

## ELECTROCHEMICAL REDUCTIONS OF AZO DYES IN AQUEOUS SOLUTIONS

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### ABSTRACT

The electrochemical reduction of azo dyes in aqueous alkaline solutions is investigated. Cyclic voltammetry, controlled potential electrolyses, chronoamperometry and steady state voltammetry at microelectrodes were used to provide insight into the reduction process. With basis on the data obtained from the experimental techniques mentioned above, a mechanism for the reduction reaction is proposed.

### 1. INTRODUCTION

The textile industry is a range of industries with operations and processes as diverse as its products. It is, thus, meaningless to speak of a "typical" textile effluent since the type of fiber involved is the main factor determining the effluent composition, that is, the type and quantities of chemicals present [1].

Most textile wastewaters contain dyes and a particularly important group of these compounds contain the N=N double bond. These dyes are well known pollutants and have to be removed or destroyed prior to discharge of the effluents. The treatment of textile effluents to the extent demanded for discharge to a stream or river is, almost without exception, based on biological processes. The reasons for the dominant position held by these processes appear to be threefold. Firstly, they have been for a considerable time the standard method of treatment of domestic sewage and, therefore, there is a solid background knowledge about them. Secondly, biological processes are more economical to run than alternative procedures capable of giving the same degree of treatment. Finally, they are environmentally compatible.

However, some compounds resist to this treatment and biological processes are no longer useful if the concentration of the contaminants is relatively high or variable. The electrochemical technology can be an alternative way for degradation of organic compounds prior to their discharge, thus contributing in many ways to a better environment [2].

In early papers, Florence [3,4] investigated by polarography the behaviour of several azo compounds and proposed that an unstable hydrazo intermediate is involved in the reduction mechanism.

In this paper a preliminary study of the electrochemical reduction of azo dyes in aqueous solutions at carbon electrodes is presented. The objective of this investigation is to set up the experimental conditions for the transformation of azo dyes into less toxic products.

### 2. EXPERIMENTAL

Chronoamperometry and cyclic voltammetry experiments were carried out using a three-electrode cell and a PAR 375 potentiostat. The data was plotted on a HP 400 printer. The working electrode was the cross section of a vitreous carbon rod ( $r = 3.5$  mm), the secondary electrode was a platinum spiral and the reference was the saturated calomel electrode (SCE). Steady state voltammograms were carried out in a two electrode cell, the working electrode being the cross section of a carbon fiber ( $r = 8$   $\mu$ m) and the reference was the SCE. Controlled potential electrolyses were carried out in a three electrode cell; the working electrode was a carbon disc ( $r = 12.5$  mm) and the secondary electrode was a platinum grid of similar area. The two compartments containing the anolyte and catholyte were separated by an ion exchange membrane. A Hi-Tek potentiostat and a home made integrator were used in these experiments.

The azo dyes used in this study are little soluble in water with exception of those having the sulphonic group as a substituent. For this reason the solutions were all prepared at  $\text{pH} \geq 11$ . All chemicals were of analytical-reagent grade (Merck) and the water used was purified with a E-pure-Barnstead system (18 M $\Omega$ .cm). The azo compounds were synthesised following literature recipes.

### 3. RESULTS AND DISCUSSION

The compounds investigated were classified in two groups, A and B, and are listed in table 1. The compounds in each group have identical electrochemical behaviour and, therefore, results presented and discussed for one of them are valid for the others.

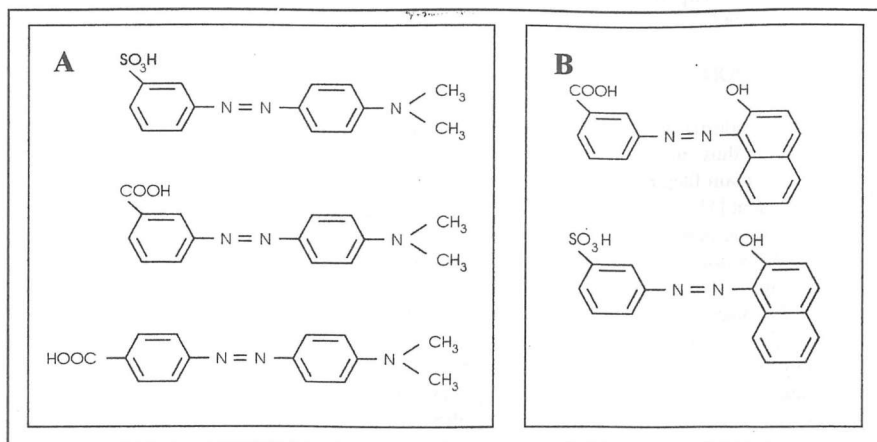


Table 1 - Compounds investigated.

Figure 1 shows a typical cyclic voltammogram of a solution of A in water containing 0.1 M KCl and KOH, pH 12, at a vitreous carbon electrode. A well defined reduction peak is observed at a potential close to -0.9 V vs SCE; when the potential scan is reversed, a broad oxidation peak is displayed at about -0.3 V which is likely to result from the oxidation of a product formed during the reduction process. Similar voltammograms were recorded for a range of scan rates from 50 to 300 mV/s and a plot of  $\log |i_p|$  vs  $\log v$  is a straight line with a slope close to 0.5. This observation indicates that the process is diffusion controlled.

It was also observed that an increase in pH shifts the reduction peak to more negative potentials and this fact suggests that protons participate in the reduction mechanism. On the other hand, a plot of the cathodic peak current vs dye concentration, between  $5 \times 10^{-4}$  and  $10^{-2}$  M, is linear and, therefore, no change in the reaction mechanism is expected in this concentration range. Furthermore, this linear relationship establishes that electrochemical methods may be used in the analytical quantification of these compounds, in this concentration range.

Figure 2 shows a typical cyclic voltammogram observed for compounds of group B, at pH 13. A reduction peak is observed at a potential close to -1.0 V and an oxidation peak appears at about -0.2 V vs SCE during the reverse scan. This oxidation peak is sharper and better defined than that obtained for compounds of group A. Another feature in the behaviour of these dyes is a cathodic peak coupled to the anodic one observed on a second consecutive cycle. This observation only occurs with compounds of group B.

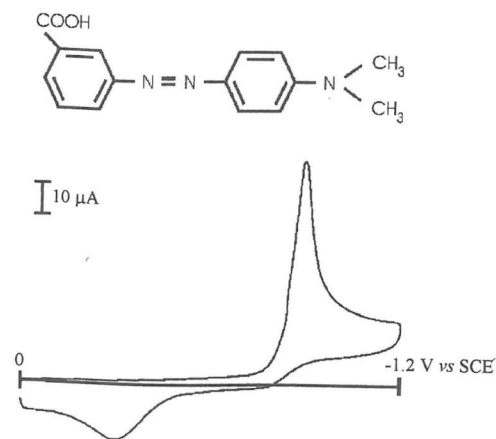


Figure 1 - Cyclic voltammogram of a solution of A  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  in water / KCl (0.1 mol  $\text{dm}^{-3}$ ) / KOH, pH = 12, at a vitreous carbon electrode recorded with a scan rate of 150  $\text{mV s}^{-1}$ .

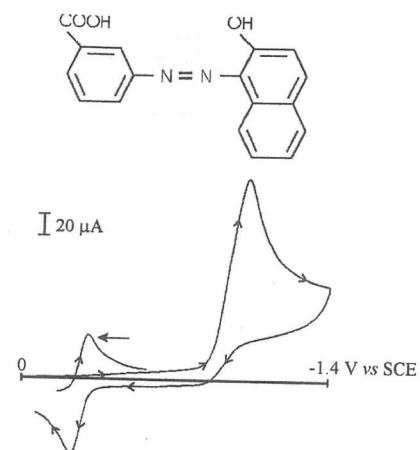


Figure 2 - Cyclic voltammogram of a solution of B  $2.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$  in water / NaOH (1 mol  $\text{dm}^{-3}$ ), pH = 13, at vitreous carbon electrode recorded with a scan rate of 300  $\text{mV s}^{-1}$ .

The number of electrons involved in the reduction process was determined for compounds of both groups, by combining chronoamperometry and steady state voltammetry employing microelectrodes. In this procedure, the electrochemical behaviour of the dye was compared to that of the couple  $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{2-}$  which is well established as a one-electron reversible system.

By combining Cottrell equation,

$$I_d = \frac{nFAD^{1/2}c}{(\pi r)^{1/2}}$$

with the limiting steady state current at a disc microelectrode given by

$$I_l = 4nFDcr$$

both applied to the dye and the reversible system, the number of electrons involved in the reduction of the azo compound is,

$$n_{dye} = \frac{\left[ \frac{I_{d,dye}}{I_{d,rev}} \right]^2}{\frac{I_{l,dye}}{I_{l,rev}}}$$

where  $r$  is the radius of the electrode,  $A$  its area,  $c$  the concentration,  $D$  the diffusion coefficient and the other variables have their usual meaning.

The value of  $n$  obtained was 2 for compounds **A** and between 3 and 4 for compounds **B**.

Controlled potential bulk electrolyses were also carried out and coulometry measurements gave  $n = 2$  for compounds **A**, confirming the results obtained by voltammetry, and  $n = 4$  for compounds **B**, a slight higher value than that obtained by the other method.

The above results may suggest the mechanism of reduction for compounds **A** presented in figure 3. The anodic peak observed on the reverse scan in cyclic voltammetry may be attributed to the oxidation of a reduction product. In figure 4, a possible mechanism for the reduction of compounds

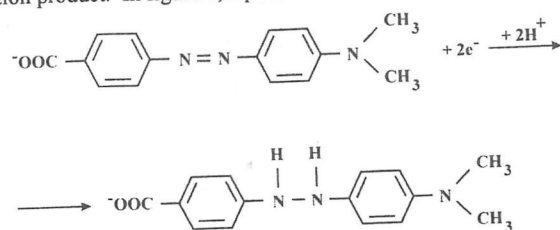


Figure 3 - Proposed mechanism for A.

**B** is suggested, assuming that the number of electrons involved in the reduction process is 4. In this case, after the hydrogenation of the N=N bond, the molecule is cleaved yielding aminobenzoic acid and *ortho*-amino- $\beta$ -naphthol. It is this last compound that is probably oxidised reversibly at approximately -0.3 V vs SCE, thus yielding a cathodic peak in a second consecutive cycle. This was confirmed by cyclic voltammetry experiments of *ortho*-amino- $\beta$ -naphthol in the same conditions; the voltammograms were reversible and the oxidation peak appeared at the above potential.

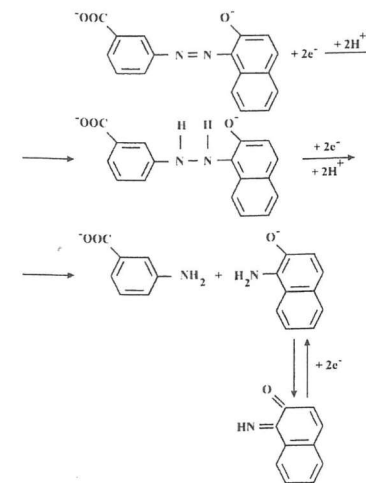


Figure 4 - Proposed mechanism for B.

It should be stressed that these conclusions need further experimental support. In particular, bulk electrolysis products should be identified by chromatography techniques and a more detailed analysis of the voltammetric data should be carried out. While more data are necessary to fully establish the reduction mechanism, it is, however, possible to conclude that, at least with compounds of group **B**, the molecule is cleaved under the used experimental conditions. It may be then possible to degrade these molecules by electrolysis.

### 3. CONCLUSIONS

The results reported here have shown that azo compounds reduce in alkaline aqueous solutions at vitreous carbon electrodes at reasonably mild potentials ( $\geq -1$  V vs SCE). The number of electrons involved was determined by different methods and it was concluded that it depends on the substituents of the azo molecule. At least compounds containing the *ortho*-amino- $\beta$ -naphthol substituent are cleaved into smaller units and the mechanism involves four electrons. Electrochemical techniques may then constitute the basis for a method of treatment of effluents containing these contaminants.

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