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Journal of Chromatography A, 889 (2000) 253–259

JOURNAL OF
CHROMATOGRAPHY A

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Electrochemical treatment of textile dyes and their analysis by high-performance liquid chromatography with diode array detection

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Abstract

Several textile dyes were individually exposed to electrochemical treatment. Chromaticity variation and the formation of degradation products were followed using a UV spectrophotometer and HPLC with diode array detection. Dyes studied belong to the azo (color index, C.I. 15 510), methine (C.I. 48 013), indigo (C.I. 73 040), natural (C.I. 75 760) and arylmethane (C.I. 42 000) classes. Aliquots of the solutions treated at constant potential were analyzed and compared with control dye solutions. The final electrolysis solutions obtained by using different electrode materials: Pt, Ti and diamond presented different chromatograms. It was found that the novel (in this application) diamond electrode is efficient in studying the degradation of various dyes. Possible fragmentation and molecule moiety rearrangement are proposed as a result of the electrochemical treatment. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dyes

1. Introduction

Water plays an important role in textile dying processes and is at the same time the principal stained waste which has to be treated to reduce ecological consequences. Dyes in wastewater can be eliminated by various methods, including flocculation, precipitation, reverse osmosis, adsorption [1] and also oxidative–reductive chemical and photochemical [2] processes. Other techniques comprise radiation and decolorization with ozone in combination with H₂O₂. At this time small-scale oxidizing methods use Fenton's reagent [3], which has lower costs in comparison with ozone process in dye

liquors treatment [4]. The oxidizing effect of the corona discharge is also known and it has been reported as an effective method to destroy biomolecules and to bleach organic dyes using a stainless steel electrode [5]. Electrochemical methods using carbon electrodes have also been tested [6,7] and results reported in Ref. [8] showed an efficient carbon fiber electrode whose performance is comparable with the Fenton's reagent. However, tests are performed by means of in situ colorimetric measurements, or determining parameters like chemical oxygen demand (COD) and total organic carbon (TOC), which are global and show an effect on the dye and on the interfering matrix material too. Therefore, when the analytical question is the dyestuff and its probable products after treatment, chromatographic methods are superior and offer identification possibilities. In this way, the breakdown

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products of three dyes after electrochemical treatment using an iron electrode has been studied in Ref. [7] by means of high-performance liquid chromatography (HPLC).

The purpose of this study was to test several electrode materials in the electrochemical treatment of selected textile dyes, to describe the reduction and oxidation feasibility of the azo and other linkages in the molecule or the formation of derived compounds by means of HPLC with diode array detection (DAD).

2. Experimental

2.1. Chemicals

Dyes were donated from a textile production facility in Puebla. These dyes were chosen as models because of their structure and dye class, extended regional use and its strong absorbance in the visible light region. The molecular structures of the dyes are depicted in Table 1. The following HPLC-grade solvents were obtained from Merck: methanol, ace-

Table 1
Structural formulae and color indices of the studied dyes

No.	Structural formulae	Name	Code	Color index	λ_{\max} (nm)
1		Sandocryl yellow (natural yellow 28)	SLY	75 760	450
2		Sandocryl blue (vat blue 41)	SLB	73 040	620
3		Sandocryl green (basic green 4)	SLG	42 000	620
4		Sandocryl red (basic violet 16)	SLR	48 013	550
5		Sandolan orange (acid orange 7)	SNO	15 510	400

tonitrile, hexane and chloroform. Purified water was obtained from a Milli-Q reagent grade water system. Phosphate buffer was prepared using reagent grade salts from J.T. Baker (Phillipsburg, NJ, USA).

2.2. Equipment

The chromatographic system consisted of a Model Constametric I pump (LDC Analytical, Riviera Beach, FL, USA), a Waters 994 programmable photodiode array detector (Waters Chromatography Division, Milford, MA, USA) operated at 220 nm, and at the maximum wavelength of each dye (see Table 1) and a Model 7125 valve injector (Rheodyne, Cotati, CA, USA) with a 20- μ l loop. The temperature control consisted of a Goldenfoil (Systec, Minneapolis, MN, USA) dual zone column temperature control system and was fixed at 29°C. The chromatographic separations were performed on Beckman columns: ODS (25 cm \times 4.6 mm I.D.) and Octyl (15 cm \times 4.6 mm I.D.). All were stainless steel columns with 5- μ m packing. Diverse mobile phase compositions of methanol–water and acetonitrile–water solutions were used and are indicated in the figures. The mobile phase was prepared by measuring separately and then mixing known volumes of the organic solvents and buffer solution KH_2PO_4 – Na_2HPO_4 with different pH values, which are indicated in the figures, as well as the flow-rate.

Batch electrochemical treatments were carried out in a glass reactor without stirring in the presence of oxygen in a phosphate buffer solution (pH 7) using a potentiostat–galvanostat UAP/LODZ and the electrodes systems described below. Start and electrolyzed solutions were analyzed utilizing a Beckman DU 7500 spectrophotometer.

2.3. Procedures

Prior to each electrolysis UV–Vis spectra of dye solutions were obtained to establish their maximum absorbance wavelength and every dyestuff was chromatographed individually at detection wavelengths λ_{max} and 220 nm. Subsequently, batch solutions of dyes were chromatographed before and after electrochemical treatment. For this purpose each dye was dissolved in a phosphate buffer solution (pH 7). The initial concentration utilized in this work was 500

mg/l and the solution volume in the batch reactor was 50 ml. Under potentiostatic conditions curves current vs. time were registered and aliquots were taken from the batch solution at determined time intervals. Optimum electrolysis time was determined from these curves and by constructing the absorption decay curve with time, which presented a plateau after 2 h. After treatment one half of the batch solution was analyzed and the other half was extracted for 48 h with a hexane–water mixture to perform later analysis of each extract. Aliquots and extracts were kept in polycarbonate or PTFE jars in the darkness under refrigeration. The auxiliary electrodes were washed with water to remove salts and the films formed on its surface were removed by immersion in chloroform or methanol. After evaporation of the organic solvent 1 ml of hexane or methanol was added to the recipient and the solution was also analyzed.

Peak identity confirmation of the electrolysis products was achieved by retention time matching of injected standards and spectra comparison by spectra index. The working electrodes were foils of platinum, titanium and diamond with geometrical areas of 4, 6.5 and 3 cm², respectively. Potentials were +2.2 V, +2.5 V and –2.5 V in the cited order. The corresponding auxiliary electrode for the platinum and titanium working electrodes was Pt and Ni. Diamond was tested both using a Ti and a Ni auxiliary electrode. In all cases a saturated calomel reference electrode was used.

3. Results and discussion

3.1. Electrolyzed samples

Fig. 1 shows representative chromatograms of initial and final solutions of the indigoid SLB, natural SLY and azo SNO dyes using a diamond electrode during the electrochemical treatment. In each case, a marked diminution of the dye peak was observed at detection wavelength 220 nm. The main reason for not selecting the dye maximum absorbance wavelength in this part of the study was the fact that decomposition components presenting absorbance bands in the UV spectral region, could be recorded. As can be appreciated in the amplified

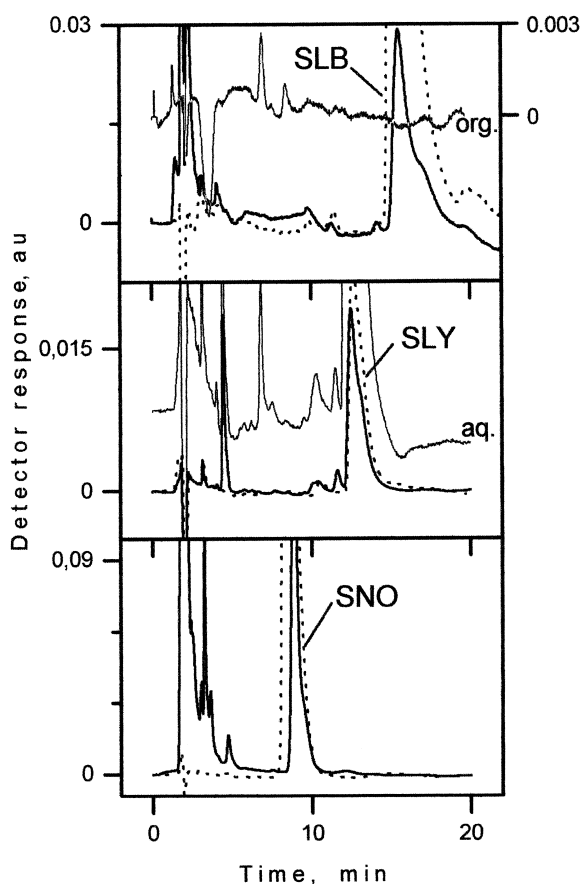


Fig. 1. Chromatograms of the batch solutions before (dotted lines) and after electrolysis (continuous lines) of three dyes on a diamond electrode. Hexane extract of SLB (org.) and aqueous extract of SLY (aq.) (right axis). Column Octyl, flow-rate 0.8 ml/min, temperature 29°C, detection wavelength 220 nm, mobile phase (aqueous phosphate buffer, pH 5)–methanol (50:50) (SLY, SNO) and linear gradient methanol–water (40:60) to (50:50) (SLB).

pictures, there is a set of new components in the solution which present smaller retention times than the dye molecule. This indicates the presence of less hydrophobic compounds regarding the reversed stationary phase and probably, smaller in size. To demonstrate the formation of electrooxidation/electroreduction products of different polarity, analysis of hexane and water extracts of the final batch solutions was carried out. This operation allowed the detection of substances present in low concentration in the mixture, using particularly a 50- μ l injection. Fig. 1 (org.) and (aq.) present some components not

observed before in the final batch solution of the electrochemically treated on a diamond electrode SLB and SLY dyes, respectively.

Detection at the maximum wavelength was used to follow the dependence of the concentration diminution on time. The results obtained for four selected dyes on diamond are shown in Fig. 2A and are compared for SLY and SNO with the chromaticity vs. time curves obtained by UV–Vis spectroscopy. An interesting observation is the similarity of the relative concentration (continuous line) and chromaticity (dotted line) curves for the azo dye

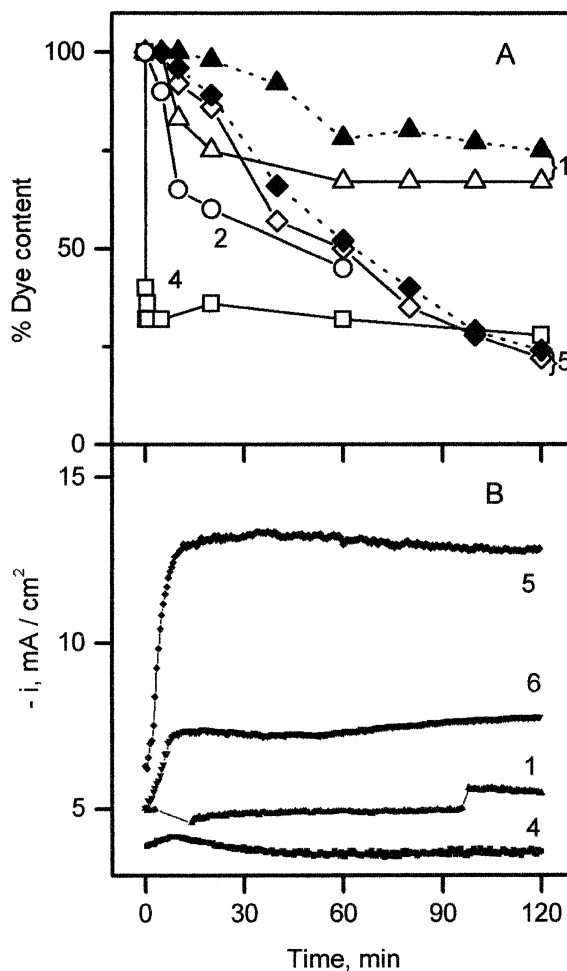


Fig. 2. Dependence of concentration diminution (A, continuous lines) and chromaticity diminution (A, dotted lines) and of current density (B) on electrolysis time on a diamond electrode for SLY (1), SLB (2) and SLR (4) and for SNO (5) and methyl orange (6).

(curve set 2), while the relative concentration curve of the natural dye lies below the chromaticity curve (curve set 1). For this dye near 30% can be decomposed in a 1-h treatment. The methine, indigoid and azo dyes undergo a greater decomposition on the diamond electrode with different velocities. The SLR dye undergoes 70% transformation in 20 min. Further we concentrated our attention on this methine group dye.

The current density curves depicted in Fig. 2B increase and reach a plateau. After a light increase observed in the SLR curve, the current density falls pointing out the formation of a passivating film on the electrode surface. When this dyestuff was treated on Pt and Ni [9] electrodes, the formation of a protective film on the electrode surface was observed. Fig. 3 shows that the composition of the film formed on the Pt electrode during treatment of this dye is a complex mixture of the original dye and its electrooxidation products. The electrochemical processes are known as very complicated phenomena. Here, where very reactive radical species can be

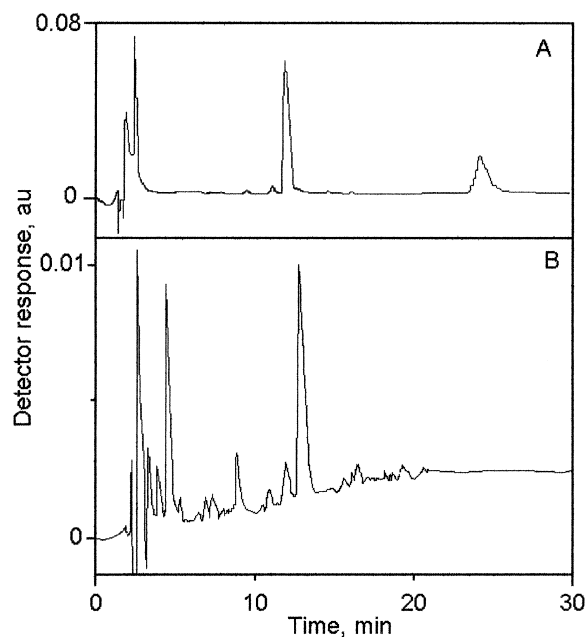


Fig. 3. Chromatograms of Sandocryl red SLR batch solution before electrochemical treatment (A) and of the hexane solution of the film (B) formed on the Pt electrode during treatment. Conditions as in Fig. 1. Mobile phase linear gradient aqueous phosphate buffer, pH 5–methanol (40:60) to (50:50).

formed in the bulk, adsorption occurrence on the electrode surface also plays an important role in the electrochemical–chemical–electrochemical mechanism. Although variations of the π -electrons system in dyes are controlled by the proton activity and concentration, it was observed [8] that the effect of pH is not very significant in the treatment of dyeing wastewater by using a carbon fiber electrode.

Sandocryl red dye SLR solutions presented very close mixture composition after electroreduction on diamond and Ti electrodes. After examination of possible redox reaction paths, probable products could be diethylamine (Fig. 4, peak a), aniline (Fig. 4, peak b), 1,2,3,3-tetramethylindoline (Fig. 4, peak c), *N,N'*-diethylaniline (Fig. 4, peak f), 1,2,3,3-tetramethylindolium and 1,3,3-trimethyl-2-methyleneindolium. Except the indolium species, the mentioned compounds were assigned in the chromatogram by matching retention times under the same conditions and by means of the spectrum index. Spectra correlation factor was higher than 0.9, while the value obtained in the electrolysis solution peaks for a λ_1/λ_2 absorbance ratio was considerably smaller than the ratio for the reference compounds, due probably to the effect of the electrolyte in the electrolyzed sample. The chromatogram in Fig. 4 shows two unidentified peaks (d, e), which present absorbance bands at 330 and 360 nm, respectively. The high stability of the indolinium ion in SLR

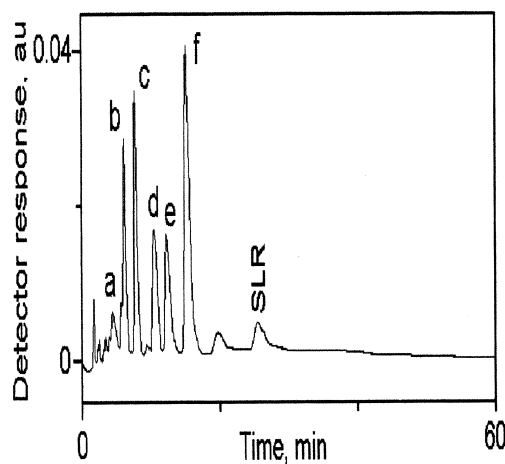


Fig. 4. Chromatograms of the organic extract of the Sandocryl red SLR batch solution after electrolysis using titanium as working electrode. Conditions as in Fig. 3.

accounts probably for the formation of 1,2,3,3-tetramethylindolium and 1,3,3-trimethyl-2-methyleindolium, but they could not be assigned to the peaks.

The chromatograms obtained after electroreductive treatments of methine, indigoid and azo dyes showed several components. As expected, aniline and alkylnilines were common products also obtained in [7,10]. Proposed products in the solution after electrochemical treatment on diamond electrode of SLB are 3,4-dichloroaniline and 3,4-dichloroaminobenzoic acid, of SLY are 2,4-dihydroxybenzoic acid and 1,2-benzenediol and of SNO, aniline and aminonaphthol. The last was confirmed in the chemical reductive cleavage of azo dyes by means of HPLC–mass spectrometry (MS) [10].

3.2. Model mixtures

We concentrated on the HPLC–DAD analytical method for Sandolan and Sandocryl type textile dyes, which cause regional concern. The calibration was calculated in triplicate using electronic integration of individual peaks at two detection wavelengths. Regression is acceptable and correlation coefficients are not less than 0.95 at λ_{\max} and vary $0.91 < R^2 < 0.99$ at λ_1 .

It is known that some dyes are irreversibly retained on ion-exchange columns. Reversed-phase [10,11] and polymeric stationary phases [12] have been used in different stages of method development for dye applications. Octadecylsilane columns using ion pairing reagents were also investigated and have been shown to be suitable for dye analysis. Although

fair resolution of the mixture components in a dye class can be obtained, capacity factor magnitude remains sometimes too large. As example we studied the effect of pH on the separation of the pair of basic dyes SLG/SLR which produced unresolved peaks on an ODS column. Examination of the chromatographic parameters R_s , α and k in Table 2 showed that reduction of the acetonitrile content in the mobile phase up to 40% gave a slight increase in α enabling a definition of two chromatographic peaks, but an increase in retention time at pH 7. The underlying trend observed with the resolution was that an increase in the acidity of the eluent produced a decrease in dye retention improving at the same time the resolution. This fact is also supported by the smaller asymmetry factors presented by the peaks at lower pH values.

We performed then the analysis of different model mixtures of Sandocryl type textile dyes at equivalent concentration levels on both C_{18} and C_8 stationary phases. The octyl stationary phase seemed to be a more convenient column packing in our case as can be appreciated in Fig. 5 when comparing the k values in Table 2 for the pair SLG/SCR. The C_8 column decreased the analysis time but did not resolve well the mixture components in the isocratic mode. Thus, in order to optimize the separation of the second pair, gradient elution was tested and is presented in Fig. 5.

4. Conclusions

Electrochemical treatment using a diamond elec-

Table 2

Resolution, selectivity capacity factor and asymmetry factor calculated at the half height ($F_{1/2}$) and at the third height ($F_{1/3}$) in the separation of Sandocryl green and Sandocryl red dyes in mass relation 1:1^a

pH Value, 40% CH ₃ CN	R_s	Acetonitrile (%), pH 7	α	k		$F_{1/2}$		$F_{1/3}$	
				SLG	SLR	SLG	SLR	SLG	SLR
				5.0	1.1	60			0.53
6.0	1.1	55			0.71	0.64	0.74	0.68	
6.5	0.9	50	1.1	13	14	0.66	0.63	0.70	0.67
7.0	0.8	45	1.1	20	22	0.70	0.68	0.69	0.71
		40	1.2	34	41	0.66	0.66	0.67	0.67

^a Column ODS Beckman, flow-rate 0.8 ml/min, temperature 30°C, detection at 205 nm. Asymmetry factor calculated as $F = w_{\text{tail}} / (w_{\text{front}} + w_{\text{tail}})$, where w is the peak width of the corresponding peak fragment.

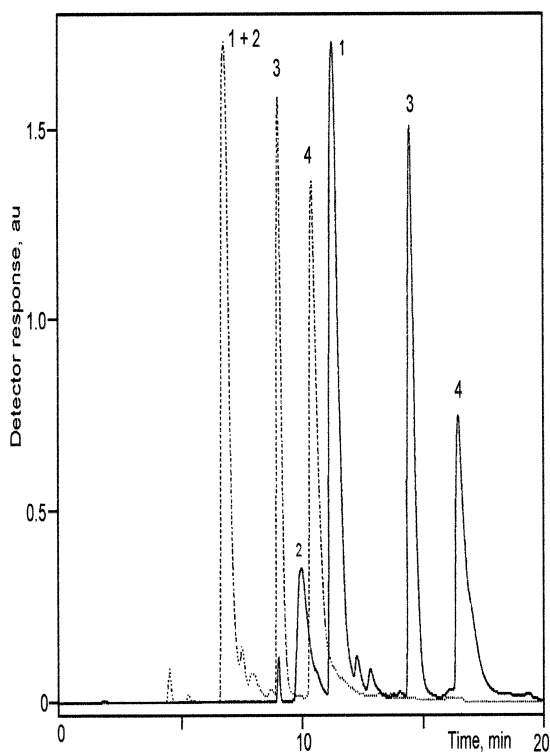


Fig. 5. Separation of Sandocryl dyes: SLB (2), SLY (1), SLG (3) and SLR (4) on Octyl stationary phase. Mobile phase methanol–water using gradient 40–100% (continuous line) and 50–100% methanol (discontinuous line), pH 7, flow-rate 1 ml/min. Detection at 205 nm.

trode is an effective method for the study of the decomposition of textile dyes of different nature. The destruction products identified were aniline and alkyanilines for the studied nitrogen containing dyestuffs. The HPLC analysis presented in this work demonstrate that diode array detection result of more utility than ex-situ extinction measurements or in-situ absorbance monitoring.

Acknowledgements

This work was supported by a research grant of the Sistema de Investigación Ignacio Zaragoza, CONACyT-Puebla (960602001). Dr. J. Juárez-Posadas is thanked for helpful discussion about degradation products.

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