VOLTAMMETRIC REDOX BEHAVIOUR AND ELECTROCHEMICAL DEGRADATION OF REACTIVE RED 2 DYE

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ABSTRACT

The removal of synthetic azo dyes has become an environmental challenge due to its hazardous effects on animal and human being. The aim of this work was to study the voltammetric redox behaviour of a azo dye Reactive Red 2 (RR2) and its removal by electrochemical method using graphite electrodes at room temperature. In the cyclic voltammetric (CV) study, the potential window was in the range between -1.0 V and +1.0 V. The effects of pH, scan rate and dye concentration were studied. The electrochemical reaction pathway of the electroactive chromophoric group was derived. This azo dye with a hydroxyl group in the ortho position with respect to the N=N group exhibited a well defined irreversible redox peaks in the pH range between 1 and 13. The CV results indicated that the electrode process was adsorption controlled. The number of electrons transferred in the redox process was calculated from the controlled potential electrolysis experiment. The dye was then subjected to electrochemical degradation by applying DC power supply with graphite electrodes. Complete decolourization was observed after two hours of electrolysis. The electrolyzed solution was subjected to UV-Visible and FT-IR analyses. UV-vis spectra showed a peak that corresponds to the diene structure. FT-IR results showed that the solubilising groups attached to the ring play a major role in the degradation of azo dye.

INTRODUCTION

In the manufacturing or processing, approximately 15-20% of the synthetic textile dyes used are lost in wastewater streams. (Pollution Prevention and Abatement Handbook, 1998.) Such textile effluents are potentially toxic because of their low removable rate, (Zollinger *et al*, 2003. Gottlieb *et al*, 2003.) and if untreated would cause long-term health concerns.(Brown *et al*., 1993, Jackpotisch *et al*, 2001.) Certain azo dyes and their precursors are suspected to be human carcinogens. The dye contaminated water produces high colour intensity. A major source for the release of the colour into the environment is due to the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process. Hence, the removal of the colour is significant. (Shu *et al*, 1995.) The textile wastewater is being treated usually by biological, physical and chemical methods. Electrochemical techniques are considered as an attractive technology for the treatment of dyeing wastewater due to its significant advantages viz., wide application, simple equipment, easy operation, lower temperature requirements and no sludge formation. (Daneshvar *et al*, 2004. Do *et al*, 1994.) The advantages of employing electrochemical processes for wastewater treatment are versatility, environmental compatibility and potential cost effectiveness. (Nava *et al*, 2008.) The azo dyes are generally electrochemically active both in the reduction and in oxidation potential region. (Jeyadevappa *et al*, 2006.) The reduction of the azo group is influenced by the nature of the substituent or solubilising attached on the aromatic ring. The electron

withdrawing group such as nitro or halogen and electron donating groups such as hydroxyl or amino play different roles in the reduction of azo groups (Yu *et al*, 2004) Consequently, chemical structure and substituent group of azo dyes significantly influenced the degradation pathway.(Kariyajjanavar *et al*, 2010.) This study presents the systematic voltammetric behaviour of RR2 dye in differ buffer conditions and its electrochemical reaction mechanism with special reference to the hydroxyl group positioned in ortho to the azo bond.

MATERIAL AND METHODS

RR2 azo dye was purchased from Atul (P) Limited, and studied in the pH range between 1 and 13. Stock solution of 1.0×10^{-2} M dye was prepared with double distilled water. Cyclic voltammetric measurements were conducted with CH-620A Electrochemical Analyzer. A three-electrode system was used with Ag/AgCl as reference electrode, platinum wire as counter electrode and glassy carbon (GC) as working electrode. The working electrode was polished using Al_2O_3 on a polishing pad. Prior to recording cyclic voltammetry, the analyte solution was purged with nitrogen gas for 15 min. Controlled potential electrolysis was carried out to calculate the number of electrons transferred in the redox reaction. For the electrochemical degradation study, an apparatus consisted of a 250 mL closed cell and two graphite electrodes, 2 cm apart from each other and dipped into the solution. 1 ml of 10^{-4} M dye solution with 5 mL of pH 1 buffer was made up to 50 mL and subjected to degradation. Potentials such as 1.2 V and

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2 V were applied at room temperature using a DC power unit (APLAB L3230). UV-Vis spectra were recorded using Jasco-V-530 instrument and FT-IR spectra were analysed using Nexus 670 instrument.

RESULTS

The structure of the RR2 dye is shown in Fig.1. This dye contains two sulphonic acid groups, an azo group, two reactive chlorine groups and one hydroxyl group in the ortho position with respect to the azo bridge. Chlorine forms covalent bond with the cellulose thereby improving the wash fastness.

Table 1

Sweep rate mV/s	Reactive red 2	
	Ep (V)	Ip (µA)
10	0.296	44
50	0.311	172
100	0.313	267
200	0.321	480
300	0.328	663
400	0.334	830
500	0.337	994
1000	0.363	1763

Effect of pH

The effect of pH on the electrode reaction was investigated in the pH range from 1 to 13 and with a potential window between -1.0 V and 1.0 V at a scan rate of 100 mV/s. The redox reaction and the nature of voltammograms obtained were strongly dependent on the pH of the medium studied. Well-defined anodic and cathodic peaks were obtained in pH 1.
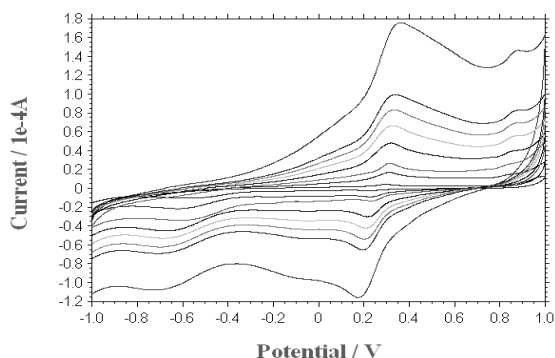

Fig. 2 Effect of scan rate on electroreduction of the dye

Effect of scan rate

 Effect of scan rate on redox reaction of the dye was recorded. When the scan rate increased from 10-1000 mV/s, the peak current also increases as shown in Table. 2 The anodic peak potential was observed at 0.3 V and cathodic peak potentials at 0.2 V and -0.7 V.

Effect of dye concentration

The concentration of the dye was increased from 1-5 ml in the buffer medium which contains 5ml of pH 1 buffer as supporting electrolyte. The anodic peak current increased

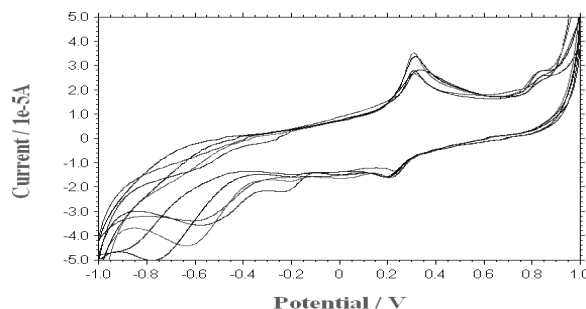gradually but no remarkable increase was observed in cathodic peak current.

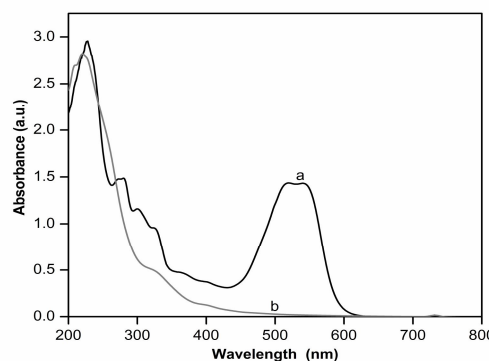**Fig.3** Effect of concentration of the dye in pH 1 buffer

Fig. 4 UV-vis spectrum of RR2 dye (a) before and (b) after electrochemical degradation.
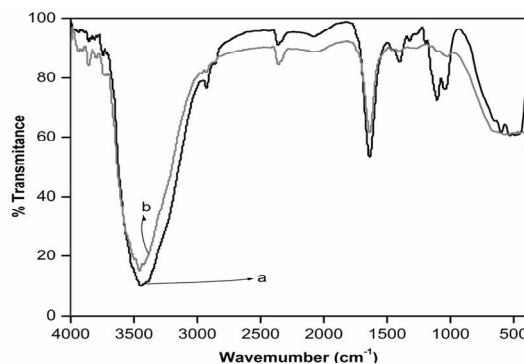

Fig. 5 IR spectrum of RR2 dyes (a) before and (b) after electrochemical degradation.

UV-Vis absorption spectrum of the RR2 dye solution at a concentration of 10-4 M was recorded. The strong absorbance band at 534 nm and the other bands at 226,278,302 were observed. The FT-IR bands were observed at 3445 cm^{-1} , 2361 cm^{-1} ,1637 cm^{-1} , 1107 cm^{-1} 532 cm^{-1} .

DISCUSSION

The peak current increased with the scan rate and the dye concentration. A single well defined oxidation peak at a potential of 0.3 V and two reduction peaks at potentials of 0.2 V and -0.7 V were obtained. From the peak potential values obtained, it was inferred that the redox process was easier and that could be due to the presence of the ortho hydroxyl group

with respect to the azo bridge. The number of electrons 'n' involved was calculated as 2, for the oxidation and two reduction potentials from controlled potential electrolysis by applying the equation $Q = nFN$, where Q is the total charge passed during electrolysis, and N is the number of moles of species initially present and F is Faraday's constant. The peak current increased with the scan rate but at the same peak potential for both oxidation and reduction as shown in fig 2. The fractional αn value obtained shows the irreversibility of the redox process. The slope value obtained by plotting log current against log scan rate is closer to 1, which is expected for ideal adsorption behaviour and hence partial adsorption can be suggested. A linear plot of peak current vs. scan rate proves the process to be adsorption controlled.

There was no appreciable potential shift for the oxidation peaks and it was around 0.3 V for all the concentration. The peak currents increased linearly with the increase in the concentration of electroactive species in dyes. It was inferred that the number of peaks is independent of dye concentration and peak current is dependent on dye concentration. From the fig. 3 it is observed that the intensity of the peak current increased with the dye concentration.

Effect of substituents

Amines and hydroxyl groups are very strongly active ortho and para directors with nonbonding electrons. Generally these electron donating substituent groups inductively take electrons from the ring and give it back by resonance. Hence, the degradation of the azo dyes strongly depends on the chemical structure and substituent groups. In RR2 two sulphonic acid groups are present, which are electron withdrawing favouring reduction. RR2 contains a hydroxyl group conjugated with azo linkage usually exists an equilibrium mixture of two tautomeric forms (azo or hydrazone) in the aqueous solution. It is reported that when the hydroxyl group is positioned in a naphthol, ortho to the azo bond, the hydrazone form is favourable at equilibrium. Hence intramolecular hydrogen bonding could be formed in the solution.[13] The larger conjugated π system of naphthalene ring is more favourable than the smaller conjugated π system of benzene ring through resonance for the delocalization of the nonbonding electron pairs of substituent groups and nitrogen in the azo bond. Hence RR2 which contains a naphthalene ring undergoes distortion thereby easier reduction. As reported in previous literature, RR2 with a hydroxyl group adjacent to an azo bridge was reduced yielding corresponding amines.[11]
The electrochemical degradation at 2V resulted in complete decolourisation of the dye in 45 minutes, while 120 mins was required for complete decolorisation at 1.2V. But considering energy cost 1.2V was taken for further study. The percentage of decolourisation was found to be ~100% in 120 min and a significant color removal is evident in this process. The degree of decolorisation was monitored through UV-Vis absorbance studies.

The strong absorbance band at 534 nm ascribed to the n-π* transition of the azo bond and the other bands at 226,278,302 were attributed to the π-π* transition related to aromatic rings. The decolourisation of dye solution was increased with electrolysis time. In Fig. 4, the UV-Visible spectra of the

decolourised dye clearly showed a complete shift of the peak at 534 nm in the visible region towards the UV range. Only a small peak at 221nm is obtained which attributes to the diene structure. During electrochemical degradation, oxidation had occurred resulting in the decrease of the absorbance band of the dye solution. The naphthalene ring in the dye structure has been changed to diene structure. The active chlorine can bring about partial mineralisation of dyes.[13]

The FT-IR results are shown in fig. 5. The band at 3445 cm^{-1} was ascribed to NH stretching and OH stretching vibrations, while the band at 2361 cm^{-1} attribute to the –N=N- vibration. The band at 1637 cm^{-1} attributes to the adsorbed water, and the strong bands at 1107 cm^{-1} attributes to the symmetric and assymmetric stretching of sulphonate anions of benzene rings.[13] The band at 532 cm^{-1} attributes to the chlorine atoms. After complete decolourisation, the same bands appeared at 3445 cm^{-1}, 2361 cm^{-1}, 1637 cm^{-1} and 532 cm^{-1} which ascribed to the NH and OH stretching vibrations, –N=N- vibration, adsorbed water with less intensity and chlorine atoms respectively. The azo groups are present even after decolourisation. This indicates that oxidation reaction has occurred at the hydroxyl position.
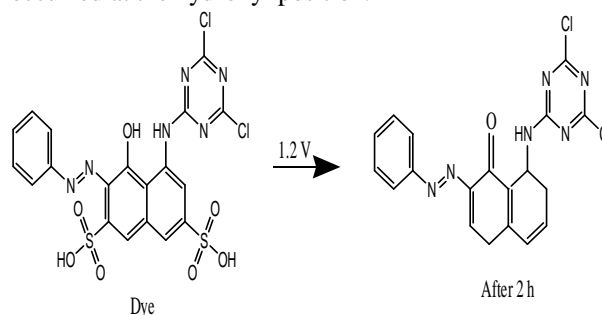

Fig. 1 A proposed mechanism of electrooxidation of the dye at room temperature under a potential of 1.2 V for 2 h

CONCLUSION

CV data provides useful information about the redox behaviour of the dye RR2. UV-Vis and FT-IR spectral studies confirm complete decolourisation and partial mineralisation. this dye species seems to be electro-active enough to undergo electro-oxidation. It is concluded that the hydroxyl substituted reactive azo dyes are more susceptible to oxidative degradation and strongly depends on the substituent groups attached to it. The proposed electrochemical degradation is an effective, facile and greener method for the above type of dyes. Further work on this study is to degrade the above type of dyes electrochemically using ITO/TiO$_2$ electrodes.

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