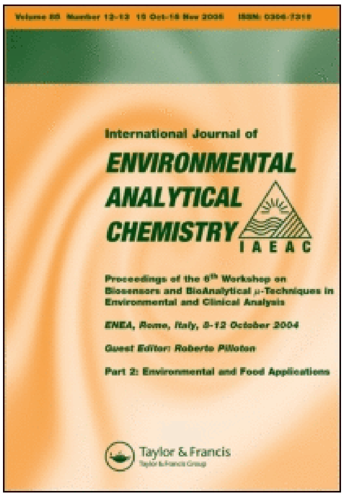

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DETERMINATION OF DIRECT ORANGE 8 IN EFFLUENT USING A POLYPYRROLE MODIFIED ELECTRODE

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Electrochemical studies of direct orange 8 were carried out with a bare glassy carbon electrode (GCE) and a polypyrrole-coated GCE in aqueous acetonitrile medium using voltammetric techniques. One reversible couple around 0.3 V due to the redox reaction of the phenol group, one reduction peak around −0.4 V due to reduction of the azo group and one oxidation peak around 1.0 V due to oxidation of the amino group were observed. Chronocoulometric studies revealed dye adsorption on the GCE. A square-wave stripping method was developed for the determination of the dye at pH 13.0, and a linear calibration equation obtained. The reproducibility in the measurement of peak currents was confirmed from the RSD value 2.8% at 0.001 mg mL^{-1} concentration. A comparison of the stripping voltammetric method with the UV-Vis spectrophotometric method was made. The determination limits are wider and the RSD value is lower in the stripping voltammetric method. The concentration of the dye present in dye effluent was determined using this method.

Keywords: Direct orange 8; Benzidine dye; Polypyrrole; Modified electrode; Stripping voltammetry

INTRODUCTION

The dye direct orange 8 is a benzidine-type dye and is suspected of releasing harmful amines that are allergenic and carcinogenic in nature [1]. Even though Germany has banned the use of benzidine-based dyes, direct orange 8 (DO8) dye is in use in many countries. The available chromatographic methods such as HPLC/UV [2] and LC/MS [3], and mass spectrometric [4] methods for the determination of dyes need expensive equipment and materials and include time-consuming extraction steps [5]. Most spectrophotometric methods [6] include complex reactions, which cause contamination and loss of substances, and all of them have lower sensitivity. Polarographic and simple voltammetric [7–10] methods also have lower sensitivity. In the literature, no stripping voltammetric method was found for the determination of DO8.

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The aim of this study was to investigate the electrochemical behaviour of DO8 and to develop a new stripping voltammetric method for its determination. The use of conducting polymer-coated electrodes overcomes the electrode-fouling problem and enhances the electrode activities [11–13]. These electrodes were employed to preconcentrate analytes prior to stripping analysis to improve sensitivity [14,15]. Polypyrrole-coated electrodes are widely used for the detection and determination of many organic compounds. In this article, electrochemical studies of DO8 at a bare glassy carbon electrode (GCE) and a polypyrrole-coated GCE and a stripping voltammetric method for determination are reported.

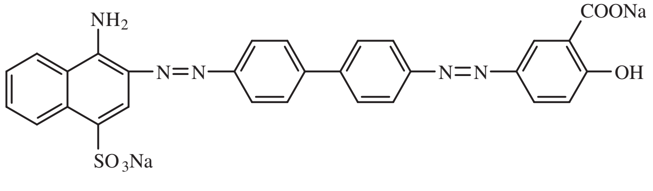
EXPERIMENTAL

Apparatus

A Bioanalytical System (BAS-100A) Electrochemical Analyser was employed for most of the electroanalytical techniques and a BAS CV 27 Voltammograph instrument coupled with BAS X-Y recorder was used in certain experiments related to the preparation of polypyrrole-coated electrode. Photometric analyses were carried out using a UV-Vis spectrophotometer, JASCO V530 model.

Reagents

The dye direct orange 8, disodium salt of 5-{[4′-(1-amino-4-sulfo-2-naphthalenyl)azo](1,1′-biphenyl-4-yl)azo}-2-hydroxybenzoic acid (C.I.22130) was donated by ATUL India Ltd. The dye was purified by recrystallisation in acetonitrile.



Since the dye is only partially soluble in water but freely soluble in acetonitrile, a stock solution of 1.0×10^{-2} M DO8 was prepared in acetonitrile. H_2SO_4, KCl, KOH and Briton Robinson (BR) buffer in 50% (v/v) aqueous acetonitrile solutions were used as media. Pyrrole was used for polymerisation studies. Acetonitrile was of HPLC grade (Merck) and other chemicals were of analytical grade (Merck). Doubly distilled and deionised water using TKA water purification system, Germany, was used.

The BAS-100A (MF-2012) glassy-carbon working electrode (2-mm dia.) was used in this study. To achieve reproducible results, great care was taken in the electrode pretreatment. The glassy carbon electrode was pretreated in two ways: (i) mechanical polishing over a velvet micro-cloth with an alumina (0.5 µm) suspension and (ii) electrochemical treatment by applying a potential of +1.5 V for 2 s. In order to avoid the complications due to anodisations, electrochemical cleaning was done only briefly. Electrochemical pretreatment was done in the same supporting electrolyte solution in which the measurement was carried out. Background currents for each of the supporting electrolyte solutions were recorded and later corrected with the current values obtained with analytes. The reproducibility of the result was often verified by recording voltammograms under identical conditions at various time intervals.

Procedure

Purging and blanketing were done for the analyte solution placed in an electrochemical cell of 15-mL capacity for 15 min with stirring. Then various voltammograms were recorded.

Preparation of Polypyrrole-coated Electrode

Polypyrrole films were obtained by electrooxidation of the 0.1 M pyrrole solution in acetonitrile containing 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP) potentiostatically at +0.90 V (*vs* Ag/AgCl). Thickness of the films was controlled coulometrically and 0.1-μm thick films were used in all cases. Care was taken to clean the glassy carbon electrode coated with pyrrole after every experiment in 1 : 1 hydrochloric acid/water and 1 : 1 hydrogen peroxide/acetic acid mixture before the usual surface treatment. Nitric acid (6 M) was used to clean the cell.

RESULTS AND DISCUSSION

Cyclic and Square-wave Voltammetry

Cyclic voltammograms were recorded for 1.0×10^{-3} M DO8 in 50% (v/v) buffered aqueous acetonitrile solution at various pH values from 1.0 to 13.0. The dye showed two cathodic and two anodic peaks at all pH media (Fig. 1). The reduction and anodic peak currents reached maximum values at pH 1.0 and 13.0, respectively. From the analytical point of view, 0.1 M KOH in 50% (v/v) aqueous acetonitrile

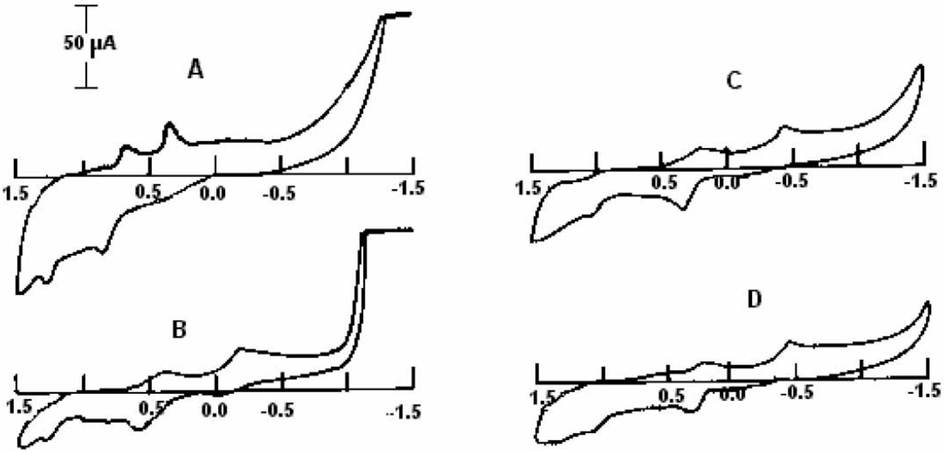


FIGURE 1 Cyclic voltammogram of 1.0×10^{-3} M^{-1} direct orange 8 at different pH values (sweep rate 250 mV s^{-1}). (A) pH 1.0; (B) pH 4.0; (C) pH 13.0; (D) pH 9.2.

TABLE I Cyclic and square-wave voltammetric behaviour of 1.0×10^{-3} M direct orange 8 at pH 13.0

	Cyclic voltammetry				*Square-wave voltammetry*			
	ν ($\mathrm{mV\,s^{-1}}$)	E_p (V)	i_p (μA)	*Current function*	F (Hz)	E_p (V)	i_p (μA)	*Current function*
1	25	0.30	0.84	2.48	10	0.31	1.00	2.04
2	50	0.36	1.00	1.82	20	0.29	1.21	1.74
3	75	0.36	1.17	1.74	30	0.27	1.56	1.84
4	100	0.36	1.40	1.80	40	0.26	1.90	1.94
5	125	0.36	1.55	1.79	50	0.26	2.04	1.86
6	150	0.37	1.65	1.74	60	0.26	2.54	2.12
7	175	0.37	1.76	1.72	70	0.24	2.90	2.23
8	200	0.38	1.92	1.66	80	0.24	3.08	2.22
9	225	0.38	2.10	1.63	90	0.22	3.58	2.43
10	250	0.39	2.23	1.60	100	0.21	3.74	2.41

(pH 13.0) and the anodic peak at potential about 0.30 V were selected owing to the good peak shape and higher current.

At pH 13.0, the dye showed two peaks at potentials about 0.30 and 1.0 V in the anodic sweep and two peaks at potentials about 0.25 and −0.4 V in the cathodic sweep. The absence of a reversible couple in the reverse scan for the anodic peak at potential about 1.0 V and cathodic peak at potential about −0.4 V indicated that these peaks were electrochemically irreversible in nature. The remaining two peaks at potentials around 0.30 V in the forward scan and around 0.24 V in the reverse scan are electrochemically reversible. An anodic shift was observed for cyclic voltammetric peak potentials when the scan rate was changed from 25 to $250\,\mathrm{mV\,s^{-1}}$ for the peak at 0.3 V (Table I). The peak current was linearly dependent on the scan rate [i_p (μA) $= 0.0061\nu + 0.724$; $R^2 = 0.9934$]. The height of the peak decreased as the scan cycle increased. These facts suggest adsorption-controlled oxidation.

In square-wave voltammetry also, two peaks were observed in the anodic scan (Fig. 2). The peak obtained around 0.30 V in the difference curve was almost identical with the forward current curve. The forward current response was higher than the reverse and difference current curves. The log i_p *versus* log frequency (Hz) plots yielded a straight line [$\log i_p = 0.6077 \log \mathrm{Hz} - 0.6716$; $R^2 = 0.9653$] with slope value around 0.6. This fact again confirms an adsorption-controlled reaction [16].

Chronocoulometry

Since adsorption facilitates the first accumulation step in stripping analysis, confirmation of adsorption of the substrate is necessary. The adsorption of the dye on the electrode was studied by double potential step chronocoulometry. The potential of the glassy carbon electrode was stepped from an initial value of 0.0 to a final value varying from 0.05 to 0.5 V in 10 mV increments. The levelling of net charge of the adsorbed species (Q_{net}) at a potential about 0.31 V indicated reactant adsorption.

Controlled-potential Coulometry

The number of electrons transferred (n) is determined coulometrically from the charge, $1.93 \times 10^5\,\mathrm{C\,mol^{-1}}$ (coulombs per mole) consumed for electrolysis at the

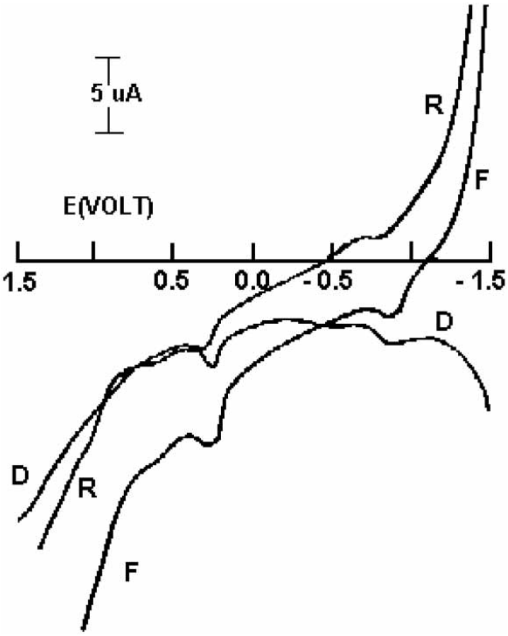


FIGURE 2 Square-wave voltammogram of 1.0×10^{-3} M direct orange 8 at pH 13.0. D = difference current curve, F = forward current curve and R = reverse current curve.

reduction potential −0.4 V. The '*n*' value is 2.0003 (rounded to 2). This may be due to the reduction of the azo group attached nearer to the phenol group. Both azo groups have either a carboxylate or a sulphonate group in the meta position. Both amino and phenoxide groups mesomerically donate electrons and retard reduction. Hence, the inductive effect is the deciding factor here. The phenoxide O is more electron withdrawing than the NH_2 group. Hence, the azo group para to the phenoxide group undergoes reduction. The second azo group may be reduced at a higher negative potential than can be achieved within the available potential window of the cyclic voltammogram. A charge of $9.7 \times 10^4\,C\,mol^{-1}$ was consumed for electrolysis at a potential about 0.30 V. The '*n*' value is 1.0053 (rounded to 1). This may be due to oxidation of the phenoxide group present in this dye molecule at alkaline pH.

Stripping Analysis at a Polypyrrole-coated Electrode

The response in cyclic voltammetry (CV) at a polypyrrole-coated GCE is presented in Fig. 3A. On a coated electrode, almost all peaks became flattened in CV. However, in differential-pulse stripping voltammetry (DPSV) (Fig. 3B) and square-wave stripping voltammetry (SWSV) (Fig. 3C), a representative sharp and narrow peak was noticed at a potential of about 0.2 V. The second peak obtained at a potential of about −0.3 V with the bare electrode was completely absent when the coated electrode was used. The stripping peak potential shifted towards the less anodic side. Peak potential differences of about 0.2 V in DPSV and about 0.1 V in SWSV were noticed between bare and coated electrode responses. This shift may be due to the catalytic effect of the polypyrrole surface on the oxidation of the phenolic group. The peak current increased from 13.7 to 19.5 μA under identical conditions in DPSV and from 28.2 to

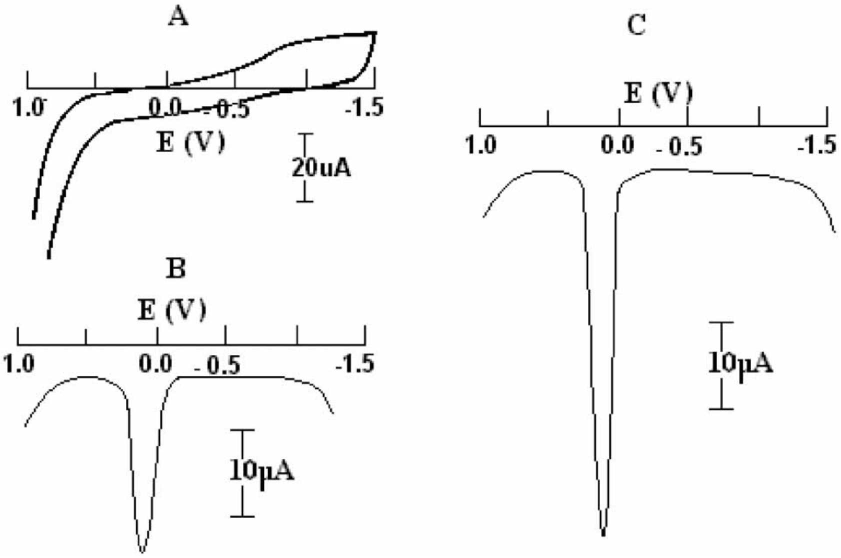


FIGURE 3 Polypyrrole-coated GCE responses of 0.11 mg mL^{-1} of direct orange 8: (A) CV; (B) DPSV; (C) SWSV.

41.0 μA in SWSV. The increase in peak current may be due to the increased surface area of the coated electrodes. Square-wave voltammeter is better for stripping studies and the polypyrrole-coating on the GCE enhances the current nearly 1.5 times. Hence, detailed stripping voltammetric studies for DO8 were carried out only with SWSV using a polypyrrole-coated GCE.

Square-wave Stripping Voltammetry

The effects of accumulation potential (E_{acc}) and initial scan potential (E_{is}) on the square-wave stripping mode were studied. E_{acc} of -1.0 V and E_{is} of -1.5 V were selected as they gave a higher current response. The stripping peak current increased with an increase in square-wave amplitude from 25 to 150 mV. The stripping peak signal gave a lower current response for higher square-wave amplitude above 125 mV. However, an amplitude of 100 mV was selected as it gave a good peak response. The dependence of the peak current on the frequency was studied between 10 and 1000 Hz. This experiment was carried out for a constant (4 mV) value of the step potential and the results showed a maximum peak current at 70 Hz. A lower current response was observed for higher frequency values between 80 and 1000 Hz. Broadening of the peak also occurred. When the step potential was given higher values (2 to 10 mV), a decrease in peak current was observed above 5 mV. Hence, a frequency of 70 Hz and a step potential of 5 mV were used, which provided a sufficiently sensitive analytical signal at a reasonable scan rate of 350 mV s^{-1}. The use of higher frequency and step potentials led to a distorted peak, resulting in poor resolution. The effects of stirring rate (100 to 2000 rpm) and rest period (2 to 30 s) were studied. The optimum values were found to be 300 rpm and 5 s respectively. Experimental conditions for the maximum signal from square-wave stripping voltammetry are given in Table II. A representative stripping voltammogram for a dye concentration of 0.11 mg mL^{-1} is given in Fig. 3C.

TABLE II Experimental conditions for maximum signal achieved in stripping voltammetry

Variable	*Range examined*	*Value at maximum signal*
pH	1.0 to 13.0	13.0
Initial scan potential (V)	0.0 to −1.5	−1.5
Accumulation potential (V)	0.1 to −1.5	−1.0
Stir rate (rpm)	100 to 2000	300
Rest period (s)	2 to 10	5
Square wave amplitude (mV)	25 to 150	100
Frequency (Hz)	10 to 90	70
Step potential (mV)	2 to 10	5

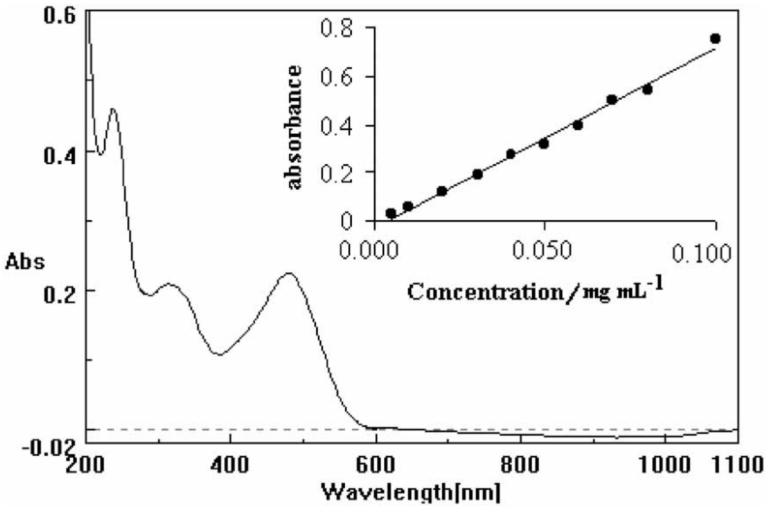


FIGURE 4 UV-Vis spectrum of direct orange 8. Insert: Calibration plot of direct orange 8 at λ_{max} 482 nm.

Analytical Characteristics

Square-wave stripping voltammograms at different concentrations of DO8 were recorded using their maximum signal conditions. From them, a linear calibration equation

$$i_p(\mu A) = 365.7C(\mathrm{mg\,mL^{-1}}) - 0.4$$

was obtained for dye concentration between 0.001 and 0.5 $\mathrm{mg\,mL^{-1}}$ under maximum signal conditions. The reproducibility of the stripping signal current was calculated in terms of the relative standard deviation (RSD) for 10 measurements carried out at a concentration level of 0.001 $\mathrm{mg\,mL^{-1}}$ and the RSD value was 2.8%.

Comparison of Results with a Spectrophotometric Method

A UV-Vis spectrophotometric method was developed for the determination of DO8 and the results were compared. Figure 4 shows the UV-Vis spectrum of DO8 and the calibration plot obtained between the concentration and the absorbance values.

TABLE III Determination of direct orange 8 using SWSV and a photometric method

Sample	*Standard sample*[a] (mg mL^{-1})		*Real effluent sample* (mg L^{-1})	
	SWSV	*Photometric*	*SWSV*	*Photometric*
1	0.0101	0.0089	3.2	2.9
2	0.0098	0.0093	3.1	2.8
3	0.0096	0.0097	3.3	2.6
4	0.0102	0.0092	3.2	2.9
5	0.0097	0.0094	3.1	3.0
6	0.0098	0.0096	3.1	2.6
7	0.0099	0.0103	3.3	2.7
RSD	2.2%	4.7%	2.8%	5.6%

[a] Concentration of dye in standard samples = 0.01 mg mL^{-1}.

The determination limits were 0.005 and 0.1 mg mL^{-1} and the RSD value at 0.01 mg mL^{-1} was 4.7%. The RSD value at 0.01 mg mL^{-1} was calculated using the SWSV method for comparison and was 2.2%. Table III gives the results obtained from the two methods for the determination of DO8. Based on the above results, we consider that the proposed SWSV method is a good technique for the determination of DO8 owing to its wider range and higher sensitivity.

Proposed Method for the Determination of Dye in Effluent

A real dye effluent sample was collected from the laboratory scale dying unit during the DO8 dying process for cotton fabrics. The effluent containing the unspent dye DO8, 1–2 g L^{-1} sodium carbonate and 3–4 g L^{-1} sodium chloride was made alkaline (pH 13.0) by adding 0.1 M KOH in 50% (v/v) aqueous acetonitrile. SWSV experiments under their maximum signal conditions were conducted for this effluent. The concentration of dye present in the effluent was calculated with the help of the calibration equation and was estimated to be 3.2 ± 0.1 mg L^{-1}, with RSD 2.8%. A similar determination was carried out using the calibration plot obtained from the UV-Vis spectrophotometric method. The concentration of the dye present in the effluent was determined as 2.8 ± 0.2 mg L^{-1} with RSD 5.6%. This again confirms the validity and greater suitability of the proposed SWSV method for the determination of DO8.

CONCLUSION

This article demonstrates that a polypyrrole-modified GCE shows a better redox response of DO8 than a GCE. The suitability of a polypyrrole-modified GCE for the electroanalysis of dyes using a stripping voltammetric determination procedure was investigated. A linear correlation was obtained between the voltammetric peak current and the concentration, and the determination limits and RSD values were determined. The sensitivity of this method was compared with a standard spectrophotometric method. The applicability of the method was confirmed by determining the dye concentration in a real effluent sample.

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