ADAM SOCHA*, ZBIGNIEW GORZKA*

RECOVERY OF ANTRAQUINONE FROM INDUSTRIAL WASTEWATERS CONTAINING DISULFONE DERIVATIVES OF ANTRAQUINONE

The paper presents the results of investigations on recovery of antraquinone from industrial wastes containing its disulfone derivatives by electrochemical method. In the investigations, different electrodes were used, i.e., mercury, zinc and lead ones, but the most desirable results were obtained for the mercury cathode. Under optimum conditions of the reactions, current density equaled to 2.1 A/dm^2 and charge 0.22 Ah; current efficiency of ca 90% and mass efficiency of ca 80% were reached with relatively low energy consumption ca 5 kWh/kg of antraquinone. When the other electrodes were applied, lower current (16–40%) and mass (15–30%) efficiencies were obtained at much higher energy consumption (15–18 kWh/kg).

1. INTRODUCTION

In the technological synthesis of disulfone derivatives of antraquinone only about 50% of antraquinone is used for obtaining desired derivatives substituted in positions 1,5- and 1,8-. Its remaining amount in the form of other disulfone derivatives is wasted by being drained into water reservoirs. The wastes result in excessive pollution of the aqueous environment and also in the loss of valuable raw materials and semi-products.

The aim of this paper was to investigate the useability of the electrochemical reduction method of recovering antraquinone from its disulfone derivatives forming the industrial waste.

2. METHODS AND MEASUREMENTS

The investigations were carried out in a glass electrolyzer with separated electrode spaces. Mercury, copper, zinc, and lead were used as cathodes. Industrial wastes being a mixture of disulfone derivatives of antraquinone, sodium salts of

* Institute of General Chemistry, Technical University of Łódź, 90-924 Łódź, Żwirki 36, Poland.

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antraquinone-1,5-disulfone acid ($1,5\,DiSO_3Na$) and antraquinone-1,6-disulfone acid ($1,6\,DiSO_3Na$) and antraquinone-1,7-disulfone acid ($1,7\,DiSO_3Na$), together with potassium salt of antraquinone-1,8-disulfone acid ($1,8\,DiSO_3K$), were dissolved in 0.5 mole sodium hydroxide. Prepared solutions of suitable concentrations were poured into the electrolyzer. After electroreduction reaction, i.e., when a required electric charge flowed through the system, the electrolytic products were aerated, and as a result a precipitate was formed. The precipitate was separated from the solution, rinsed with distilled water until the reaction characteristic of SO_3^{2-} ions ceased, and then dried. After drying the precipitate was crystallized from CCl_4 so that practically pure antraquinone was obtained, as confirmed by melting point $t_m = 285°C$ and IR spectrum, which agrees with IR spectrum of pure antraquinone.

3. RESULTS AND DISCUSSION

The investigations were started from determining the dependence of the mass of obtained antraquinone on electrode potential under potentiostatic conditions. Change in the mass of obtained antraquinone due to the charge in the potential of mercury cathode for electroreduction of $1,5\,DiSO_3Na$ is presented in fig. 1.
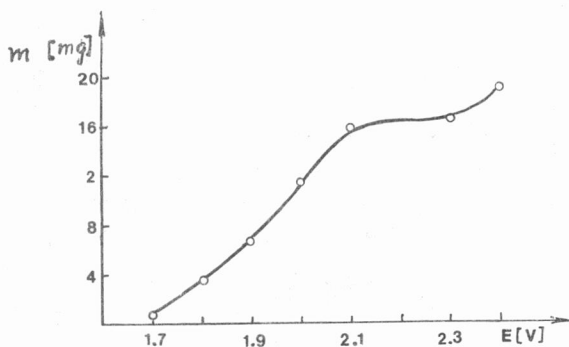

Fig. 1. Dependence of the change in mass of the prepared antraquinone on cathode potential

From the dependence presented in this figure it follows that at the potential as low as $-1.7\,V_{SCE}$ antraquinone can be obtained. The mass of obtained antraquinone increases linearly with a potential increase to about -2.1 V and then is maintained at a constant level, and starting from -2.4 V it again rises. The obtained dependence (fig. 1) allowed determination of the potential value which should be applied in further investigations and corresponding value of current intensity. The most desirable potential value was equal to -2.1 V and it allowed maximum yield before electrolysis of the basic electrolyte took place, and the current intensity value corresponding to it was about 1A [1], [2].

Using the above current intensity and initial concentration of disulfone derivatives of antraquinone equal to 0.0116 mole/dm^3 it was possible to determine the dependence of the mass and current yield of the reaction on the electric charge. Changes in the above dependences are presented in fig. 2. The dependences presented in fig. 2 show that for a constant of substrate the change in current yield accompanying the change in charge reaches the maximum for $Q = 0.1944$ Ah. Further increase of charge results in the lowering of current yield. Mass yield increases also with higher charge up to 0.1944 Ah. Further increasing of the charge brings about a slight increase in mass yield.
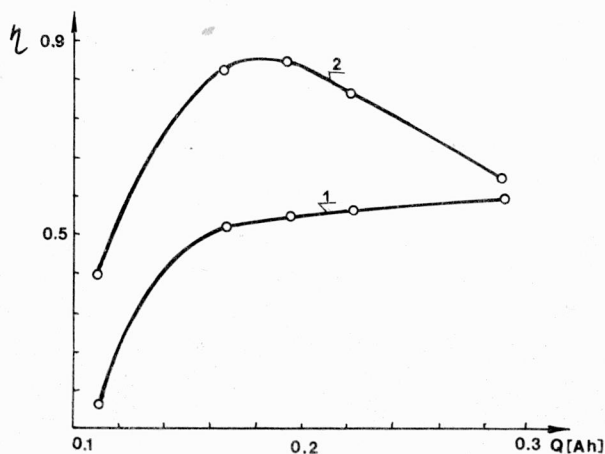

Fig. 2. Changes in mass (curve *1*) and current (curve *2*) yield of electroreduction depending on the electric charge

In order to determine the effect of substrate concentration on the yields obtained, investigations of changes in the reaction yield, depending on the changes in substrate concentration, were carried out.

Concentration of the substrate was changed within the range from 0.006 to 0.052 mole/dm^3, which corresponds to the substrate contents from 2.5 g/dm^3 to 21.5 g/dm^3, respectively. Electroreduction reaction was carried out using a constant electric charge $Q = 0.1944$ Ah and current intensity 1 A, which under experimental conditions corresponds to current density $j = 1.22$ A/dm^2. The results of the measurements are presented in tab. 1.

From the data presented in tab. 1 it is evident that an increase in concentration of a substrate up to $C = 0.0122$ mole/dm^3 is accompanied by a rapid increase in current yield. Further increase of concentration does not result in substantial changes. Mass yield grows with increasing concentration, reaching the maximum for $C = 0.0122$ mole/dm^3. Further increase of concentration brings about the lowering of the mass yield. It is a result of insufficiently high charge flowing through the

electrolyzer. Taking into account the above dependences, i.e., the effect of electric charge, substrate concentration and current density on mass and current efficiencies, their mutual relationship was determined basing on the Brandon method of multiple regression [3], [4].

Table 1

Values current (η_j) and mass (η_m) yields for different concentrations of a substrate

C mole/dm^3	η_j	η_m
0.00626	0.1128	0.1327
0.01221	0.9599	0.5699
0.03120	0.9602	0.4577
0.04550	0.9841	0.3134
0.05200	0.9883	0.1080

The process of electrolysis was considered a three-parameter one and the following parameters were assumed: electric charge Q, substrate concentration C, and current density j. The experiments were carried out within the range of parameter values presented above and assumed the most favourable for the reaction yield. The charge ranged from 0.1111 Ah to 0.45 Ah, substrate concentration from 0.06 to 0.052 mole/dm^3, and current density from 1.22 to 2.84 A/dm^2.

In accordance with the method of estimating regressions of that type, equations describing current and mass efficiencies of the investigated reaction on mercury electrode were derived [3], [4] as follows:

for current efficiency

$$\eta_j = 0.999 \times (139.2\,Q^3 - 124.2\,Q^2 + 32.9\,Q - 1.9)$$
$$\times (94341.2\,C^3 - 9402.7\,C^2 + 281.6\,C - 1.2) \qquad (1)$$
$$\times (0.30\,j^2 - 1.27\,j + 2.3);$$

and for mass efficiency

$$\eta_m = 0.999 \times (32173.2\,C^3 - 3598.05\,C^2 + 110.3\,C - 0.38)$$
$$\times (1280.3\,Q^4 - 1242.6\,Q^3 + 393.4\,Q^2 - 43.3\,Q + 1.85) \qquad (2)$$
$$\times (0.3\,j^2 - 1.26\,j + 2.3).$$

The above equation parameters allow determining the following maximum current and mass efficiencies:

for current efficiency

$$Q = 0.1986 \text{ Ah}, \ C = 0.015 \text{ mole/dm}^3, \ j = 2.1 \text{ A/dm}^2;$$

and for mass efficiency

$$Q = 0.2539 \text{ Ah}, \quad C = 0.0215 \text{ mole/dm}^3, \quad j = 2,1 \text{ A/dm}^2.$$

Electric energy consumption at parameters for maximum current efficiency was about 4.79 kWh/kg of the recovered antraquinone.

Adequacy of the above equations was estimated by comparison of the efficiencies obtained in the experiments for selected parameters with those calculated from equation (1) or (2). Exemplary results are given in tab. 2. Relative error calculated from the dependence $(\eta_{jc} - \eta_{je})/\eta_{jc} \times 100\%$ is small, thus the obtained equations may be assumed to describe the process correctly within the range of applied parameters.

Table 2

Values of current efficiency: experimental ones (η_{je}) and those calculated from equation (1) (η_{jc}) for corresponding Q, C and j

Q Ah	C mole/dm^3	j A/dm^2	η_{jc}	η_{je}	Relative error (%)
0.1944	0.0122	2.26	0.814	0.855	4.86
0.2222	0.0122	2.26	0.794	0.787	0.93
0.4444	0.0122	2.26	0.402	0.410	2.12
0.1111	0.0122	2.26	0.415	0.414	0.34

Measurements with cathodes of amalgam copper, lead and zinc were carried out in the way analogous with the investigations of electroreduction of disulfone derivatives of antraquinone on mercury electrode. The reaction parameters were planned in such a way as to allow different charge flowing through the electrolyzer, i.e., higher and lower than the theoretical one for the reduction of the substrate.

Equations describing dependences of current and mass efficiencies on the parameters applied for individual electrodes were determined by means of the

Table 3

Value of current (η_j) and mass (η_m) efficiencies, electric energy consumption and parameters in electroreduction of disulfone derivatives of antraquione on different electrodes

Electrode	Q Ah	C mole/dm^3	j A/dm^2	η_j		η_m		E kWh/kg
				η_{je}	η_{jc}	η_{me}	η_{mc}	
Mercury	0.199	0.015	2.1	0.87	0.88	–	–	4.8
	0.254	0.022	2.1	–	–	0.74	0.77	–
Amalgam	0.215	0.007	1.03	0.16	0.13	–	–	–
Copper	0.244	0.007	2.69	–	–	0.31	–	26
Zinc	1.26	0.035	0.5	0.38	0.41	–	–	–
	1.38	0.009	0.93	–	–	0.15	0.17	15
Lead	0.333	0.052	2.09	0.16	0.17	–	–	–
	0.333	0.02	1.5	–	–	0.26	0.31	18

Brandon method of multiple regression. Basing on the equations, parameters for obtaining maximum current and mass efficiencies on individual electrodes were calculated. The results of experiments and calculations are presented in tab. 3.

4. CONCLUSIONS

Investigations of electrochemical reduction of disulfone derivatives of antraquinone suggest the following conclusions:

1. Application of the above method allows about 80% recovery of antraquinone industrial wastes containing its disulfone derivatives.

2. The reaction is mostly effective when mercury electrode is applied. Mass efficiency is then ca 80%, current efficiency, ca 90%, and electric energy consumption, ca 5 kWh/kg of the recovered antraquinone.

3. Other cathodes, i.e., zinc or lead ones, can also be used. Application of lead cathode is justified when the process is carried out by means of continuous method.

4. Application of electrodes other than the mercury ones results in about a threefold increase in energy consumption.

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ODZYSKIWANIE ANTRACHINONU ZE ŚCIEKÓW PRZEMYSŁOWYCH
ZAWIERAJĄCYCH JEGO DISULFONOWE POCHODNE

Przedstawiono wyniki badań metodą elektrochemiczną odzyskiwania antrachinonu ze ścieków przemysłowych zawierających jego disulfonowe pochodne. Stosując różne elektrody, a mianowicie: rtęciową, cynkową i ołowianą, najkorzystniejsze rezultaty uzyskano z katodą rtęciową. W optymalnych warunkach reakcji, tj. gęstości prądu 2,1 A/dm^2 i ładunku 0,22 Ah, uzyskano wydajność prądową ca 90% oraz wydajność masową ca 80% przy stosunkowo nieuiżym zużyciu energii równym ca 5 kWh/kg antrachinonu. W przypadku stosowania pozostałych elektrod uzyskiwano niższe wydajności prądowe (16–40%) oraz masowe (15–30%) przy znacznie wyższym zużyciu energii (15–18 kWh/kg).

РЕГЕНЕРАЦИЯ АНТРАХИНОНА ИЗ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД, СОДЕРЖАЩИХ ЕГО ДИСУЛЬФОННЫЕ ПРОИЗВОДНЫЕ

Представлены результаты исследований электрохимическим методом регенерации антрахинона из промышленных сточных вод, содержащих его дисульфонные производные. Применяя разные электроды, а именно: ртутный, цинковый и свинцовый, самых полезных результатов достигли с ртутным катодом. В оптимальных условиях реакции т.е. плотности тока 2,1 А/дм² и заряде 0,22 ампер-час, получили производность тока ок. 90% и производность массы ок. 80% при относительно небольшом потреблении энергии равным ок. 5 кВч/кг антрахинона. В случае применения остальных электродов получили низшую производность тока (16–40%) и массы (15–30%) при значительно большем потреблении энергии (15–18 кВч/кг).