock solution, and 8.0 mL of appropriate BR buffer/distilled water. Solutions of different concentrations were prepared. Dissolved oxygen was removed from the solution by passing nitrogen gas for about 15 min. The polarograms and cyclic voltammograms were then recorded. The redox behavior was studied at varying pH (2.5 – 12.0), concentrations and sweep rates (100 – $2,000$ mV s^{-1}). Controlled potential electrolysis of the dye solution was performed at slightly more negative potential than the peak potential of the respective peak. Absorbance of the solution was measured at different time intervals at 520 nm. The value of the rate constant k was calculated from the \log_{10} (absorbance) vs time plots. The number of electrons transferred was calculated from the decrease in current with time during electrolysis. Controlled potential coulometry was also carried out at different pH values. The progress of electrolysis was monitored by recording cyclic voltammograms at regular intervals of time. The end products of electrolysis were identified by TLC. For COD studies, the experiments were carried out as per standard methods.

2.4 Coulometry

For the coulometric determination of number of electrons “ n ” consumed in the reduction, a solution of depolarizer, potassium chloride, and buffer/distilled water was mixed in the same ratio as that for CV and DPP studies. The solution was de-aerated by passing nitrogen gas for 15 min and cyclic voltammograms were recorded at slightly more negative potential than the peak potential. With the progress of electrolysis the color of the solution gradually faded and finally a colorless solution was obtained. The number of electrons “ n ” transferred at the platinum electrode was determined from the formula $Q = nFN$.

3 Results and discussion

3.1 Cyclic voltammetric (CV) studies

The cyclic voltammogram of amaranth in distilled water (2×10^{-4} M) exhibits reduction peak at -0.872 V and corresponding oxidation peak at -0.779 V at scan rate of 100 mV s^{-1} . The cathodic peak can be safely assigned to the reduction of the azo ($-\text{N}=\text{N}-$) group. The separation between cathodic and anodic peak potentials is more than

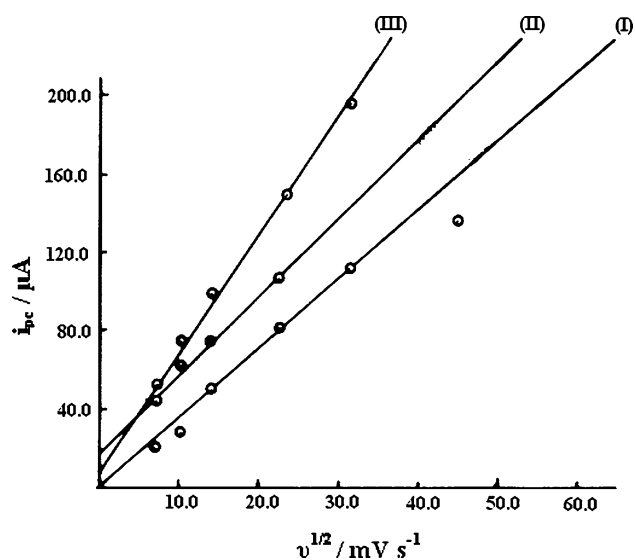


Fig. 2 Plot of i_{pc} vs $v^{1/2}$ amaranth solution at (I) pH 6.5, (II) distilled water, (III) pH 8.8 at platinum working electrode, concentration = 2×10^{-6} M

60 mV, indicating the irreversible nature of the electrode process [30]. As the scan rate (v) is increased, the reduction peak potential shows negative shift and the oxidation peak potential shows positive shift. At higher scan rate of $1,000 \text{ mV s}^{-1}$ the reduction peak appears at -1.0 V and the oxidation peak at -0.697 V . The peak potential separation (ΔE_p) increases gradually from 0.093 to 0.306 V as the scan rate is increased from 100 to $1,000 \text{ mV s}^{-1}$ suggesting the irreversible nature of the electrode process.

The plot of $i_{p,c}$ vs $v^{1/2}$ in the 6.5 pH solution is a straight line passing through the origin indicating the diffusion controlled nature of the electrode process (Fig. 2 (I)). This proportionality may be attributed to the fact that a steeper concentration gradient is established thereby increasing the rate of diffusion at faster scan rates. Reduced species will diffuse away from the electrode faster as the scan rate is increased [31, 32]. A similar plot for the dye solution in neutral aqueous medium and at pH 8.8 (Fig. 2 (III)) is, once again, a linear behavior, however, not passing through the origin. This indicates adsorption effects contributing to diffusion current. In such a case an adsorbed species may undergo electron transfer.

3.2 Effect of pH

Well-defined cathodic peaks in the acidic pH range are obtained with both platinum and glassy carbon electrodes. With increase in pH the cathodic peak shifts negatively and the anodic peak positively with increasing pH, which indicates that proton transfer occurs as a step consecutive to an irreversible electrode process [33]. The plot of $E_{p,c}$ vs pH is linear up to pH 6.5 (Fig. 3) as also above 6.5.

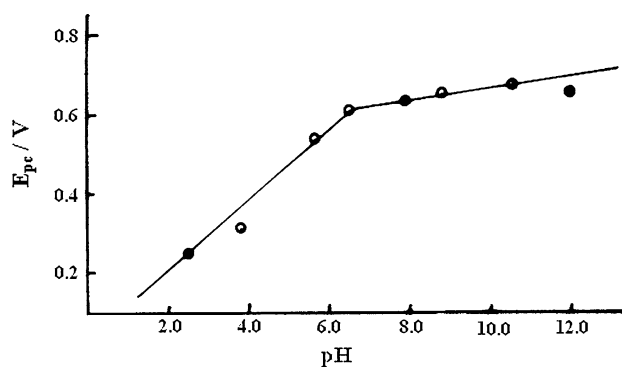


Fig. 3 Plot of $E_{p,c}$ vs pH of amaranth solution at pulse amplitude of 25 mV at dropping mercury electrode, concentration = 2×10^{-3} M, drop time = 2 s, column height = 60 cm

Table 1 Voltammetric characteristics of amaranth dye solution at varying pH, concentration 2×10^{-4} M, $v = 200 \text{ mV s}^{-1}$

S.No	pH	$-E_{p,c}/V$	$-i_{p,c}/\mu A$	$-E_{p,a}/V$	$i_{p,a}/\mu A$
1	2.5	0.491	18.32	0.570	29.50
2	4.0	0.783	35.90	0.541	62.98
3	5.6	0.577	4.780	0.674	22.08
4	6.5	0.957	73.87	0.668	59.29
5	7.9	0.989	68.91	0.641	74.88
6	8.8	0.954	97.50	0.676	95.24
7	10.5	0.986	934	0.651	89.13

However, the two linear segments have different slopes. The value of pH 6.5, is in accord with the pKa value. Above pH 6.5, the $E_{p,c}$ becomes practically independent of pH. This indicates the reduction of unprotonated species [34]. These results are presented in Table 1.

3.3 Differential pulse polarographic studies

A single four-electron irreversible reduction peak is observed in the pH range 2.5 to 12.0 at the mercury electrode. This may be attributed to reduction of the azo group ($-N=N-$). A shift in $E_{p,c}$ towards more cathodic potential with pH, along with a break at pH 6.5, is observed. Beyond this there is near constancy in $E_{p,c}$ (Fig. 3). This suggests participation of protons in the rate determining process. Analysis of the peak $E_{d.e.}$ vs $\left[\log \left(\frac{i}{i_d - i} \right) - 0.546 \log t \right]$ plot and shifting of the peak potential towards more negative value with concentration suggests the irreversible nature of the electrode process [35, 36]. The results of DPP studies are thus in close agreement with those of the CV studies.

3.4 Controlled potential coulometric studies

By using controlled potential coulometry, the number of electrons transferred “ n ” at platinum electrode were

Table 2 The number of electrons “*n*” value at different pH values at Pt

S.No	pH	Pot/V vs SCE	N*
1	2.5	-1.20	2.20
2	5.6	-1.20	1.96
3	8.8	-1.20	1.80
4	Dye solution in distilled water	-1.20	2.07

N*: Average of three replicate measurements

calculated and this lies in the range 2 ± 0.2 (Table 2). The value of “*n*” lies in the range 4 ± 0.2 at the steel electrode. Controlled potential electrolysis of amaranth (2×10^{-4} M) at platinum and steel electrodes was carried out at -1.20 V. Bench scale electrochemical treatment was carried out. Electrolysis results in complete disappearance of color which is fairly faster in case of platinum where the solution is decolorized within 10 min of electrolysis leading to the complete disappearance of the cathodic peak current. With steel, the colored solution took 80 min for complete color removal. The data are summarized in Table 3. A comparative overlay of the dye solution of pH 8.8 before and after electrochemical treatment is presented as Fig. 4.

3.5 Spectral studies

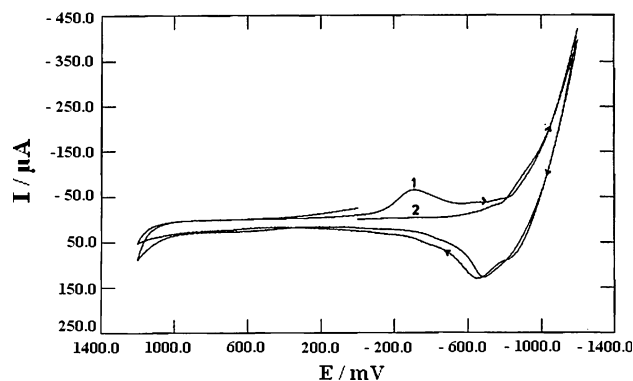
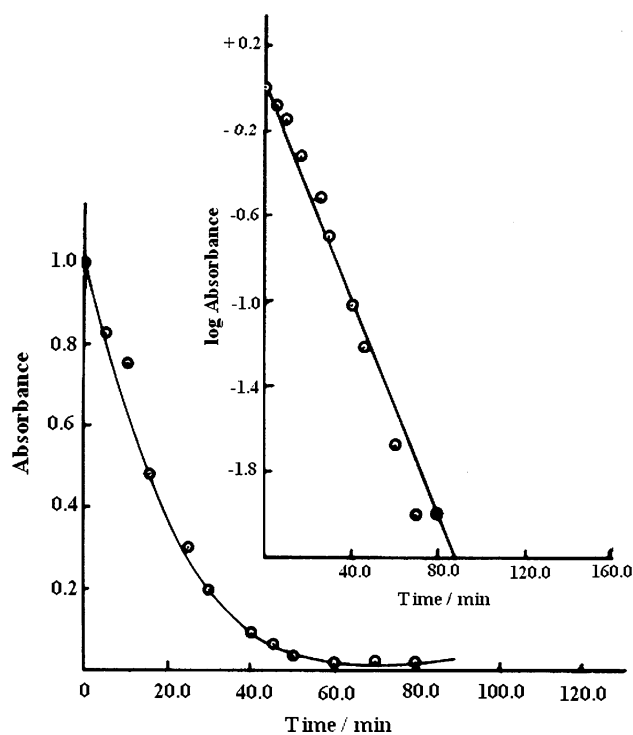
UV-visible spectra of amaranth (2×10^{-4} M) in distilled water were recorded at $\lambda_{\max} = 532.5$ nm. The progress of controlled potential electrolysis was monitored by recording spectral changes at different time intervals. At $\lambda_{\max} = 532.5$ nm, absorbance decreases systematically with the progress of electrolysis. The kinetic measurements were conducted at steel electrodes. The observed rate constant, $k = 5.75 \times 10^{-2}$ abs min $^{-1}$ was determined from the first-order kinetics plot of log absorbance vs time (Fig. 5).

3.6 COD removal

The electrolyzed solution shows a substantial decrease in COD from an initial value of 2,680 ppm to a final value of 96 ppm at platinum and to 142 ppm at steel.

Table 3 Controlled potential electrolysis results of amaranth (concentration = 2×10^{-4} M in distilled water) at two different working electrodes, scan rate = 200 mV s $^{-1}$

	Working electrode used	Scan rate/mV s $^{-1}$	$-E_{p,c}/V$	$-i_{p,c}/\mu A$	$-E_{p,a}/V$	$i_{p,a}/\mu A$	Time taken
Before electrochemical treatment	Platinum foil	200	0.890	40.80	0.758	86.88	10 min
After electrochemical treatment			–	–	–	–	
Before electrochemical treatment	Steel foil	200	0.890	40.80	0.758	86.88	1 h 20 min
After electrochemical treatment			0.203	28.53	0.829	83.03	

**Fig. 4** Cyclic voltammograms of amaranth (2×10^{-4} M, 8.8 pH) at platinum working electrode, scan rate 500 mV s $^{-1}$; (1) Before electrochemical treatment (2) After electrochemical treatment**Fig. 5** Plots of absorbance vs time and log absorbance vs time at 521 nm during electroreduction of amaranth at steel working electrode, concentration = 2×10^{-4} M in distilled water

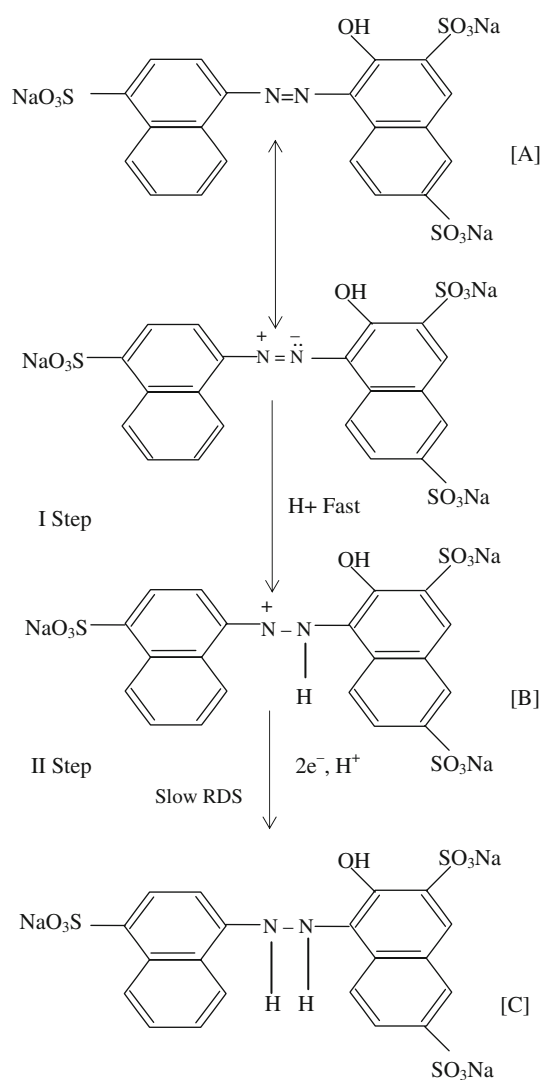


Fig. 6 Reduction mechanism of amaranth at platinum electrode

3.7 Proposed mechanism

On the basis of the coulometry, controlled potential electrolysis, chromatographic and spectral analysis, two reduction mechanisms are proposed. One is the two electron reduction to hydrazo compound at platinum (Fig. 6). A four electron reduction at steel (Fig. 7) may be favored by the presence of the strong electron releasing substituent, the $-OH$ group [37].

In Fig. 6, amaranth undergoes $2e^-$ reduction in acidic as well as alkaline medium. The reduction process proceeds by the protonation of the polarized molecule resulting in the formation of (B). In the second step, which is slow and rate determining, (B) accepts $2e^-$ and a proton and results in the formation of stable hydrazo (-NH-NH-) form (C).

In Fig. 7, $4e^-$ reduction takes place at the steel foil electrode. The I and II steps of reduction proceed in the

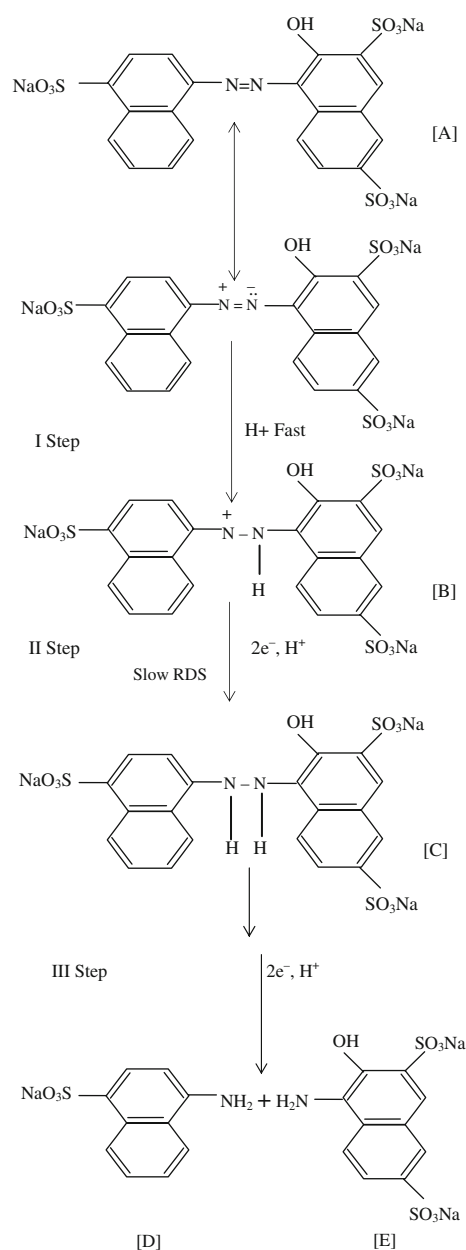


Fig. 7 Reduction mechanism of amaranth at steel electrode

same way as described in Fig. 6. In step III, (C) the hydrazo moiety undergoes a further two electron reduction resulting into two products (D) and (E).

4 Conclusion

The newly developed electrochemical method gives satisfactory and promising results. The electrochemical reduction of amaranth under the experimental conditions described in this work is an irreversible process controlled by diffusion. Both platinum and steel electrodes exhibit

great stability and resistance to redox and acidic/basic environments showing no deactivation. During the electrochemical degradation process, the COD decreases by approximately 97% at the platinum electrode and by 95% at the steel foil electrode with complete color removal. The electrochemical treatment developed achieves higher decoloration and COD removal than that reported previously through the ACF electrode treatment method [26] which gives only 60% COD removal. Hence, the present electrochemical procedure is a better alternative approach for wastewater treatment resulting in significant lowering of toxicity.

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