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Brizola Santos, Lídia; Santos Domingues, Fernando; Rosseto, Fernando; de Cinque Almeida, Vitor;
Garcia, Juliana Carla; Evelázio de Souza, Nilson

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Simultaneous determination of textile dyes by Adsorptive Cathodic Stripping Voltammetry

Lídia Brizola Santos, Fernando Santos Domingues, Fernando Rosseto, Vitor de Cinque Almeida, Juliana Carla Garcia and Nilson Evelázio de Souza*

Departamento de Química, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900, Maringá, Paraná, Brazil.
*Author for correspondence. E-mail: nesouza@uem.br

ABSTRACT. The Adsorptive Cathodic Stripping Voltammetry (ACSV - differential pulse) proved to be an efficient method in the separation and quantification of two reactive textile dyes, Procion Yellow (PY) and Procion Red (PR), each containing two azo groups as chromophores and two monochlorotriazine reactive groups, at nanomolar level. The linearity of the method obtained for each reactive dye was 30.15 – 633.15 nmol L⁻¹ for PY in B-R buffer pH 8.0, and 62.56 – 982.291 nmol L⁻¹ for PR in B-R buffer pH 8.0, using preconcentration at -0.1 V during 60 s.

Keywords: stripping voltammetry, reactive dyes, textile dyes.

Determinação simultânea de corantes têxteis por Voltametria Adsorptiva de Redissolução Catódica

RESUMO. A técnica de voltametria adsorptiva de redissolução catódica (VARC – pulso diferencial) mostrou-se eficiente na separação e quantificação de dois corantes têxteis reativos, Amarelo Procion (PY) e Vermelho Procion (PR), cada um contendo dois grupos azo como cromóforos e dois grupos reativos monoclora-triazina, a nível nanomolar. A linearidade do método obtida para cada corante reativo foi 30,15 – 633,15 nmol L⁻¹ para AP em tampão B-R pH 8,0 e 62,56 – 982,291 nmol L⁻¹ para VP em tampão B-R pH 8,0, usando pré-concentração em -0,100 V por 60 s.

Palavras-chave: voltametria adsorptiva, corantes reativos, corantes têxteis.

Introduction

The textile industry produces large volumes of effluents containing dyes that have not been fixed to the fiber during the dyeing process (KUNZ et al., 2002). Serious aesthetic and environmental problems arise from the presence of these dyes in wastewater because of their color and high chemical oxygen demand (Further, the discharge of untreated effluents may generate toxic aromatic amines under the anaerobic conditions of the water, which may contaminate soil and subterranean areas (VAJNHANDL; LE MARECHAL, 2005; BESINELLA JUNIOR et al., 2009; PIVA et al., 2011; CONCEIÇÃO et al., 2013).

The textile industry is one of the largest producers of liquid effluents (SILVA et al., 2010). Approximately 80 L of water is required to produce 1 kg of cloth, although reference has been made to values of the order of 150 L, with 80% of this volume being discharged as effluent and only 12% of this total is lost due to evaporation (regional data). The effluent characteristics depend on the technology and

industrial processes used, as well as the type of fiber and chemicals involved. The textile sector could achieve substantial savings if dye-rich wastewater could be reused in new dyeing baths. Unfortunately, it is very difficult to quantify the residual dyes, principally because non-uniform color batches can result from the mixing of the dyes used and from the lack of bath concentration uniformity, making it impossible to reuse the water in subsequent baths. In this way, this study aimed to develop an analytical methodology able to quantify binary mixtures of dyes with similar chemical structures.

The most commonly used methods to monitor dyes during the dyeing process are spectrophotometry and voltammetry (BERGAMINI et al., 2005; CARBÓ et al., 2010; CATANHO et al., 2006; THOMAS; AURORA, 2006; ZANONI et al., 2006). Processes based on UV-VIS spectral absorption analysis are the instrumental methods most frequently used in laboratory, once the cost and the availability of equipments are the principal advantages of these processes. A limitation is related to the fact that absorptions for certain compounds may appear in the

same range of the electromagnetic spectrum, causing spectral interference operational steps (SOZGEN; TÜTEM, 2004; ZANONI et al., 1999). Some sensitivity and selectivity improvement can be achieved through the use of spectrophotometrically selective reagents, reactions with masking agents, or by separating the analyte from the matrix. However, introducing additional increases of the risks of contamination and loss of the analyte (KARPINSKA, 2004).

Derivative spectrophotometry (DS) is an advanced, modern spectrophotometric technique. In DS, the spectra are obtained by plotting the values of the first or second derivative of the zero-order spectrum as a function of wavelength (ALMEIDA et al., 2009; KARPINSKA; SZOSTAK, 2005; OJEDA; ROJAS, 2004).

Voltammetric methods are used for environmental, food, and pesticide analyses, among others (PAULINO et al. 2008). There are reports in the literature of their use in determining dyes in textile effluents (CARNEIRO et al., 2005; GUARATINI et al., 2001; LI et al., 2007; VIANA et al., 2006; YANG et al., 2007; ZANONI et al., 1999). However, there is little information about simultaneous determination of textile dyes in wastewater using voltammetric techniques. A possible limitation of the use of such techniques is that the chemical similarity of the compounds may lead to voltammetric peak overlapping. This may occur because the voltammetric signal for the analyte arises from the electroactive chemical groups in the molecule. However, a study of the electrochemical behavior of dyes is possible by separation of the peaks

with significant resolution. Thus, adsorptive cathodic stripping voltammetry (ACSV) has become a powerful analytical tool for determining the speciation of textile dyes in a mixture.

In this study, we proposed to carry out the simultaneous voltammetric determination of two dyes: Procion Yellow HE4R (PY) and Procion Red HE7B (PR) (Figure 1), which are classified as reactive AZO dyes and are used in dyeing cotton fibers. These dyes were chosen because they are commonly used in the region and because their similar structures make them difficult to separate.

Material and methods

Adsorptive Cathodic Stripping Voltammetry (ACSV)

Voltammograms were obtained with a Potentiostat - Galvanostat Autolab GPES 663 VA Stand. A system of three electrodes consisting of an Ag/ AgCl (KCl saturated) as reference electrode, a glassy carbon auxiliary and a hanging mercury drop (HMDE) as working electrodes were used. Supporting electrolytes and stock solutions were prepared using demineralized water obtained from a Milli-Q system (Millipore). Stock solutions of PY and PR dyes (100 mg L⁻¹) were prepared from direct dissolution of the solid samples gently supplied by MR Malharia (Brazil). Studies were carried out in Britton-Robinson (B-R) buffer (0.40 mol L⁻¹ in each of acetic, phosphoric, and boric acids) adjusted to the required pH, using sodium hydroxide solution 0.20 mol L⁻¹ (BERGAMINI et al., 2005).

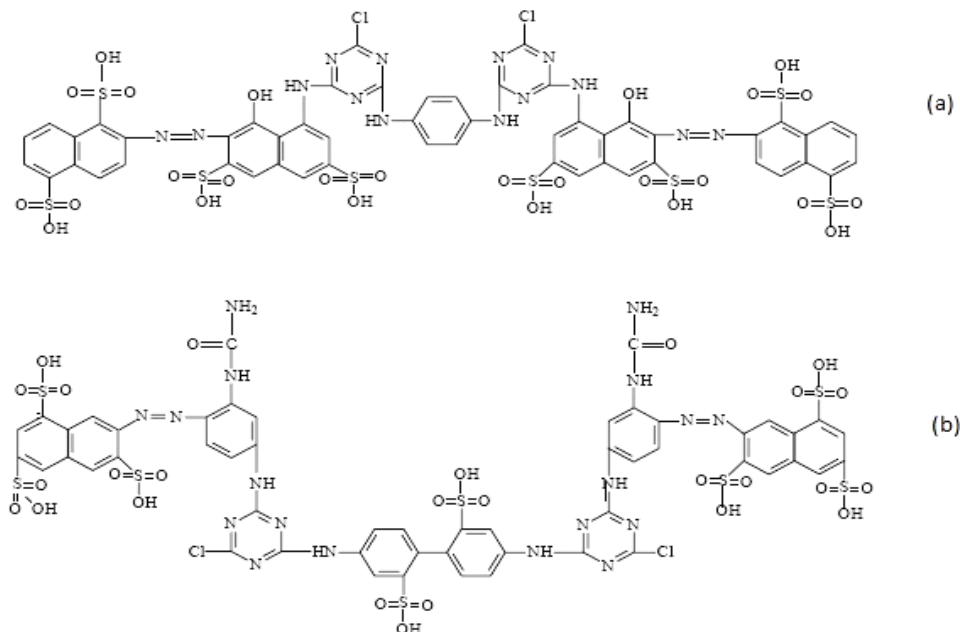


Figure 1. Chemical Structures of the dyes: (a) Procion Red HE7B (PR) and (b) Procion Yellow HE4R (PY).

Sample preparation of dye baths

In 250 mL-beakers, solutions were prepared from the baths of dye-based manufacturer's process. To the solutions of individual dyes and the mixture was added 17.5 g NaCl pa and 5 g Na₂CO₃. After total dissolution, solutions were transferred to 250 mL-beakers, where volume was measured with deionized water. An aliquot of 100 mL was transferred to a 250 mL-beaker, where occurred the dyeing process of cotton fabric at 85°C for 2h. After the dyeing process of the tissue, the waste generated was collected and the dyes were measured by voltammetry and the results compared with the spectral analysis (ALMEIDA et al., 2009).

Results and discussion

Optimization of the voltammetric parameters for the PR and PY dyes

The reduction potentials found for the dyes (Figure 2) were -0.272 V (PR) and -0.181V (PY) (vs. Ag/AgCl) in B-R buffer pH 4.0. Before investigating the ACSV parameters, such as the accumulation potential, accumulation time and scan rate, the voltammetry conditions were studied. The characteristics of individual voltammograms for PY and PR dyes were first studied in order to develop the procedure for the dye mixture analysis.

The voltammograms obtained for PR and supporting electrolyte (Figure 2a) pre-adsorbed on the mercury electrode revealed two reduction peaks. The peaks can be attributed to the reduction of the azo group. Figure 2b showed the voltammograms obtained for PY and supporting electrolyte, which showed one reduction peak. As with PR, the first peak was attributed to the reduction of the azo group.

The difference in the values for the reduction potential for the azo groups of the two dyes can be assigned to the different chemical groups bonded to the azo group in the molecules. One azo group is bonded to an ortho-hydroxyl group, while the other is bonded to an ortho-amide group. These substituents affect the electron density of the azo group to different degrees and, therefore, the voltages at which reduction occurs are different.

Effect of the accumulation potential

Figure 3 shows the effect of the accumulation potential on the current intensity for the reduction peaks of the PR and PY dyes. For these dyes, the

effect was investigated in the potential range from -0.300 to 0.200 V. The maximum peak current value was reached at -0.100 V, enabling determination to be achieved with greater sensitivity due to the greater accumulation. Accordingly, this potential was selected as the optimum value.

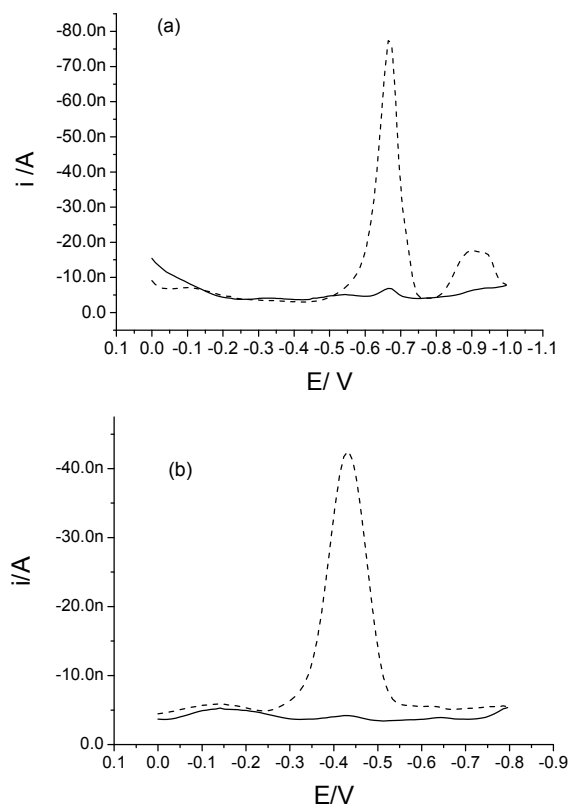


Figure 2. Voltammograms of the: (a) PR dye and (b) PY dye. Experimental conditions: B-R buffer pH 8.0, scan rate: 50 mV s⁻¹, accumulation potential: -0.100 V.

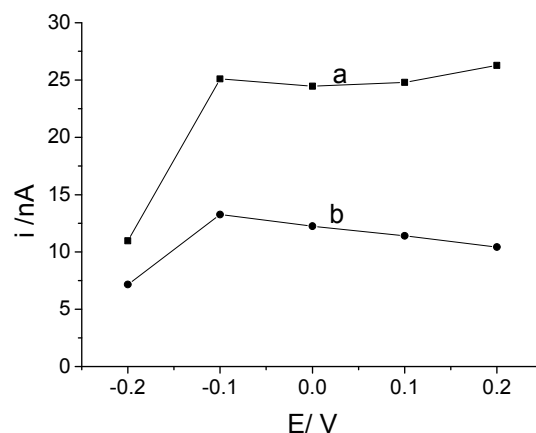


Figure 3. Effect of accumulation potential on the height of the current for the (a) PY (1.51.10⁻⁸ mol L⁻¹) and (b) PR dye (1.87.10⁻⁸ mol L⁻¹). Deposition time 60 s; scan rate 50 mV s⁻¹; B-R buffer pH 8.0.

Effect of the scan rate

The effect of the scan rate (v) was evaluated and illustrated in Figure 4, the peak current signals for PR and PY dyes increased as the scan speed increased, stabilizing above a scan speed of 50 mV s^{-1} .

In the studies of the effect of scan rate on the peak current, it was found to be linearly dependent on the square root of the speed, with a linear correlation coefficient of 0.9917 ($i = 22.24 + 0.835 v^{1/2}$) for PY and 0.9733 ($i = -15.21 + 4.19 v^{1/2}$) for PR (Figure 4b), demonstrating that the mass transport is controlled by diffusion (ROSA et al., 2003).

The scan rate selected for subsequent voltammetric studies was 50 mV s^{-1} for the best accuracy in analyzing the dye mixtures by the ACSV.

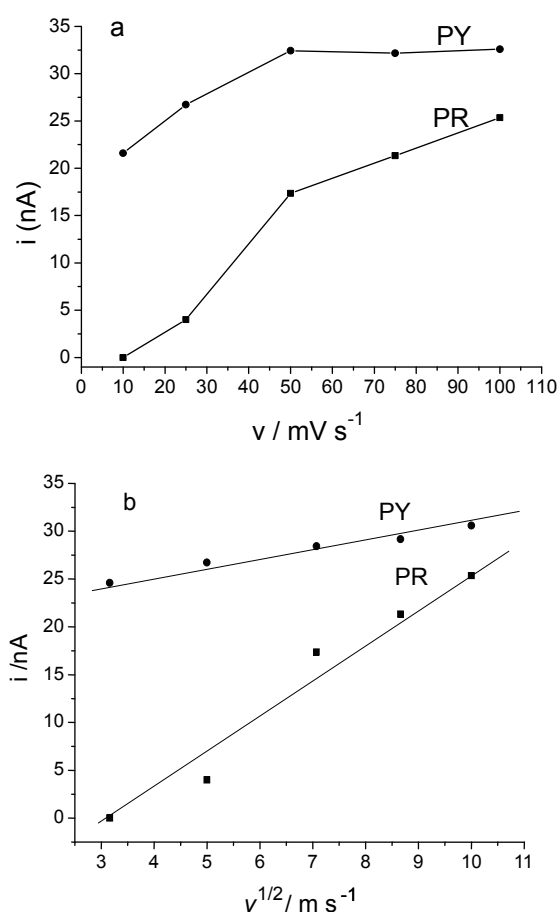


Figure 4. Effect of the scan rate on peak current reduction for dye PR and PY. Deposition time 60 s; accumulation potential - 0.100 V; PR concentration $1.87 \cdot 10^{-8} \text{ mol L}^{-1}$, PY $1.51 \cdot 10^{-8} \text{ mol L}^{-1}$.

Dye mixtures

Figure 5 (a) shows the overlapping voltammetric profiles for PR and PY in pH 4.0. The analyte interferes with PR for the PY signal and vice versa. In other words, a positive interference occurs in the current signal for each dye, which is undesirable for the chemical speciation, identification and quantification of the dyes in the wastewater. Accordingly, interference from the PR peak signal with the PY signal was investigated, together with the interference of the PY peak in the PR signal.

Was also performed to study the variation of pH for the binary mixture of the dyes.

The literature reports the use of voltammetry in the quantification of mixtures of dyes. However, there is the derivatization of the voltammograms (NI; BAI, 1997). Through the procedure we have proposed, the derivatization step is not necessary.

Analysis of binary mixtures

Using the optimized instrumental conditions found previously with working solutions, calibration graphs for the two dyes, were constructed by plotting the absolute values of the current height (i) at -0.422 V and -0.583 V for PY and PR, respectively as a function of concentration. Table 1 lists typical calibration equations, and the correlation and other coefficients of analytical merit, such as detection limit, quantification limit and dynamic linear range.

The estimated detection limits for the ACSV procedure for the PY and PR dyes were, respectively, $30.15 \text{ nmol L}^{-1}$ ($S/N = 3$) and $62.56 \text{ nmol L}^{-1}$, ($S/N = 3$), which were obtained from the signal/noise (S/N) ratio (RIBANI et al.; 2004).

The same detection limit criterion may be adopted for the quantification limit, using the ratio 10:1, i.e., the QL can be calculated using the visual method, the signal-noise ratio.

The proposed procedure was applied to the binary mixtures samples as described in the Experimental Procedure. The degree of closeness between the results obtained using the proposed voltammetry procedure and a reference method was evaluated. The comparison method was UV-Vis molecular absorption spectrophotometry (ALMEIDA et al., 2009). The analyses were conducted in triplicate, from the preparation of three different solutions. Table 2 gives the results obtained.

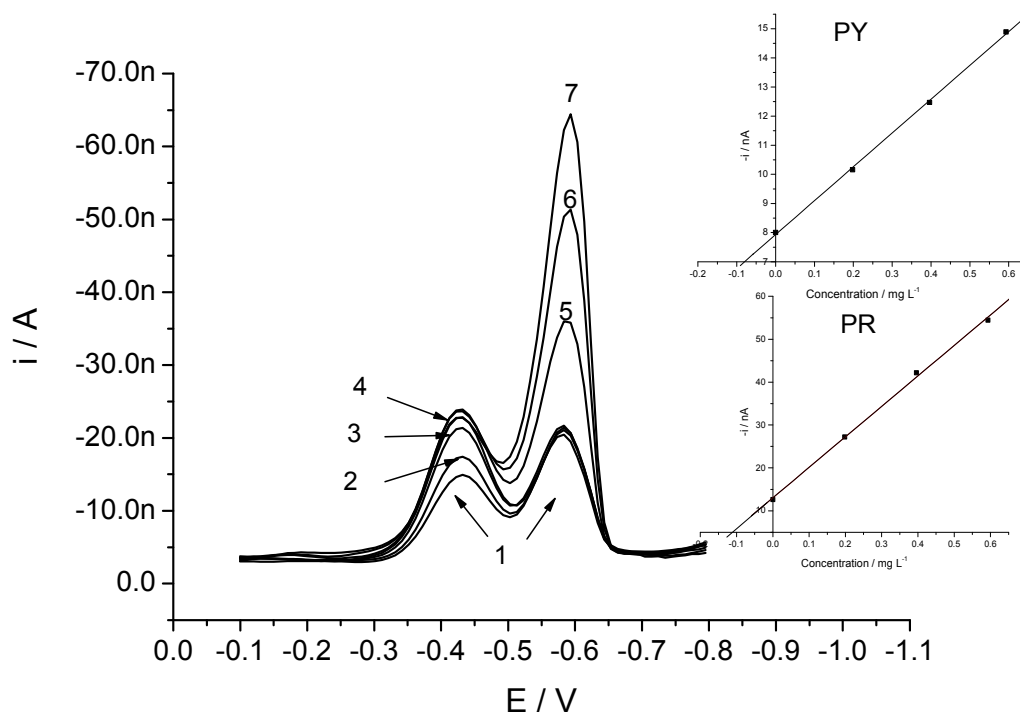
Table 1. Analytical parameters, linear regression equation, correlation coefficient (R), standard deviation (S), limit of detection (LD), limit of quantification (LQ) and linear dynamic range (LDR).

Analyte	Equation	N	R	S	LD nmol L^{-1}	LQ nmol L^{-1}	LDR nmol L^{-1}
PY	$i = 0.3287 + 1.3478 \cdot 10^{-8} C$	17	0.9986	1.104	30.15	101.63	30.15 – 633.15
PR	$i = -2.162 + 1.224 \cdot 10^{-8} C$	11	0.9996	0.719	62.56	208.47	62.56 – 982.291

Table 2. Determination of PY and PR in single samples and binary mixtures.

Sample / Method	Concentration of the dyes \pm S.D. (10–4) mol L ⁻¹ **			
	ACSV*	DS*	ACSV*	DS*
PR	14.11 \pm 0.115a	13.85 \pm 0.431 a	-	-
PY	-	-	14.91 \pm 0.125 b	14.56 \pm 0.214 b
BM	8.922 \pm 0.161 a	9.247 \pm 0.375 a	7.790 \pm 0.226 b	7.902 \pm 0.201b

*ACSV: Adsorptive Cathodic Stripping Voltammetry; *DE: Derivative Spectrophotometry; ** Average of three determinations. Same letters in the same row represent means not significantly different at a confidence level of 95% by t-test.

**Figure 5.** Voltammograms for the mixture of dyes in B-R buffer pH 8.0 (1 – sample; 2, 3 and 4 – subsequent additions of PY dye; 5, 6 and 7 – subsequent additions of PR dye).

The efficiency of the industrial dyeing process was estimated from the concentration of the dyes before and after the process. Table 3 shows the concentrations of the dyes used in the dyeing baths and the concentrations determined using the proposed method.

Table 3. Voltammetric quantification of dyes isolated, and PY and PR in the mixture before and after dyeing process.

Sample	Concentration of dyes		effluent %
	(before) dyeing bath mg L ⁻¹	(after) Waste generated mg L ⁻¹	
PR	6000	2273	37.9
PY	6000	2511	41.9
BM (PR/PY)	5852 / 6196	2487 / 2118	42.5 / 34.2

From the results, it is estimated that more than 34% dye is lost in the effluent.

Conclusion

The proposed derivative voltammetric method was successfully applied to the samples of textile dyes. ACSV proved to be an efficient technique for

the determination and quantification of PR and PY dyes, despite the similarity in their structures, once they can be determined at distinct reduction potentials. The proposed method enables simple, rapid and direct determination of PR and PY dyes in the wastewater resulting from fabric dyeing.

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