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Utilization of Industrial Waste Liquors from the Production of Sulphonated Derivatives of Anthraquinone

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ABSTRACT

The results are presented of investigations on the recovery of anthraquinone from industrial waste liquors containing its disulphonated derivatives, by means of electroreduction. Using a mercury electrode as cathode, a current density of $5{\cdot}6\ A\,dm^{-2}$ *and a pH of 8–9, about 80% of the anthraquinone was recovered. Energy consumption was about* $40\,kWh\,kg^{-1}$ *of recovered anthraquinone. When a zinc cathode was used, about 30% of the anthraquinone could be recovered, but at a much higher energy consumption (about* $1240\,kWh\,kg^{-1}$*).*

1 INTRODUCTION

In the technological synthesis of disulphonated derivatives of anthraquinone, the 1,5-isomer is isolated after dilution of the reaction liquor. On further dilution to *c.* 30% H_2SO_4 and treatment with KCl, the potassium salt of the 1,8-isomer is obtained. The waste liquors from the disulphonation contain about 4–5% of sulphonated products namely:

0·64% sodium salt of anthraquinone-1,5-disulphonic acid (1,5DiSO$_3$Na);
0·65% sodium salt of anthraquinone-1,6-disulphonic acid (1,6DiSO$_3$Na);
0·60% sodium salt of anthraquinone-1,7-disulphonic acid (1,7DiSO$_3$Na);
2·3% potassium salt of anthraquinone-1,8-disulphonic acid (1,8DiSO$_3$K);
0·30% salt of anthraquinone sulphonic acid.

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The components in the waste liquor were determined in the COBR (Research Centre of the Dye Industry) for the Dye Industry in Zgierz by HPLC.[1] The presence of considerable amounts of disulphonated derivatives in the waste liquors results in losses of raw material and in potential pollution problems.

The high toxicity of such wastes and their resistance to biodegradation in the aqueous environment, since none of the presently known systems of biological neutralization can be applied, thus necessitates further purification of the liquors and removal of the disulphonated derivatives.

Investigations carried out by the author indicate that anthraquinone can be recovered in good yield from such industrial wastes.[2,3]

The object of this present paper is to investigate the applicability of electrochemical reduction in recovering anthraquinone from its disulphonated derivatives contained in industrial waste liquors, and to determine the basic parameters of the desulphonation.

2 METHODS OF MEASUREMENT

Investigations were carried out by the potentiostatic method, in order to determine the dependence of the mass of the recovered anthraquinone on the electrode potential. Parameters used were as follows: 200 cm^3 of solution containing 1×10^{-3} mol dm^{-3} 1,5DiSO$_3$Na or 1,8DiSO$_3$K was poured into the electrolyser. The solution was carefully deoxygenated with argon. After reaching a temperature of 298 K, the required potential of the electrode was established. The potential changed from $-1{\cdot}7$ V to $-2{\cdot}4$ V every 100 mV in relation to a saturated calomel electrode. After the reaction was complete, i.e. when a charge of 92 A s had passed through the electrolyser, the solution of the electrolyte was aerated and anthraquinone was formed according to the mechanism shown below. The investigations were carried out in a glass electrolyser with separated electrode compartments, the current being controlled. Mercury and zinc were used as the cathode. The waste liquors, after the precipitate had been separated by sedimentation, were made alkaline with saturated NaOH, and diluted (*r*-fold), to an extent that sodium sulphate did not crystallize. Solutions of the waste liquors thus prepared were placed in the electrolyser and the current was switched on.

In this series of investigations the solutions were not deoxygenated. After electroreduction, i.e. when the required charge had passed through the system, the electrolytic products were aerated, giving a precipitate. The precipitate was separated from the solution, washed with distilled water until the characteristic tests for SO_3^{2-} and SO_4^{2-} ions were negative, and then dried. After drying the precipitate was crystallized from CCl_4 and pure

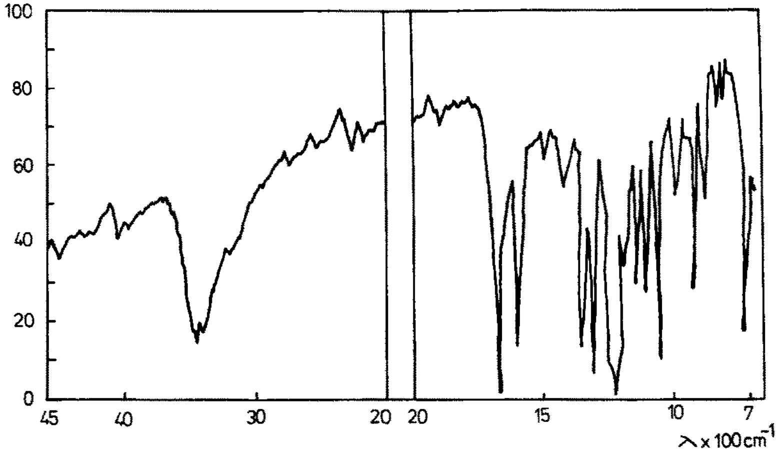


Fig. 1. IR spectrum of the recovered anthraquinone.

anthraquinone was obtained, as confirmed by the melting point $T_t = 558$ K and IR spectrum (Fig. 1) which agrees with that of the pure reference sample.

3 RESULTS AND DISCUSSION

Basic information about the course of the electrochemical process is given by study of the dependence of the current on the potential, carried out in this case by the derivative pulsed volt–amperometry method. The dependence of current on potential for the electroreduction of sodium anthraquinone-1,5-disulphonate is shown in Fig. 2.

From the dependence apparent in this figure, reaction of $1,5DiSO_3Na$ by reduction proceeds in at least three electrode stages. The process of electroreduction is preceded by adsorption of the substrate.[4]

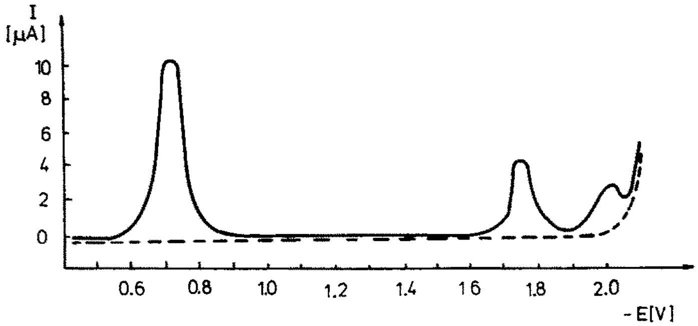
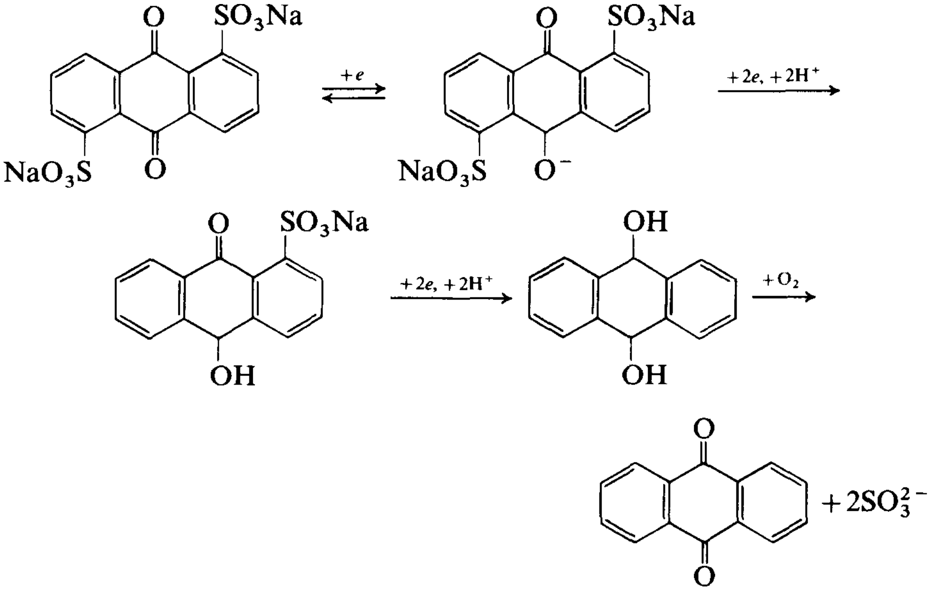


Fig. 2. Differential pulse voltammogram of the reduction of $1,5DiSO_3Na$ on a hanging mercury drop (amplitude 50 mV, time of measurement 100 ms).

Within the potential range from −660 mV to −800 mV the quinone system is reduced and anion radicals are formed, then two sulphonic acid groups are eliminated, the first one in the potential range −1650 mV to −1790 mV and the second one in the range −1870 mV to −1980 mV.[5]

The following scheme of reaction is thus suggested. After electroreduction of the first oxygen in the quinone system, reduction of the other is also possible before desulphonation or during it.



Investigations were carried out to determine the dependence of the weight of the recovered anthraquinone on the electrode potential under potentiostatic conditions.

Analytically pure 1,5DiSO$_3$Na and 1,8DiSO$_3$K diluted in 0·5M NaOH were selected as most representative for the measurements. The change in weight of the recovered anthraquinone in the reduction of 1,5DiSO$_3$Na and 1,8DiSO$_3$K in relation to the change in electrode potential is shown in Fig. 3. From the relationship shown in this figure it follows that at potential −1·7 V$_{SCE}$ anthraquinone can be obtained, as a result of electroreduction of the disulphonated derivatives.

The weight of recovered anthraquinone increases linearly with change in potential to −2·1 V for 1,5DiSO$_3$Na reduction and less regularly for 1,8DiSO$_3$K reduction. Within the range −2·1 V to −2·3 V the amount of anthraquinone slightly decreases, and above −2·4 V again increases. For energetic reasons it is preferred to apply a potential of about −2·1 V. At this potential, reduction of the disulphonic acid derivatives contained in the prepared waste liquors occurred, but under these conditions small yields of about 10–20% were obtained. Therefore further investigations under controlled current intensity were carried out at electrode potentials higher than $-2{\cdot}4$ V. Typical conditions and results of the experiments are presented in Table 1.

Using the Brandon method of multiple regression, a mathematical dependence of the mass yield on the electric charge (Q), current density (j) and dilution (r) was determined.[6] The form of the equation is as follows:

$$\eta_m = 0{\cdot}97(0{\cdot}55r^2 - 1{\cdot}25r + 1{\cdot}12) \times (0{\cdot}03Q^2 - 0{\cdot}19Q + 1{\cdot}23) \times (-0{\cdot}0044j^2 + 0{\cdot}056j + 0{\cdot}85)$$

Based on this dependence, the parameters Q, j and r which allowed maximum yield were determined. These values were: $Q = 5$ A h, $r = 2$, $j = 5{\cdot}7$ A dm^{-2}; and for these parameters the yield obtained was about 82% at an energy consumption about 40 kW h kg^{-1} of recovered anthraquinone, whereas the yield calculated from the above equation is 87%.

Analogous experiments on the electroreduction of disulphonated derivatives contained in waste liquors were carried out using a zinc

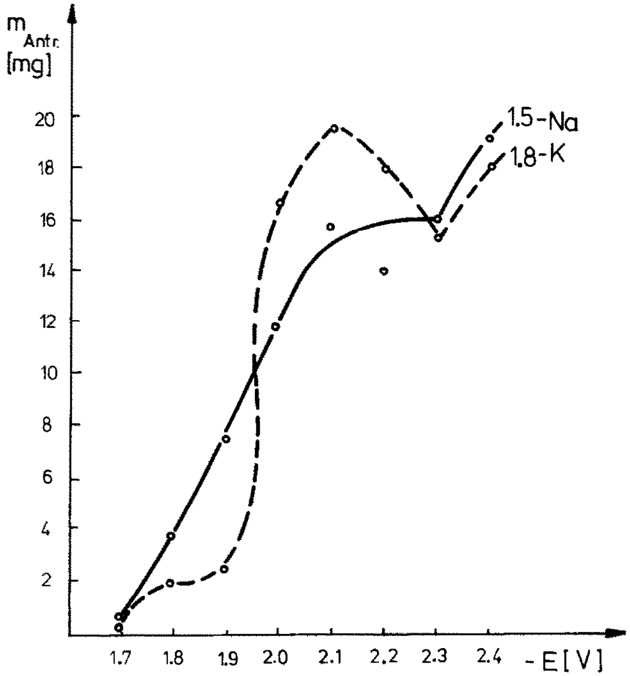


Fig. 3. Dependence of the mass of the recovered anthraquinone on electrode potential during the electroreduction of 1,5DiSO$_3$Na and 1,8DiSO$_3$K.

TABLE 1

Electroreduction of Disulphonated Derivatives of Anthraquinone Contained in Industrial Waste Liquors Using a Mercury Electrode[a]

Lp	Q ($A\,h$)	r	j ($A\,dm^{-2}$)	η_m
1	6·82	0·71	8·18	0·705
2	2·70	0·75	11·33	0·434
3	2·5	0·82	7·87	0·326
4	3·2	0·84	10·07	0·382
5	2·1	0·97	4·41	0·408
6	3·5	1·07	8·81	0·432
7	2·3	1·40	7·24	0·490
8	2·5	2·00	7·87	0·782
9	2·5	2·00	7·87	0·800

[a] Symbols: Q, electric charge; r, dilution; j, current density; η_m, mass yield.

electrode. It was found that maximum recovery was about 30% at a much higher energy consumption of about 140 kW h kg^{-1}.

These experiments thus confirm the possibility of the recovery of anthraquinone from industrial waste liquors containing its disulphonated derivatives.

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