DETERMINATION OF DRIMARENE BLUE X-BLN AT A GLASSY CARBON ELECTRODE BY DIFFERENTIAL PULSE VOLTAMMETRY

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The electrochemical oxidation behaviour of Drimarene Blue X-BLN (DB) has been investigated in phosphate buffers (pH 2.54–10.18) by cyclic and differential pulse voltammetry (DPV) at a glassy carbon electrode (GCE). The oxidation of DB dye generated well-defined pH-dependent two pairs of quasi-reversible anodic-cathodic peak couples. DB exhibited the second redox couple over the entire pH range, while the first redox couple disappeared for pH ≥ 6.70. The redox processes were adsorption-controlled. An electroanalytical method was developed for the determination of DB in phosphate buffer solution (pH 2.85) as supporting electrolyte using DPV. The anodic current heights varied linearly with DB concentrations in the ranges 2×10^{-6}–3×10^{-5} and 6×10^{-6}–3×10^{-5} mol l^{-1} with limits of detection (LOD) of 8.7×10^{-7} and 5.7×10^{-7} mol l^{-1} and limits of quantification (LOQ) of 2.9×10^{-6} and 1.9×10^{-6} mol l^{-1} for the first and second anodic peaks, respectively. Validation parameters, such as accuracy, precision and recovery were evaluated. The proposed method was successfully applied to the determination of DB in tap water and the analytical results compared well with those obtained by the spectrophotometric method.

Keywords: Voltammetry; Electrochemistry; UV-Vis spectroscopy; Differential pulse voltammetry; Glassy carbon electrode; Electrochemical oxidation; Drimarene Blue X-BLN; Spectrophotometry; Reactive blue 198.

Waste water from textile dyeing and finishing factories is a significant source of environmental pollution. Reactive dyes are extensively used in textile industry, fundamentally due to the ability of their reactive groups to bind to textile fibres by covalent bonds formation via their hydroxy or amino groups[1]. This characteristic facilitates the interaction with the fibre and reduces energy consumption[2]. Drimarene blue (DB) is reactive dye presents a brilliant blue colour which is extensively used in textile fibres colouring. It is necessary to develop analytical methods for the dye deter-

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mination to help the industries to control their effluent remediation and to help the environmental agencies to control the aquatic system contaminations. Drimarene Blue X-BLN (Fig. 1), chlorotriazine reactive dye containing several sulfonic groups is a very polar compound. Spectrophotometric and chromatographic methods are not straightforward; major problems are spectral interferences and low affinity by the solid phase, even when ion-pair liquid chromatography is exploited[3]. For these reasons, quantitative methods for determination of dyes with several sulfonic groups are few in the literature[4]. However, there are several analytical methods such as UV-Vis spectrophotometry[5], immunoassays[6], and chromatography[7,8], capillary electrophoresis[9–11] and Raman spectroscopy[12] have been reported for other dyes determination. Voltammetric techniques have been reported for the determination of several azo dyes based on the electrochemical reduction of azo dyes groups[13–18].

The aim of the present work is to develop a voltammetric method for DB dye determination based on the electrochemical oxidation behavior of DB on a glassy carbon electrode. The electroanalytical technique provides the advantage of simplicity, low cost, relatively short analysis time and direct analysis, without any extraction, clean-up or pre-concentration steps.

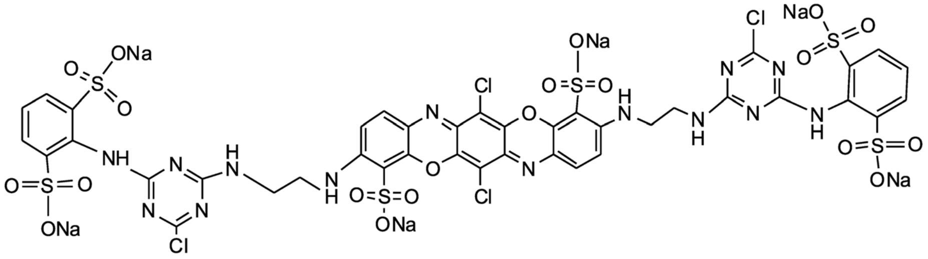

FIG. 1
Molecular structure of Drimarene Blue X-BLN

EXPERIMENTAL

Apparatus

The voltammetry experiments were performed using CHI610C Electrochemical Analyzer controlled by CHI Version 9.09 software (CH Instruments, USA). A three-electrode system was composed of a glassy carbon (BAS model MF-2012, Φ = 3 mm) working electrode, an Ag|AgCl|3 M KCl (BAS model MF-2063) reference electrode and a platinum wire (BAS model MW-1032) counter electrode. The UV-Vis absorption spectra were recorded on a double beam Perkin–Elmer UV-Visible spectrophotometer equipped with a PC for data processing UV Winlab-Ver 2.80.03 (Perkin–Elmer, USA) using a 1.0 cm cell at 0.2 nm intervals, in the range of 200–700 nm. A CG 808 (Schott Gerate, Germany) digital pH-meter with glass combination electrode served to carry out the pH measurements.

Reagents

A commercial reactive dye, Drimarene Blue X-BLN dye (CI Reactive Blue 198, empirical formula $C_{41}H_{30}Cl_4N_{14}Na_4O_{14}S_4$, 1682.60 g mol^{-1}), kindly provided by Dakahlia Spinning and Weaving (DETEX) Company, Egypt, was used without further purification. Stock solution (1×10^{-3} mol l^{-1}) was prepared in double distilled water, and stored in a dark bottle. Phosphate buffer solutions (0.2 mol l^{-1}) prepared by adding appropriate amounts of *o*-phosphoric acid, potassium dihydrogen phosphate and disoduim hydrogen phosphate[19] were used as supporting electrolytes. High-purity reagents were employed in all experiments. All solutions were prepared using bi-distilled water.

Procedure

For voltammetric measurement, 5 ml of the electrolyte solution were transferred into the voltammetric cell. After measurement of the blank solution in the anodic direction from –0.8 to +0.8 V, the appropriate amount of DB dye solution was added and the anodic potential sweep was carried under different operational parameters. Before each measurement the glassy carbon electrode was polished manually with 0.5 mm alumina dispersed in bi-distilled water on a smooth polishing cloth and gently dried with a tissue paper. The peak heights were evaluated as the differences between each voltammogram and the background electrolyte voltammogram. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

There were no previous electrochemical data available concerning the redox behaviour of DB dye. Therefore, DB was subjected to cyclic and differential pulse voltammetric (DPV) studies with the aim to characterize its electrochemical redox behaviour in detail over a wide pH range (2.54–10.18) on the glassy carbon electrode. It was found that DB dye is an easily oxidizable molecule. There was no report in the literature about the voltammeric oxidation of this dye, but one could predict that the oxidation process occurs for any of the several nitrogenous groups in the molecular structure of the drimarene blue dye.

The influence of solution pH on the differential pulse voltammetric response of 2×10^{-5} mol l^{-1} DB dye was examined between pH 2.54 and 10.18 (Fig. 2). The dye gave two well-defined oxidation signals (I and II), the first one was strongly displaced to less positive values with increasing pH from 2.54 to 6.70, then disappeared at pH ≥ 6.70, while the second peak was shifted to lower potential with increasing pH in the whole pH range. Experiment results indicated that only the measurements in acidic media produced the highest responses and the best defined peak was at pH 2.85. This pH value was selected as the optimum value for quantitative analysis.

Cyclic voltammetry (CV) can provide general information about the electroactivity and possible surface activity of various compounds. Typical cyclic voltammograms of 3.75×10^{-5} mol l^{-1} DB dye at a glassy carbon electrode in phosphate buffer at pH 2.85 and 6.70 are shown in Fig. 3, the cy-

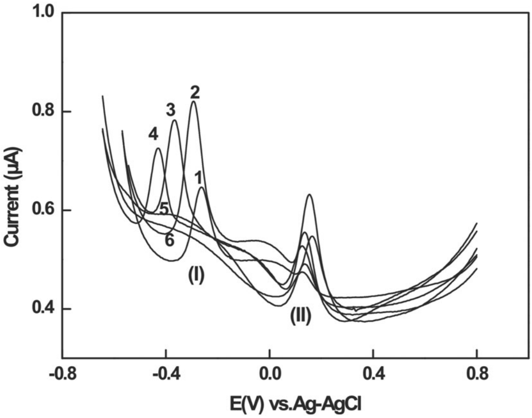

FIG. 2
Differential pulse voltammograms of 2×10^{-5} mol l^{-1} Drimarene Blue X-BLN solution at a glassy carbon electrode in phosphate buffer at different pH values: 2.54 (1), 2.85 (2), 3.12 (3), 4.70 (4), 6.70 (5) and 8.7 (6). Pulse amplitude 50 mV, pulse width 30 s, sample width 0.02 s

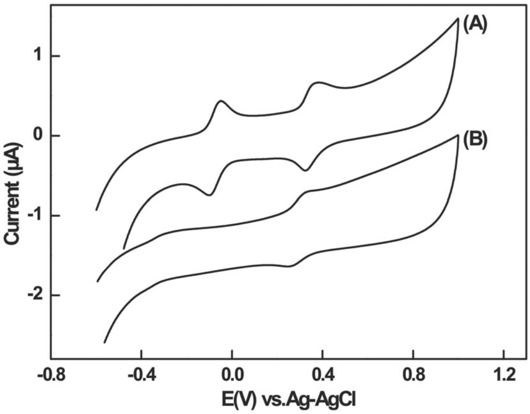

FIG. 3
Cyclic voltammograms of 3.75×10^{-5} mol l^{-1} Drimarene Blue X-BLN solution at a glassy carbon electrode in phosphate buffer (0.2 mol l^{-1}) at pH 2.85 (A) and 6.7 (B). Scan rate 50 mV s^{-1}

clic voltammogram for oxidation of DB dye at pH 2.85 shows two pairs of quasi-reversible anodic-cathodic peak couples, the first one at –0.052/–0.093 V and the second at 0.385/0.325 V vs Ag|AgCl|3 M KCl. At pH 6.70 the first couple almost vanished, while the second couple appeared with the peak potentials of 0.327/0.264 V at scan rate of 50 mV s^{-1}.

Cyclic voltammograms were then recorded for 5.0×10^{-5} mol l^{-1} DB at different potential scan rates (10–500 mV s^{-1}) in phosphate buffer at pH 2.85. The potentials of the two peak couples were found to be independent of the scan rate over the whole range studied, which indicated the reversibility of the processes. Simultaneous increases in peak heights with the scan rate (v) were observed. The intensity values of the anodic and cathodic peaks are similar in magnitude, which also clearly confirmed the reversibility of the electrochemical oxidation of DB dye.

The separations of the redox peak potentials of the two couples ($\Delta E_p = E_{pa} - E_{pc}$) at scan rate v = 100 mV s^{-1} was found to be 67.2 and 24.9 mV for first and second couples, respectively which is close to $2.3RT/nF$ (or $59/n$ mV at 25 °C). The number of electrons involved in the reaction were $n = 0.88 \approx 1$ and $2.37 \approx 2$ for first and second couples, respectively[20]. The redox behaviour could be ascribed to the triazine groups.

Scan rate studies were also carried out to assess whether the oxidation at GCE electrode under diffusion or adsorption controlled. The voltammetric peak currents increased with the scan rate over the range of 10–500 mV s^{-1}. The plots of logarithm of the peak currents (log i_p) vs logarithm of the scan rate (log v) for the first and second anodic peaks were straight lines with slope values close to the theoretical value of 1.0, suggesting that the oxidation processes are predominantly adsorption-controlled in the whole scan rate range studied[21].

Based on the voltammetric oxidation behaviour of DB dye, a quantitative electroanalytical method was developed. The differential pulse mode was selected, as the DPV has well-established advantages, including good discrimination against background current and low detection and determination limit[20]. The optimum instrumental conditions were obtained at pulse amplitude 50 mV, pulse width 50 ms and sample width 0.02 s.

A set of DP voltammograms in phosphate buffer (0.2 mol l^{-1}, pH 2.85), illustrating the variation of the two anodic peak heights (I and II) with the dye concentrations is shown in Fig. 4. The variations of current heights with dye concentrations are represented by the linear regression equations: i_{pa} (μA) = 0.007 + 0.006 C (μmol l^{-1}), $R = 0.999$ ($n = 8$) and i_{pa} (μA) = 5.019×10^{-4} + 0.005 C (μmol l^{-1}), $R = 0.999$ ($n = 8$) for concentrations ranges 2×10^{-6}– 3×10^{-5} and 6×10^{-6}–3×10^{-5} mol l^{-1} for the first and the second anodic peaks, respectively. The limits of detection (LOD) and the limits of quantification (LOQ) of DB dye were calculated to be 8.7 × 10^{-7} and 2.9 × 10^{-6} mol l^{-1} for peak I and 5.7 × 10^{-7} and 1.9 × 10^{-6} mol l^{-1} for peak II, based upon the definition: LOD = $3S_{y/x}/b$, LOQ = $10S_{y/x}/b$ [22], where $S_{y/x}$ is the standard deviation of y-residuals and b is the slope of the calibration plot.

In order to determine the accuracy and precision of the method, oxidation peak II of DB dye was chosen. Three different concentrations at low, medium and high concentrations of linear range (i.e. 9.09 × 10^{-6}, 13.04 × 10^{-6} and 16.67 × 10^{-6} mol l^{-1}) of DB dye were prepared and ana-

TABLE I
Accuracy and precision data for Drimarene Blue X-BLN obtained by DPV method

Added mol l^{-1}	Found $\bar{x}^a$ mol l^{-1}	SD[b]	RSD, %[c]	Accuracy bias, %[d]	Recovery, %
9.09 × 10^{-6}	9.06 × 10^{-6}	0.187	2.064	0.330	99.66
13.04 × 10^{-6}	13.09 × 10^{-6}	0.102	0.779	–0.382	100.38
16.67 × 10^{-6}	16.64 × 10^{-6}	0.154	0.925	0.179	99.82

[a] $\bar{x}$, mean. [b] SD, standard deviation. [c] RSD, relative standard deviation: RSD (%) = (SD/$\bar{x}$) × 100%. [d] Bias (%) = [(added – found)/added] × 100%.

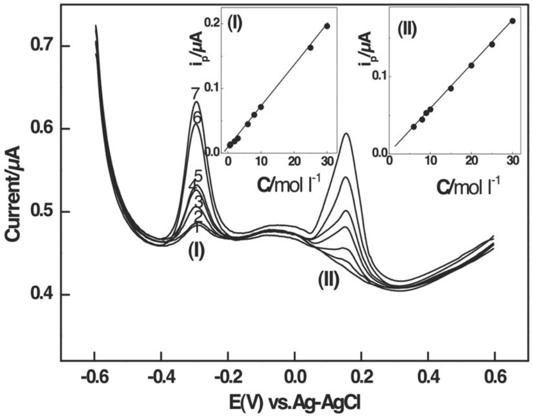

FIG. 4
Differential pulse voltammograms of Drimarene Blue X-BLN at different concentrations (in mol l^{-1}): 2 × 10^{-6} (1), 3 × 10^{-6} (2), 8 × 10^{-6} (3), 10 × 10^{-6} (4), 15 × 10^{-6} (5), 20 × 10^{-6} (6) and 30 × 10^{-6} (7) in phosphate buffer (0.2 mol l^{-1}) at pH 2.85. Pulse amplitude 50 mV, pulse width 30 s, sample width 0.02 s. Insets: Calibration plots: current heights of anodic peak (I) vs. dye concentrations and current heights of anodic peak (II) vs. dye concentrations

lysed. The analytical results obtained from this investigation are summarized in Table I. The relative standard deviation (RSD, %), recovery and Bias values can be considered satisfactorily at levels of concentrations examined. Relative standard deviation usually does not exceed 2.064% for concentration range of 9.09×10^{-6}–16.67×10^{-6} mol l^{-1}.

Spectrophotometric measurements of 3×10^{-6} to 6×10^{-5} mol l^{-1} DB dye in the range of 200–800 nm showed two maxima absorbances at 264.43 and 624.98 nm (Fig. 5). The visible band at 624.98 nm is attributed to the

TABLE II
Data of DPV and UV-spectrophotometric methods for determination of Drimarene Blue X-BLN dye

Parameter	DPV	Spectrophotometric method
Mean, %	99.67	99.78
Standard deviation	0.624	0.508
Number of measurements	5	5
t-test of significance	0.266 (2.26[a])	
F-test of significance	1.511 (6.388[a])	

[a] The tabulated *t*- and *F*-values, respectively, at *P* = 0.05.

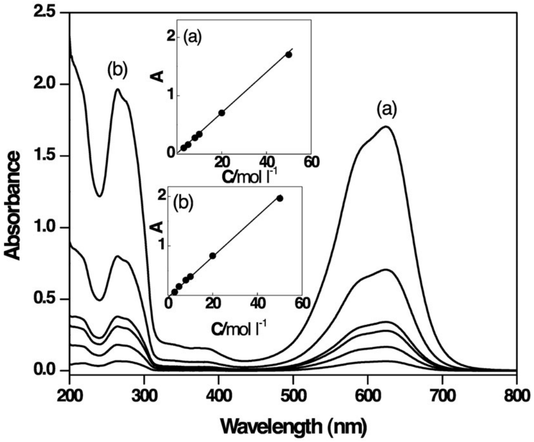

FIG. 5
UV-Vis spectra of Drimarene Blue X-BLN at different concentrations ranging from 3.00×10^{-6} to 6.00×10^{-5} mol l^{-1} in phosphate buffer at pH 8.51. Insets: Calibration plots of Drimarene Blue X-BLN at λ = 624.94 (a) and 264.98 nm (b)

reactive triphenodioxazine bonded to two monochlorotriazine groups which give the brilliant blue colour of the solution[23].

A UV-Vis spectrophotometric method was developed for the determination of DB dye and the variation of absorbance with concentration was studied in phosphate buffer at pH 8.51 (0.1 mol l^{-1}) at 264.43 and 624.98 nm and the corresponding linear calibration curves (Fig. 5, Inset) were constructed. The linear calibration ranges obtained at 264.43 and 624.98 nm were from 3.00×10^{-6} to 5.00×10^{-5} mol l^{-1}. The detection limits, reached according to $3S_{y/x}/b$, were 2.31×10^{-6} and 2.92×10^{-6} mol l^{-1} at 264.43 and 624.98 nm, respectively.

The differential pulse voltammetric technique has been applied to determine DB dye sample containing 84 mg dye per 50 ml. The results of the proposed technique have been evaluated statistically and compared with results of UV-spectrophotometeric methods (Table II). There was no significant difference between the mean values and precision of the two methods at 95% confidence level.

The proposed voltammetric method was successfully applied for the assay of DB dye in spiked tap water. Seven determinations of this dye concentration gave an average DB dye concentration of 1.67×10^{-5} mol l^{-1} corresponding to a mean recovery of 100.13%. The relative standard deviation was 1.05% indicating adequate precision and accuracy of the proposed method.

In summary, the electrochemical behaviour of DB dye was investigated at a glassy carbon electrode by cyclic and differential pulse voltammetry. The oxidation of DB generated well-defined pH-dependent two pairs of quasi-reversible anodic-cathodic peak couples. The redox processes were adsorption-controlled. The developed proposed differential pulse voltammetric method proved to be sensitive, precise, accurate and rapid enough to be used in the routine analysis of low concentrations of DB in environmental samples.

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