Rapid determination of the fouling of electrodialysis membranes by industrial effluents

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Abstract

A simple membrane fouling cell was evaluated to determine the fouling potential of industrial effluents for treatment by electrodialysis (ED). Membrane fouling was found to be highly sensitive to dodecylbenzene-sulphonate (DBS) concentration. Severe fouling was obtained with 100 and 50 mg/lDBS while very little or no fouling took place with 10 mg/lDBS. The real fouling situation appears to be much more complicated than envisaged. A bleaching effluent showed a low fouling potential while a soap and detergent effluent showed severe membrane fouling. From these preliminary experiments it appears that a simple membrane fouling cell can be used to determine rapidly the fouling potential of industrial effluents to evaluate their suitability for treatment by ED.

Introduction

Electrodialysis is largely used for the demineralization of brackish waters that do not contain a high content of organic material. Large organic anions tend to foul anion-permeable membranes (Korngold, 1976) and this can be a serious problem in the practical application of electrodialysis. Fouling causes an increase in membrane resistance which, in turn, causes an increase in power consumption and adversely affects process economics. Many potentially promising electrodialysis applications for the treatment of industrial effluents or contaminated surface waters are rendered ineffective by this type of organic fouling. It is useful, therefore, to have a simple method available to rapidly determine the fouling potential of a particular feed water.

Several cells for measuring membrane fouling by synthetic foulants are described in the literature (Korngold et al., 1970); Kusumoto et al., 1973). These 'fouling cells' have been used to study the mechanism of fouling or to compare the fouling behaviour of different membranes under different conditions in the laboratory. A disadvantage of the static fouling cell described by Kusumoto et al. (1973) is that very little effluent (± 200 ml) can be tested, and that pH changes which originate in the electrode compartments of the two-cell unit may interfere with fouling measurements. Large volumes of effluent (50 l and more) can be tested with the multi-cell flow-through fouling cell described by Korngold. Such a cell was constructed and in preliminary experiments evaluated for the determination of the fouling potential of industrial effluents prior to electrodialysis treatment. The test cell was first evaluated on a common foulant, viz. dodecylbenzene-sulphonate (DBS) before it was applied to industrial effluents for evaluation.

Fouling

Organic fouling of anion-permeable membranes could take place in a number of ways (Korngold, 1976):

- (a) The anion is small enough to pass through the membrane by electromigration but causes only a small increase in electrical resistance and a decrease in permselectivity of the membrane;
- (b) the anion is small enough to penetrate the membrane, but its electromobility in the membrane is so low that its holdup in the membrane causes a sharp increase in the electrical resistance and a decrease in the permselectivity of the membrane; and
- (c) the anion is too big to penetrate the membrane and accumulates on the surface (to some extent determined by the hydrodynamic conditions and also by a phase change which may be brought about by the surface pH). The decrease in electrical resistance and permselectivity of the membrane are slight. The accumulation can be removed by cleaning.

In case (c) the electrodialysis process will operate without serious internal membrane fouling and only mechanical (or chemical) cleaning will be necessary. Case (b) would make it almost impossible to operate the electrodialysis process. In case (a), the electrodialysis process can be used if the concentration of large anions in solution is low or if the product has a high enough value to cover the high electrical energy costs.

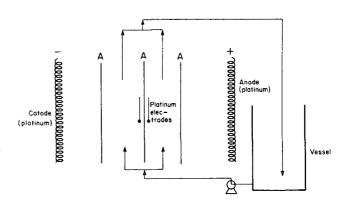


Figure 1
Flow-through fouling cell with tangential inflows. A = anion permeable membrane

TABLE 1 MEMBRANE RESISTANCE $\Omega.\text{cm}^{-2}$, BEFORE AND AFTER FOULING WITH DIFFERENT DBS CONCENTRATIONS

Fouling time,	DBS concentration in feed		
	10 mg.ℓ ⁻¹ DBS	50 mg.ℓ ⁻¹ DBS	100 mg.ℓ ⁻¹ DBS
0	58,0	58,0	58,0
1,5	•	·	95,5 (90,0*)
3,5			163,0 (138,0)
4,5		94,6 (93,6)	210,0 (191,0)
10		163,0 (162)	536,0 (376,0)
44	59,2		, ,

^{*}Values between brackets show resistance values after membranes have been mechanically cleaned.

TABLE 2 AMOUNT OF DBS $\mathrm{mg.\ell^{-1}}$ IN ANODE COMPARTMENT, I.E. DBS MIGRATED THROUGH THE ANION PERMEABLE MEMBRANES

Fouling time,	DBS concentration in feed			
	10 mg.ℓ ⁻¹ DBS	50 mg.ℓ ⁻¹ DBS	100 mg.ℓ ⁻¹ DBS	
2	0	0	0	
4	0	0	0	
6	1,5	0	0	
8	5,8	0	0	
10	7,2	0	0	
12	7,9	0	-	
14	13,1	0	-	
16	14,9	3	-	
18	18,0	9	-	

Experimental

A simplified diagram of the fouling cell with tangential inflows and a photograph of it are shown in Figures 1 and 2 respectively.

The fouling apparatus consists of four perspex cells which can be clamped together to hold the membranes $(7.1 \text{ cm}^2 \text{ exposed area})$ in position. Approximately $100 \, \ell$ of solution is circulated through the two middle compartments and a $0.1 \, \text{M}$ sodium

chloride solution through the electrode compartments (not shown in Fig. 1). Where necessary, the conductivity of the test solution is increased by addition of a solution containing about 5 or 10 g/ ℓ NaCl. A DC current density of 20 mA/cm² membrane area is used to supply the motive force for ion migration. The voltage drop across the central membrane is measured with platinum electrodes connected to a high resistance vacuum tube voltmeter. An increase in potential drop across the membrane in-

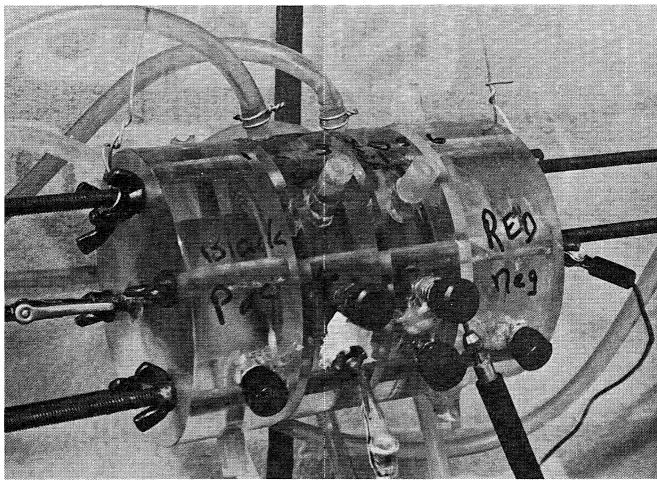


Figure 2
Photograph of flow-through fouling cell.

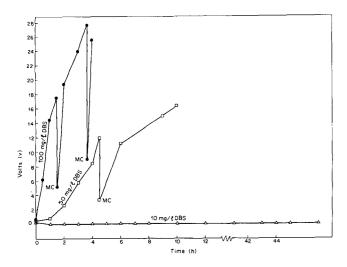


Figure 3

Effect of different DBS concentrations and mechanical cleaning (MC) on the fouling of Selemion AMV membranes.

dicates fouling. The AC membrane resistance before and after fouling were measured in a 0,5 N NaCl solution. DBS concentrations were measured with a spectrophotometer at 223 nm.

Results and discussion

Membrane fouling with different DBS concentrations

The fouling of Selemion AMV (anion permeable) membrane with different DBS concentrations is shown in Figure 3. The AC membrane resistance (ohm.cm⁻²) before and after fouling is shown in Table 1 and the amount of DBS that passed through the anion membrane is shown in Table 2.

The results (Figure 3 and Table 1) demonstrate that in this case membrane fouling is highly sensitive to DBS concentration. Severe fouling was obtained with 100 and 50 mg/ ℓ DBS while very little or no fouling took place with 10 mg/ ℓ DBS. A high fouling potential can therefore be determined quickly with the simple fouling test in the laboratory.

Mechanical cleaning (removal of surface fouling) only had a temporary effect on membrane resistance (Figure 3) and the membrane resistance could not be reduced to what it originally was (Table 1). At the elevated concentrations both surface fouling and internal fouling took place. As fouling proceeded, membrane fouling occurred at approximately the same rate as before cleaning. DBS passed through the anion permeable membrane to a substantial degree only at the lowest DBS concentration of 10 mg/ ℓ (Table 2).

In this case a situation in between categories (a) and (b) (mentioned before) occurs with the addition of surface accumulation at the higher concentrations. At the lowest DBS concentration the DBS ions are relatively few compared to the inorganic ions. They may move through the membrane at a lower speed than the chloride ions but there are too few DBS ions to impede overall ionic transfer. At an elevated DBS concentration the frac-

tion of the ionic paths containing slow-moving DBS ions is so high that it has a marked effect on membrane resistance. The ionic flow through unobstructed paths increases but also the entry of DBS ions into these 'open' paths. The obstruction is thus accelerated. Furthermore, as more ions try to enter fewer 'open' paths at the surface, a surface accumulation of the relatively large DBS ions occurs. In addition, it is likely that the presence of closely spaced DBS ions in a membrane pore may cause local structural (swelling) changes which decrease the mobility of ions in the area. The real fouling situation thus appears to be considerably more complicated than envisaged in Korngold's categorization.

The fouling potential of industrial effluents

The fouling potential was determined also with a bleaching effluent from a paper factory with a COD of approximately 800 mg/ ℓ and with a soap and detergent effluent from a detergent factory with a COD of approximately 5 300 mg/ ℓ (Figure 4). For the bleaching effluent membrane fouling potential was low or nil. Therefore, pilot tests could be considered to determine the economics of treatment by electrodialysis. For the soap and detergent effluent severe membrane fouling occurred and electrodialysis treatment should not be considered.

Conclusions

- Membrane fouling is highly sensitive to DBS concentration. Severe fouling was obtained with 100 and 50 mg/ ℓ DBS while very little or no fouling took place with 10 mg/ ℓ DBS. A high fouling potential can therefore be determined quickly in a sample fouling cell in the laboratory.
- DBS causes internal and surface membrane fouling. The real fouling situation appears to be much more complicated than envisaged in Korngold's categorization.

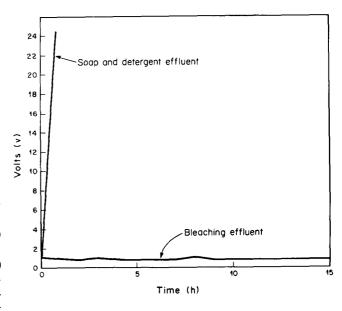


Figure 4

Effect of a bleaching and a soap and detergent effluent on the fouling of Selemion AMV membranes.

 It appears that a simple membrane fouling cell can be used to determine rapidly the fouling potential of industrial effluents to evaluate their suitability for treatment by electrodialysis.

Acknowledgement

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