

## Employment of One and Two-Dimensional Nuclear Magnetic Resonance Technique in the Identification of Direct Electrochemical Degradation Products of Textile Reactive Blue 4 Dye

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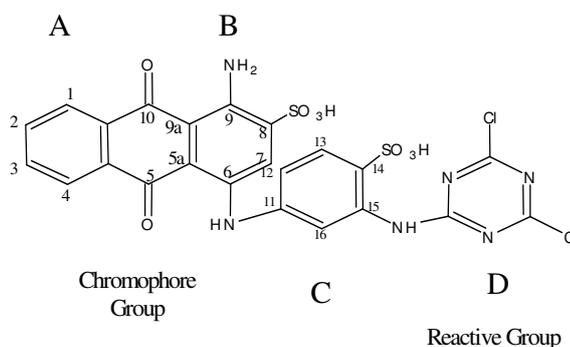
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**Abstract:** Anthraquinone dyes are the most employed class of synthetic colorants in the textile industry, but their effluents can be harmful to the health of living organisms. For this reason, methods for effective color removal and remediation of these textile colours have been strongly requested, such as electroreduction and electrooxidation. In this context, the present work investigates the application of NOESY1D and gCOSY, gHMBC, gHMBC NMR techniques and complementary techniques for the identification of degradation products generated by electrochemical reduction and oxidation of Reactive Blue 4 (RB4), which are employed as treatment methods.

Electrochemical reduction/oxidation was carried out in a Potenciostat/Galvanostat EG&G PAR 283 using a three compartment cell and reticulated glassy carbon electrode, Pt gauzes and Ag/AgCl (3.0mol L<sup>-1</sup>) as working, auxiliary and reference electrodes, respectively. The studies were carried out in a HCl/KCl solution (0.2mol L<sup>-1</sup> pH 2.0) and NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> buffer (0.1mol L<sup>-1</sup> pH 10.0). The products yielded after complete dye reduction and oxidation were extracted and analyzed by NMR spectroscopy in a VARIAN INOVA-500 spectrometer. UV-Vis and Infrared

spectra were obtained in an HP 8453 diode-array spectrophotometer and a Nicolet-Impact 400 spectrometer, respectively. TOC (total organic carbon) measurements were made using a Shimadzu 5000A Total Organic Carbon analyzer. The molecular structure of Reactive Blue 4 dye (RB4) is presented in Figure 1.

The assignment of unidimensional (<sup>1</sup>H NMR and NOESY1D) and bidimensional (gCOSY, gHMBC and gHMBC) spectra of reduced dye at pH 10.0 at potential (E) – 0.9 V are presented in Table 1.



**Figure 1.** Molecular structure of Reactive Blue 4 dye (RB4).

**Table 1.** Chemical shifts and bidimensional correlations obtained from 1D and 2D NMR spectra in CD<sub>3</sub>OD of reduced dye at pH 10.0 at E = -0.95 V.

H	$\delta(1H)$ m J(Hz)	$\delta(C)$ by gHMQC	C correlated by gHMBC	H correlated by NOESY1D
1	7.71 m	132.4		8.22 (2,3)
2	8.22 m	127.0	133.7 (4 a or 10 a)	7.71 (1,4)
3	8,22 m	127.0	133.7 (4 a or 10 a)	7.71 (1,4)
4	7.71 m	132.4	-	8.22 (2,3)
4a	-	133.7	-	-
5	-	n. a	-	-
5a	-	112.6	-	-
6	-	143.0	-	-
7	7.56 d 8	126.8	112.6 (5 a) , 149.2 (9)	7.09 (8)
8	7.09 d 8	129.1	110.2 (9 a) , 143.0 (6)	7.56 (7)
9	-	149.2	-	-
9a	-	110.2	-	-
10	-	n. a	-	-
10a	-	133.7	-	-
11	-	143.6	-	-
12	6.5 dl	111.5	124.8 (14), 110.6 (16)	7.56 (7)
13	7.66 d 8	130.1	143.6 (11), 146.7 (15)	6.50 (11)
14	6.63 d 8	124.8	-	-
15	-	146.7	-	-
16	-	110.6	124.8 (14) , 111.5 (12), 1433.6 (11)	-

The main difference observed between the original dye and its reduced form at pH 2.0, at E = -0.6 V, and at pH 10.0, at E = -0.9 V, is the loss of the sulphone group at position 8 which can be evidenced by the appearance of two doublets, one -at 7.56 and another at 7.09  $\delta$  in the <sup>1</sup>H spectra. In addition, the reduced samples at pH 2.0 at -0.6 V and oxidized at +1.0V present a cleavage of the dye molecule, indicating the disappearance of signals relative

to H12, H13 and H16 of the C ring and consequently loss of the reactive group. The results were also confirmed by spectrophotometry, IR and TOC analysis.

### Reference

1. H. Zollinger, Color Chemistry, 2<sup>nd</sup> ed., V. C. H. Publisher: New York, 1991.