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Assessment of the application of cathodic stripping voltammetry to the analysis of diazo reactive dyes and their hydrolysis products

Claudia C.I. Guaratini[a], Arnold G. Fogg[b,c], Maria Valnice B. Zanoni[a,*]

[a]*Instituto de Química, UNESP, C. P. 355, 14801-970 Araraquara, SP, Brazil*
[b]*Sensors and Cryobiology Research Group, The Research Centre, University of Luton, 2 Adelaide Street, Luton LU1 5DU, UK*
[c]*Chemistry Department, Loughborough University, Loughborough LE11 3TU, UK*

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Abstract

Two reactive dyes, C.I. Reactive Red 120 (RR120) and C.I. Reactive Green 19 (RG19), each bearing two azo groups as the chromophoric moiety and two monochloro-*s*-triazine groups as reactive groups, can be detected at nanomolar levels using cathodic stripping voltammetry. Linear calibration graphs were obtained for both reactive dyes, from 0.015 to 0.14 μmol l^{-1} for RR120 in pH 4 buffer and from 0.012 to 0.26 μmol l^{-1} for RG19 in pH 3 buffer, using a pre-concentration at 0 V during 180 and 240 s on the mercury electrode, respectively.

Keywords: Reactive dyes; Cathodic stripping voltammetry; Dye hydrolysis; Dye determination

1. Introduction

In the dyeing of cellulosic fibres with reactive dyes, the addition of alkali to the dyebath not only promotes formation of a covalent bond between the dye and the cellulosic substitute but also causes some hydrolysis of the reactive group of the dye [1]. Once dyeing is completed, the dyed material is washed-off several times to remove unfixed and/or hydrolysed dye. The extent of the fixation is calculated using a simple mass balance based on the total amount of dye added to the initial dyebath and the amount remaining in the final bath together with that removed by wash-off. Thus, the reactions necessary to introduce the substances onto the fibre do not run to total completion and residual reactive and hydrolysed dyes remain in the process water and are discharged in waste water [2]. Few, if any, studies appear to have been concerned with how much unreacted reactive dye is discharged along with hydrolysed dye. The waste water (effluent) is discharged either to the sewer, which is then treated by municipal sewage treatment works, or directly to watercourses (in some countries). Despite their inherent problems,

* Corresponding author. Fax: +55-16-222-7932.
E-mail address: boldrinv@iq.unesp.br (M.V.B. Zanoni).

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reactive dyes are effective and are widely used [3]. However, their usage has attracted the critical attention of both the public and the authorities with respect to the toxicological and environmental aspects.

The development of reactive dyes with two or more functional groups of the same or of different types, whilst altering the position or substituents in the dye molecule, has been used as a way of achieving higher fixation ratios and, therefore, of reducing environmental problems [4,5]. C.I. Reactive Red 120 (RR120) and C.I. Reactive Green 19 (RG19) (Fig. 1) are examples of reactive dyes bearing two azo groups as the chromophoric moiety and two chlorotriazine groups as reactive (groups in different sites on the molecule). A corresponding increase in the use of this type of reactive dye has highlighted the need to develop rapid and reliable analytical methods for evaluating unfixed dyes or hydrolysed dyes with sufficient sensitivity to quantify it in water samples obtained from various sampling points. Several analytical methods have been employed for these purposes, namely, UV-vis spectrophotometry [4], immunoassays [6] and chromatography [7,8]. The use of voltammetric methods in the analysis of reactive dyes has been investigated [9–11] and the results displayed satisfactory selectivity and sensitivity for monitoring low levels of reactive dyes. However, few electrochemical studies involving reactive dyes with multifunctional groups are available and no analytical methods have thus far been proposed [12–14].

The aim of the present work was to investigate the possibility of using adsorptive/cathodic stripping voltammetry for the determination of low levels of two multifunctional reactive dyes, RR120 and RG19 and their hydrolysis products in aqueous solution using a hanging mercury drop electrode.

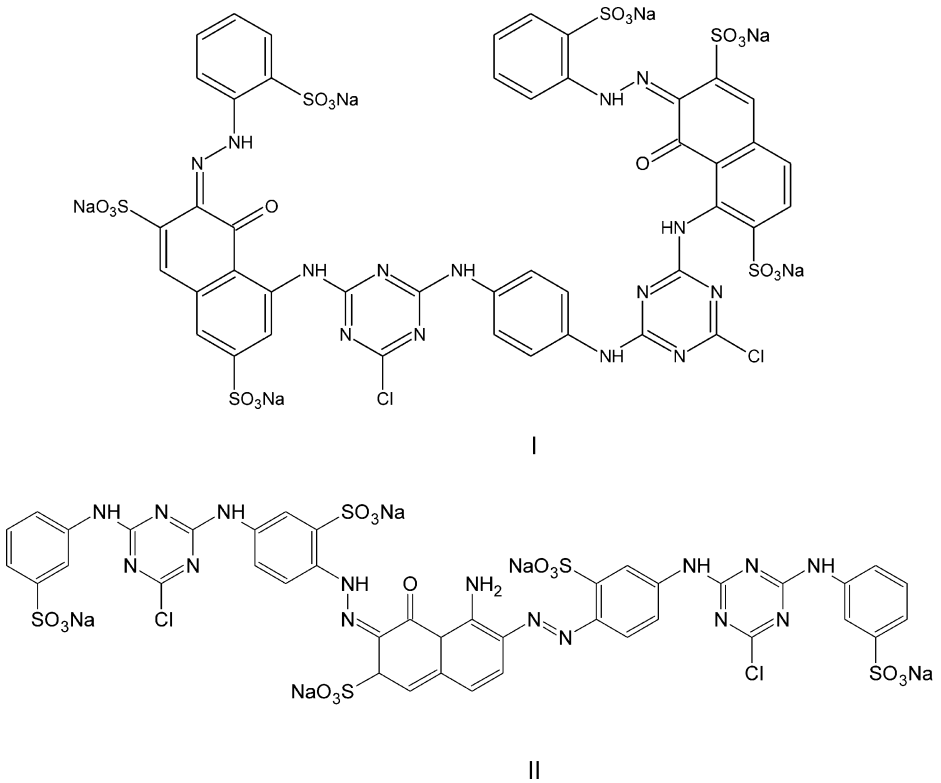

Fig. 1. Molecular structures of Procion Red HE-3B (I) and Procion Green HE-4BD (II) reactive dyes.

2. Experimental

Voltammetric measurements were made using a Potentiostat/Galvanostat EG&G PARC model 284; a EG&G PARC model 303A was used in the HMDE mode. The three-electrode system was completed by means of a glassy carbon auxiliary electrode and an Ag/AgCl (3M) electrode was used as the reference electrode. All pH measurements were made using a Metrohm E500 pH meter with a Metrohm EA 121 glass electrode which had been calibrated previously. Supporting electrolytes and stock solutions were prepared using demineralized water obtained from a Milli-Q system (Millipore).

Stock solutions of RR120 and RG19 (1×10^{-3} mol l^{-1}) were prepared from solid samples obtained from Aldrich. The studies were carried out in Britton–Robinson (B–R) buffer (0.4 mol l^{-1} in each of acetic, phosphoric, and boric acids) adjusted to the required pH using 0.2 mol l^{-1} sodium hydroxide solution.

Supporting electrolyte (10 ml) was placed in a voltammetric cell and the required volume of stock solution was added by micropipette. The solution was purged with nitrogen for 15 min and the voltammetric curves were recorded. The general procedure for carrying out cathodic stripping voltammetry was as follows. The stirrer was switched on and the solution was purged with nitrogen gas for 12 min. The accumulation potential was then applied to a new mercury drop, whilst still stirring the solution. After a 10 s quiescent period, with the stirring stopped, a potential scan was applied. Unless otherwise stated the following parameters were used; accumulation time 30 s, accumulation potential 0 V; pulse amplitude 50 mV; a maximum drop size of 0.40 mm^2 and constant stirrer speed 3 (1000 rpm) were used.

Hydrolysis reactions were carried out by treating the dye at an appropriate concentration in aqueous sodium hydroxide solution (pH 12) by heating at a controlled temperature of 80 °C in an ultra-thermostatic bath. After cooling in an ice bath, an aliquot of the dye solution was removed and diluted with 10 ml of buffer solution in a thermostatic cell at room temperature.

3. Results and discussion

3.1. Cathodic stripping voltammetry of the original dyes

Cyclic voltammetric studies showed that RR120 and RG19 were rapidly accumulated on an HMDE from stirred solutions, but the peak heights were found to be much greater with differential pulse cathodic stripping voltammetry than with linear scan voltammetry. Typical reduction curves obtained for 5.0×10^{-7} mol l^{-1} RR120 dye in 0.004 mol l^{-1} buffer at pH 4.0 and RG19 dye in pH 3.0 buffer after 30 s accumulation at 0 V are shown in Figs. 2 and 3, respectively. RR120 (Fig. 2) was reduced in three reduction cathodic processes in acidic solution, assigned as peaks I, II and III, respectively. The first step (I) can be attributed to the simultaneous reduction of both azo groups: both azo groups have hydroxyl groups in the ortho position [15]. The two other peaks (II and III) at more negative potentials can be attributed to the reduction process of the bis-monochlorotriazine groups.

The voltammograms obtained for RG19 (Fig. 3) pre-adsorbed on the mercury electrode, revealed four reduction peaks. The first two peaks can be attributed to the sequential reduction of the two azo groups (peaks I and II): one azo group has an ortho hydroxyl group whereas the other has an ortho amine group instead. These substituents affect the electron density of the azo group to different extents and, therefore, their reduction potentials occur at different values. The process was followed by two peaks at more negative potential (peaks III and IV) which are consistent with the reduction of the –C=N– bonds of the bis-monochlorotriazine rings [15], as observed for RR120.

The effect of pH on the peak potential and peak current obtained from differential pulse adsorptive stripping voltammograms of RR120 dye (5.0×10^{-7} mol l^{-1}) is shown in Fig. 4. With increasing pH, peak I is shifting towards more negative values, indicating that the azo group was being reduced in the protonated form of RR120. The peak current obtained from this process has a maximum current intensity at $pH<5$, showing

that the protonated form favours the adsorption of the species on the electrode surface. For RR120, peaks II and III were present in the cyclic voltammograms only up to pH 4 and the peak potential shifts as the pH is varied. This behaviour is similar to that of other monochlorotriazine reductions [9–11], where protonation has previously been observed to promote a easier reduction.

Fig. 5 shows the influence of pH on the peak potential and peak current of RG19 (5.0×10^{-7}

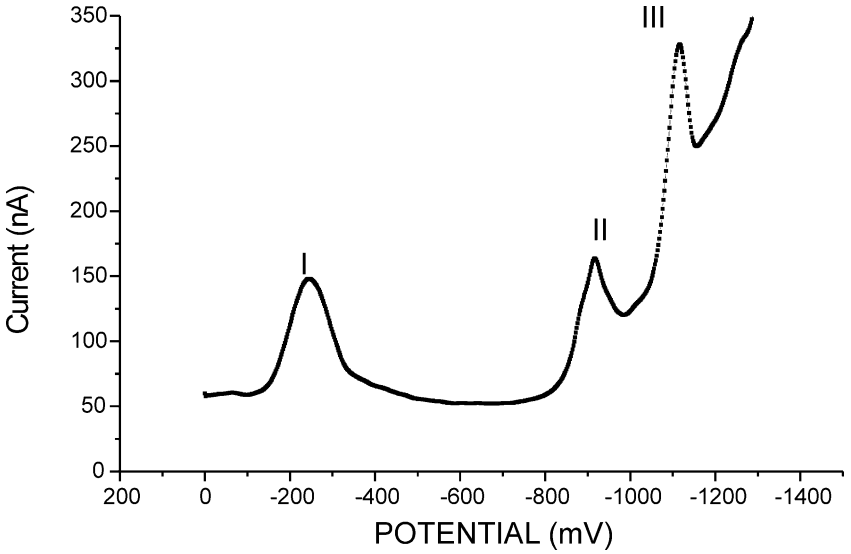

Fig. 2. Differential pulse cathodic stripping voltammograms of 5×10^{-7} mol l^{-1} of RR120 dye in B–R buffer pH 4.0. $E_{acc}=$ 0 V and $t_{acc}=$ 30 s.

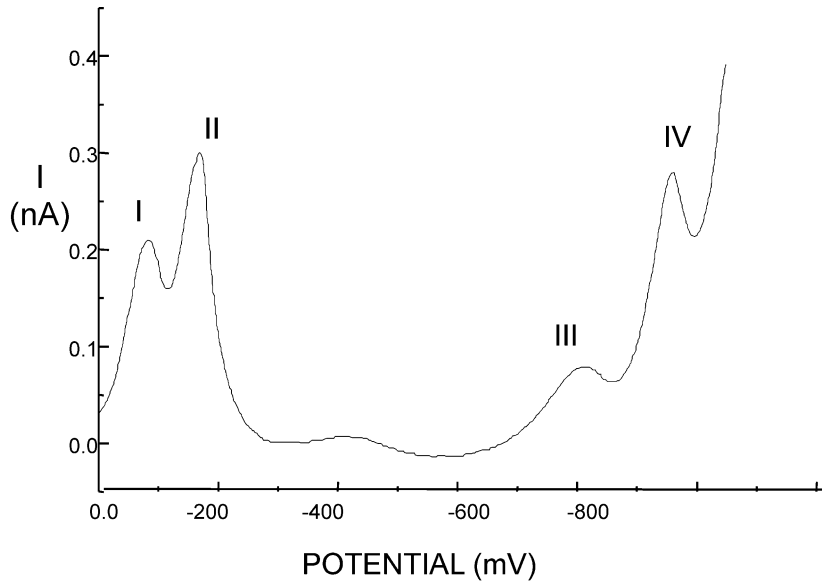

Fig. 3. Differential pulse cathodic stripping voltammograms of 5×10^{-7} mol l^{-1} of RG19 dye in B–R buffer pH 3.0. $E_{acc}=$ 0 V and $t_{acc}=$ 30 s.

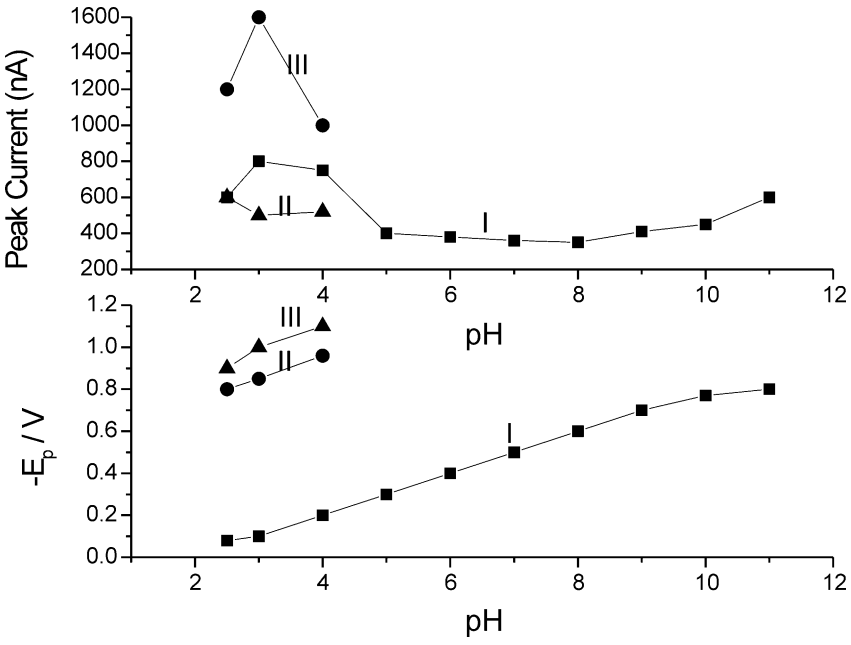

Fig. 4. Graphs of E_p vs pH and i_p vs pH for 5×10^{-7} mol l^{-1} of RR120 dye in B–R buffer. $E_{acc}=0$ V and $t_{acc}=30$ s.

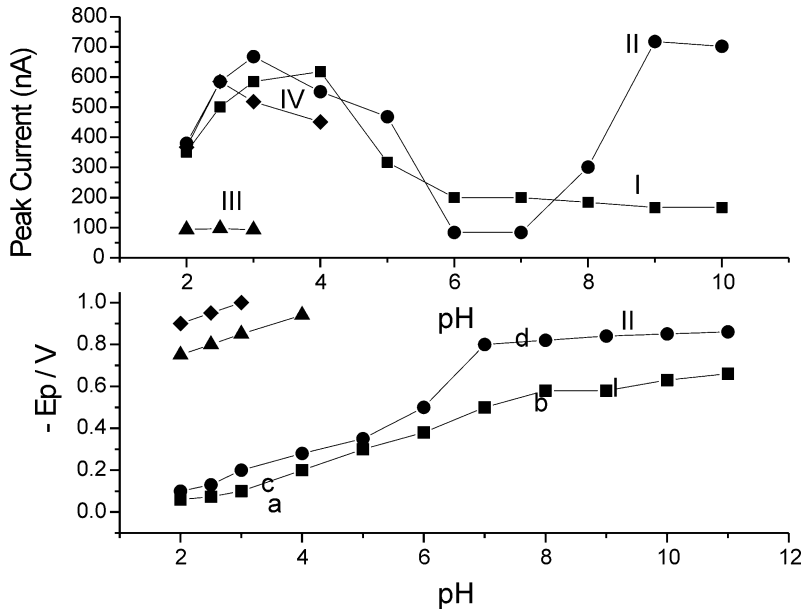

Fig. 5. Graphs of E_p vs pH and i_p vs pH for 5×10^{-7} mol l^{-1} of RR120 dye in B–R buffer. $E_{acc}=0$ V and $t_{acc}=30$ s.

mol l^{-1}). The reduction of the bis-azo groups (assigned peaks I and II) exhibited different behaviour when the pH was varied. The graph of peak I shows a linear portion with a break at pH 8.0 and the peak potential was pH-independent above this value. The process was accompanied by a lowering of peak height, clearly indicating that both protonated and unprotonated forms are preponderant at $pH \leqslant 8$ and $pH \geqslant 9$, respectively. Peak II also shows a linear portion with a break at pH < 6.0 followed by constant values of peak potential above pH 7.0. The intensity of this peak (II) shows a drop at pH 6.0 and increases again at the extremes of pH, indicating that the reduction of both azo groups in the molecule are influenced by pre-protonation reactions [16].

The different behaviour observed for reduction of the chromophore group in RR120 and RG19 can be explained by taking into consideration the electron-donating substituents at the ortho position in the reactive dyes. In the case of RR120, the –OH substituent ($\sigma = -0.37$) in this position increases the electron density of the azo group and the consequent increased basicity of the nitrogen atoms of the azo group, facilitate their protonization. Thus, the azo groups close to the –OH function in the ortho position are typically reduced in a unique reduction process involving a pre-protonated form up to pH 9.0. At higher pH values, ionization (deprotonization) of the hydroxyl group occurs and so reduction of the azo group occurs in a non protonated form.

The bisazo group reduction in RG19 occurs in two subsequent steps. The first peak (I) can be attributed to a reduction of the azo group with the ortho hydroxyl group. This is similar to that observed for RR120, for which the peak potential shifted linearly to more negative values up to pH 8, despite ionization of the –OH group occurring at a lower pH. On the other hand, the occurrence of a second reduction step at slightly more negative potential for RG19 up to $pH < 10$, indicates that the 0-amino group ($\sigma = -0.66$) affects the electron distribution in the azo group and its reduction is more difficult. In conclusion, the effect of different electron releasing substituents such as hydroxyl and amino group introduced on the naphthalene ring in the ortho position, with respect to the azo group, can promote a marked change in the electrochemical behaviour of bis-azo compounds. Despite similar planar configuration and extent of conjugation, variation in the electron density of the azo groups in the RG19, due to the proximity of different substituents, leads to a electrochemical reduction at different potentials.

The reduction of the bis-monochlorotriazine groups in both reactive dyes at very negative potentials is consistent with electrochemical reduction involving a pre-protonation reaction and the released of the chlorine substituent; for this reason, the peak intensity was higher in acidic solution [9–11]. Although the azo group reduction could be followed at all pH values in the range 2–12, the optimum pH value chosen to monitor the triazine group reduction were pH 4.0 for RR120 and pH 3.0 for RG19, for which maximum intensity was obtained.

To optimise the cathodic stripping voltammetry technique as an analytical method for determining reactive dyes in aqueous solution, the effect of some experimental parameters on the peak current for both reactive dyes were investigated.

The dependence of stripping peak currents on the accumulation time was studied using concentration levels of 5.0×10^{-8} mol l^{-1} and 5.0×10^{-7} mol l^{-1} of RR120 dye in pH 4 buffer and RG19 in pH 3 buffer. The analytically useful range of accumulation time was from 0 to 60 s at 5.0×10^{-7} mol l^{-1}. Within this range, the peak current corresponding to the bis-azo group reduction or bis-monochlorotriazine reduction rose linearly with increasing accumulation time for both reactive dyes. It was confirmed that for low concentrations (5×10^{-8} mol l^{-1}) a longer accumulation ($t_{acc} > 300$ s) was required for saturation of the electrode surface to be observed.

The influence of accumulation potential on the stripping peak currents was investigated using an accumulation time of 30 s and a potential of 0 V was adopted as the optimum accumulation potential to pre-concentrate both reactive dyes investigated.

The height of the reduction peaks for either of the two reactive dyes depends on concentration. A linear dependence of the peak current as a function of concentration of RR120 in pH 4.0 buffer

was observed in the concentration range of 1.5×10^{-8}–1.4×10^{-7} mol l^{-1} for an accumulation time of 240 s and a pre-concentration potential of 0 V, as shown Table 1. For RG19, a linear calibration curve was obtained from 1.2×10^{-8}–2.0×10^{-7} mol l^{-1} in pH 3.0 buffer using an accumulation time of 180 s. These plots show that cathodic stripping voltammetry can be used to monitor the reduction of the chromophore group or the chemically reactive group. With an accumulation time of 240 s, limits of detection around 7×10^{-10} mol l^{-1} can be obtained for RR120 and 5×10^{-10} mol l^{-1} for RG19. Mean standard deviations of 2.1% and 3.8% were obtained by measuring seven dye solutions of 5.0×10^{-7} mol l^{-1} of RR120 and RG19, respectively.

The findings show that cathodic stripping voltammetry can be an accurate, quick, simple and precise technique to determine traces of RR120 dye or RG19 dye by monitoring both the chromophoric system or the specific reactive group, where chemical reaction occurs.

3.2. Cathodic stripping voltammetry of the hydrolysis product of the reactive dyes

One of the most fundamental problems associated with reactive dye technology is the loss of potential dye–fibre reaction because of the competing hydrolytic processes [4]. This manifests itself in reduced dye fixation levels and a general incomplete utilisation of colour which is clearly uneconomical and which gives rise to associated effluent problems. Even after a substrate has been dyed successfully, problems can still arise, if dye fibre bond scission occurs under alkaline conditions, such as encountered during routine laundering. Therefore, competing hydrolysis is a significant problem, and for this reason, an analytical method to quantify a reactive dye needs to be capable of distinguishing between reactive and hydrolysed dye and also of determining low levels of the reactive dye in the presence of its hydrolysed counterpart.

Triazinyl reactive dyes are usually recommended for fixation to cellulosic fibres using batchwise conditions under alkaline conditions at a temperature of 80 °C. Under these conditions, complete reaction of the electrophilic group present in any remaining reactive dye with an hydroxyl ion would be expected to occur after some time [17].

Therefore, in order to develop an electroanalytical method capable of determining low levels of reactive dyes present amongst in the original and hydrolysed forms, a study was made to see whether cathodic stripping voltammetry could be used effectively to monitor the alkaline hydrolysis products of RR120 and RG19.

To obtain solutions of the fully hydrolysed dyes, standard solutions of the two reactive dyes were prepared by treating a 1.0×10^{-3} mol l^{-1} solution of RR120 or RG19 in 0.1 M of sodium hydroxide and in pH 12.0 buffer at a controlled temperature of 80 °C during heating from 0 to 5 h. The solution

Table 1
Calibration curves for the cathodic stripping voltammetric determination of RR120 and RG19 and their hydrolysed derivative

Reactive dye	E_p, V	pH[a]	C, μmol l^{-1}	Slope, nA μmol^{-1} l	Intercept, nA	Correlation coefficient	T_{acc}, s	E_{acc}, V	N
RR120	−0.22	4.0	0.015–0.14	1937	16.29	0.994	240	0	10
	−0.91	4.0	0.015–0.14	3239	22.46	0.997	240	0	10
	−1.09	4.0	0.015–0.14	9612	3.64	0.999	249	0	10
RR120 hydrolysed[b]	−0.28	4.0	0.10–0.70	1995	31.8	0.998	120	0	13
RG19	−0.09	3.0	0.012–0.26	1624	8.160	0.989	180	0	13
	−0.20	3.0	0.012–0.16	1574	1.810	0.995	180	0	12
	−1.04	3.0	0.012–0.22	1778	17.80	0.995	180	0	11
RG19 hydrolysed[b]	−0.18	3.0	0.10–0.60	1332	10.29	0.1000	240	0	11
	−0.28	3.0	0.10–0.60	1310	29.5	0.996	240	0	11

[a] pH* = B–R buffer.
[b] Hydrolysis condition = pH 12 (NaOH), temperature = 80 °C, heating time = 240 min.

was allowed to cool to room temperature and the pH was adjusted to pH 7.0 by the addition of 0.1 M hydrochloric acid. Aliquots of this solution were removed and added directly to the voltammetric cell containing appropriate supporting electrolyte. To obtain comparative results, an UV–vis spectrophotometric study was carried out of both reactive dyes using different pH values and heating times and temperatures.

The RR120 absorption spectrum at pH 4.0 (5×10^{-5} M) exhibited four bands. Main bands at 542 and 514 can be attributed to the long conjugated π system of the aromatic rings connected by two azo groups and the two bands in the UV region at 294 nm are characteristic of the two adjacent rings [1,18]. The absorption band at 233 nm can be attributed to the bis-monochlorotriazine groups. These attributions were confirmed by comparison with the UV–vis spectra obtained for a dye base compound containing only the azo group as chromophore and a monochlorotriazine compound used as a precursor in the synthesis of the studied reactive dye [1]. The spectra of RR120 was unchanged in the pH range 2–10. At higher pH (i.e. pH > 11), the peak at λ_{max} = 542 and 514 nm, decreased in height and gave just one peak at the shorter wavelengths of 480 nm, it is hypsochromic shift confirming that ionization of the hydroxyl group adjacent to the azo group had occurred; this was, however, only a temporary effect. The absorption spectrum of RR120 can be fully restored after addition of acid which had been to the RR120 dye solution at pH 12.0 without heating. Aliquots removed from the hydrolysed samples, which would have neutralised and added to a volummetric flask containing pH 4 buffer did not show significant changes indicates the nucleophilic substitution of –Cl by–OH in the triazine ring.

The UV–vis spectra recorded for aliquots removed from RG19 also did not show significant variation in the absorption bands at 628, 416 and 328 nm due to the azo groups in the spectra of the original dye, on hydrolysis. The absorption band attributed to the bis-monochlorotriazine groups at 268 nm exhibited a small hypsocromomic shift to 258 nm upon hydrolysis.

As the hydrolysis reaction does not promote significant changes in the UV–vis spectra of the dye molecules, stripping voltammetric curves for both the hydrolysed and original dyes were compared, with the intention of finding a way of discriminating between the two dye forms. Aliquots of the hydrolysed dye obtained by the experimental method described previously were analysed at a concentration of 1×10^{-7}mol l^{-1}, using an accumulation time of 30 s and an accumulation potential of 0 V.

The voltammograms for RR120 hydrolysed dye at pH 4.0 and RG19 at pH 3.0 are shown in Figs. 6 and 7, respectively. The peak potential corresponding to the first reduction process (azo group reduction) shifted around 60 mV to more negative values for RR120, and 70 mV, for both peaks, to more positive potentials after hydrolysis of RG19, respectively, but the peak current was not significantly changed. However, the second (bis-monochlorotriazine) reduction process showed a continual decrease in peak height and was completely eliminated after 240 min (RR120) and 330 min (RG19) at pH 12 at 80 °C (Figs. 6 and 7). Thus, the replacement of the active chlorine by hydroxyl during the hydrolysis removed the reducible monochlorotriazine group and produced an electrochemically inactive product, or shifting it to a potential more negative than the electrolyte discharge. The presence in the voltammetric response of amounts of the chlorotriazine groups at levels less than 1.0×10^{-7} mol l^{-1} could be used as a sensitive method to indicate incomplete hydrolysis at concentrations below that at which they cause perceptible coloration.

Using the optimum conditions to follow the voltammetric signal for both reactive dyes, the effect of heating time on the peak current intensities corresponding to reductive peaks at −1.0 and −1.1 V for RR120 and RG19 hydrolysed in pH 10 and 12 buffer were investigated and are shown in Fig. 8. A comparison of Curves A and C, illustrate that both reactive dyes were rapidly hydrolysed at pH 12, but in pH 10 buffer, RR120 dye was more stable than RG19.

Taking into account the fact that no significant alteration occurred in the chromophoric group after hydrolysis, the remaining reduction peak which is due to the bis-azo reduction, can be used successfully to measure low levels of the hydro-

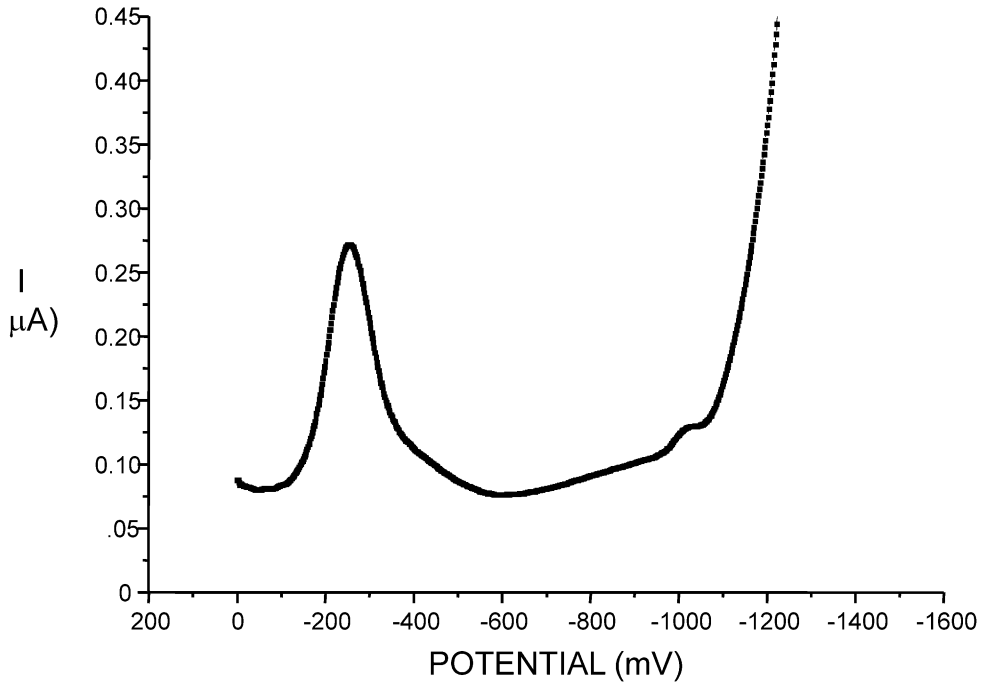

Fig. 6. Differential pulse cathodic stripping voltammograms obtained for 5×10^{-7} mol l^{-1} of RR120 dye in B–R buffer pH 4.0, after previous hydrolysis reaction in alkaline medium pH 12, $T=$ 80 °C, heating time 330 min. $E_{acc}=$ 0 V and $t_{acc}=$ 30 s.

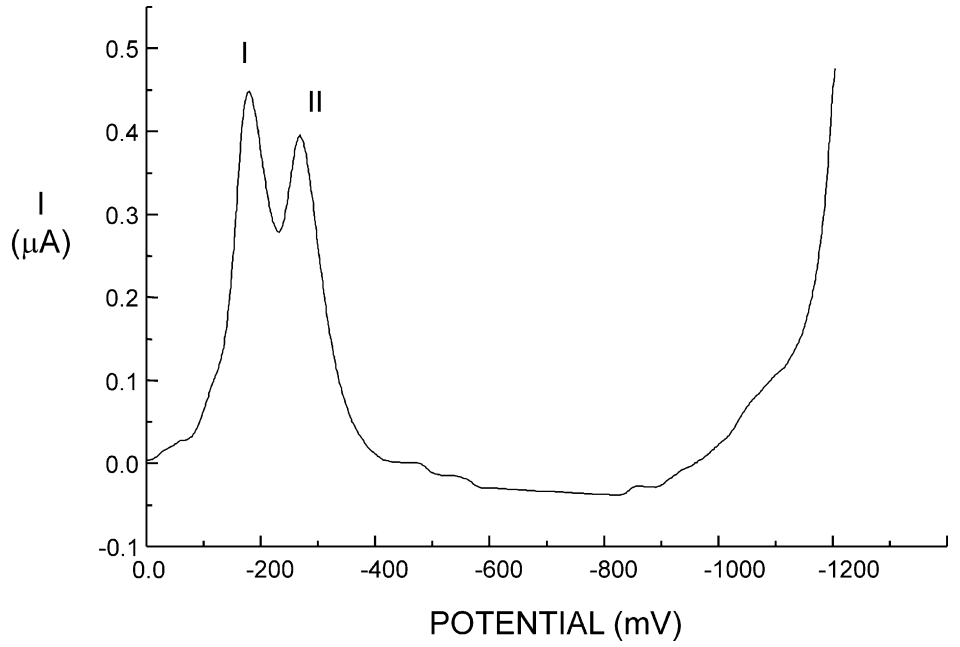

Fig. 7. Differential pulse cathodic stripping voltammograms obtained for 5×10^{-7} mol l^{-1} of RG19 dye in B–R buffer pH 3.0, after previous hydrolysis reaction in alkaline medium pH 12, $T=$ 80 °C, heating time 330 min. $E_{acc}=$ 0 V and $t_{acc}=$ 30 s.

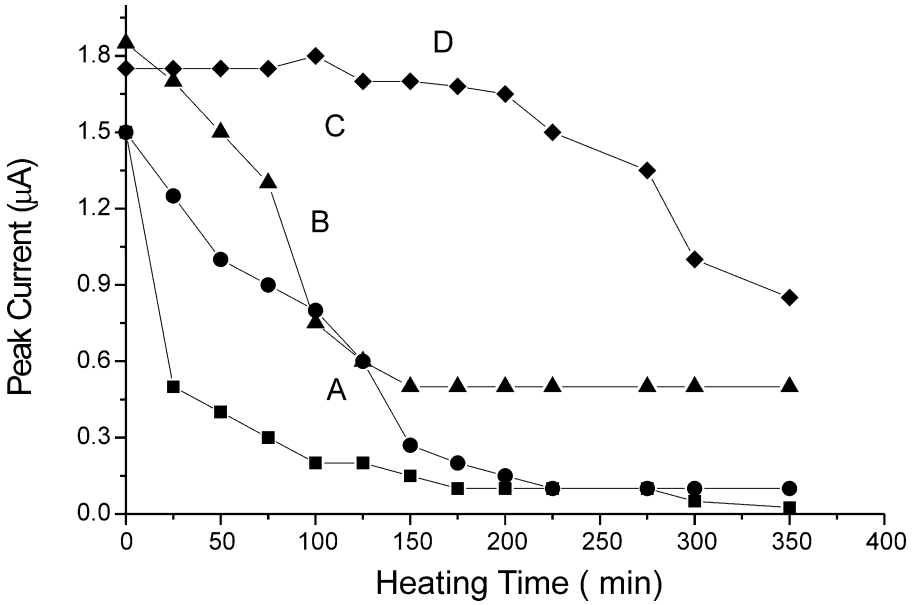

Fig. 8. Effect of heating time on the peak current intensities correspondent to reductive peaks at −1.0 and −1.1 V from stripping voltammograms obtained for RR120 dye and RG19 under hydrolysis conditions. RG19 in B–R buffer pH 12 (Curve A) and 10 (Curve B). RR120 in B–R buffer pH 12 (Curve C) and pH 10 (Curve D).

lysed dyes. Thus, experimental conditions were optimised for their determination.

Hydrolysed RR120 can be pre-accumulated on the mercury electrode surface and maximum signal was obtained at an accumulation potential at $E_{acc} = 0$ V. A linear relationship was observed up to 50 s accumulation at 5.0×10^{-7} mol l^{-1} and up to 300 s at 1.0×10^{-7} mol l^{-1}. A rectilinear relationship was observed for 5.0×10^{-7} mol l^{-1} of RG19 up to 240 s, above these times saturation occurs at the surface of the mercury drop.

In pH 4.0 buffer, the peak height corresponding to the simultaneous azo group reduction of RR120 after fully hydrolysis increased linearly with concentration of the hydrolysed dye from 1.0×10^{-7} mol l^{-1}–7.0×10^{-7} mol l^{-1} after 120 s of accumulation time at 0 V of accumulation potential. The respective parameters are shown in Table 1. The reproducibility of the method was determined by successive measurements of ten solutions of 1.0×10^{-7} mol l^{-1}, a relative standard deviations of 1.8% was obtained with a pre-concentration time of 120 s.

Linear calibration plots were obtained for both azo group reductions from 1.0×10^{-7} to 8×10^{-7} mol l^{-1} of hydrolysed RG19 at pH 3.0 (Table 1). Both peaks showed great analytical potential at an accumulation time of 240 s and an accumulation potential of 0 V. The relative standard deviation for determination of hydrolysed RG19 at 5.0×10^{-7} mol l^{-1} was calculated to be 3.50% ($n = 5$). The detection limit was calculated to be 1.0×10^{-9} mol l^{-1}, where a measurable signal was obtained for both hydrolysed dyes.

4. Conclusions

There is strong consumer demand for reactive dyes and both dyers and dye manufacturers have increasingly opted for reactive dyes with two or even three reactive groups in a given dye molecule with the aim of increasing dye fixation levels. Cathodic stripping voltammetry has been shown to be capable of determining both reactive dyes and their hydrolysis products at very low levels, well below those achievable spectrophotometrically [19]. Thus, the method is ideally suited to environmental control situations. There is also the possibility of distinguishing unhydrolysed reactive

dye in the environment, which might occur if unreacted reactive dye is discharged into a neutral pH environment. Additionally, the method could be adapted for following the dyeing process, by monitoring the ratio of reactive dye to hydrolysed dye.

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