FLUOROCARBON COATING OF ION-EXCHANGE MEMBRANE SURFACES TO OVERCOME FOULING AND GENERAL SCALING

BY

S PETERS

CONTRACT REPORT TO THE

WATER RESEARCH COMISSION

BY

ESKOM TECHNOLOGY RESEARCH AND INVESTIGATIONS
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CLEVELAND
2022

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EXECUTIVE SUMMARY

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1. BACKGROUND AND MOTIVATION FOR THE PROJECT

In South Africa, and in particular at Eskom, electrodialysis (ED) is used largely for the desalination of saline waters. One of the major problems in the ED process is the fouling of permselective membranes. This may be caused by the precipitation of colloids on the membranes. In addition, as most of the colloids present in natural waters are negatively charged, it is generally the anionic membranes which are affected.

Poisoning of membranes may be defined as the fixation of organic, multivalent and/or counter-ions within the membranes. These ions have a molecular mass of between 200 and 600 g mole^{-1}. If the ion is small enough to pass through the membrane by electromigration, a slight increase in the electrical resistance of the membrane, and a corresponding decrease in the permselectivity of the membrane can be expected. Therefore, the ED process is then economic, only if a high value product is produced. If the anion is small enough to penetrate the membrane, but has a low electromobility within the membrane, poisoning occurs. The retention of ions in the membrane causes a sharp decrease in permselectivity, and a sharp increase in electrical resistance of the membrane. The ED process then becomes virtually impossible to operate economically. If the anions are too large to penetrate the membrane, they will accumulate on the surface, and can then be removed by mechanical cleaning. Therefore, decreases in electrical resistance and permselectivity are negligible. Fouling or poisoning of membranes decreases their lifespan, resulting in more frequent replacement costs.

2. OBJECTIVES OF THE PROJECT

The objective of this research programme was to develop a suitable coating for anionic electrodialysis membranes, to prevent fouling and general scaling thereof by organic colloids present in natural waters. The aims of the study were as follows:

- To determine the effects of coating thickness of a fluorocarbon or polyvinyl alcohol (PVOH) layer on the reduction of flux.
- To provide a membrane with an extended operating life and a reduction in mechanical cleaning requirements.
- To determine the ion-exchange capacities and electrical resistance of the coated membranes.
- To perform a feasibility study into the full-scale implementation of the coating technique, by means of a pilot plant.

3. SUMMARY OF THE MAJOR RESULTS AND CONCLUSIONS

The major results of the project are summarised as follows:

- Upon application of the fluorosurfactants and PVOH as surface coatings, membrane ion-exchange capacities, and therefore permselectivities decreased below the required limit.
- In all cases, desalination properties decreased upon application of surface coatings. An increase in coating layer thickness resulted in a decrease in flux or desalination properties.
- Only in certain cases, was a greater resistance to fouling exhibited, when compared to the uncoated reference membrane.
- Membrane electrical resistance decreased with increasing fluorocarbon and PVOH layer thickness (coating concentration).
- The application of coatings to membranes did not provide the desired enhancement of mechanical cleaning requirements.

4. STATE OF THE PROJECT

Achievement of Contract Objectives

The contract objectives were met.

Contribution Made to the State of the Art

Previous work concentrated on the change in electrodialytic properties of ion-exchange membranes when the electrodialysis was carried out in the presence of the surface active agent. The change in electrical resistance of the membrane, the current efficiency of the ED system and the amount of surface active agent that permeated through the membrane, was investigated.

This research programme was aimed at developing a surface coating for membranes utilising PVOH and fluorocarbon surface active agents. After application of the coating, the desalination and anti-fouling properties of the membranes were determined.

Actions to be Taken as a Result of the Findings

Based on the findings of this project, it is considered that the use of fluorocarbon surfactants and PVOH as surface coatings for anion transfer, electrodialysis membranes is unsuitable.

5. RECOMMENDATIONS FOR FURTHER RESEARCH AND TRANSFER OF TECHNOLOGY

It is recommended that more emphasis be placed on pretreatment of feed water to the ED system, to alleviate the problem of membrane fouling. If membrane fouling did not occur, organic foulants would pass through the ED system. The presence of organics in cooling water would aid the growth of bacteria, thereby increasing biocide dosage requirements.

The effect of the reduction in membrane electrical resistance with increasing coating concentration on the current efficiency of the ED system, should be investigated. A financial feasibility study will have to be undertaken, to establish if the decrease in desalination or flux, warrants the increase in current efficiency of the ED process, as well as the increase in anti-fouling properties of the membranes.

It is proposed that Mr Peters use the research results for the attainment of a higher degree.

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1. INTRODUCTION

In South Africa, and in particular at Eskom, electrodialysis (ED) is used largely for the desalination of saline waters. One of the major problems in the ED process is fouling of permselective membranes. This may be caused by precipitation of colloids on the membranes. In addition, as most of the colloids present in natural waters are negatively charged, it is generally the anionic membranes which are affected.

Poisoning of membranes may be defined as the fixation of organic, multivalent and/or counter-ions on or within the membranes. These ions have a molecular mass of between 200 and 600 g $mole^{-1}$. If the ion is small enough to pass through the membrane by electromigration, a slight increase in the electrical resistance of the membrane, and a corresponding decrease in the permselectivity of the membrane can be expected. Therefore, the ED process is then economic, only if a high value product is produced. If the anion is small enough to penetrate the membrane, but has a low electromobility within the membrane, poisoning occurs. The retention of ions in the membrane causes a sharp decrease in permselectivity, and a sharp increase in electrical resistance of the membrane. The ED process then becomes virtually impossible to operate economically. If the anions are too large to penetrate the membrane, they will accumulate on the surface, and can then be removed by mechanical cleaning. Therefore, decreases in electrical resistance and permselectivity are negligible. Fouling or poisoning of the membranes decreases their lifespan, resulting in more frequent replacement costs [1, 2, 3].

The objective of this research programme was to develop a suitable coating for anionic electrodialysis membranes, to prevent fouling and general scaling thereof, by organic colloids present in natural waters.

The aims of the study were as follows:

- To determine the effects of coating thickness of a fluorocarbon or polyvinyl alcohol (PVOH) layer on the reduction of flux.
- To provide a membrane with an extended operating life and a reduction in chemical or mechanical cleaning requirements.
- To determine the ion-exchange capacities and electrical resistance of the coated membranes.
- To perform a feasibility study into the full scale implementation of the coating technique, by means of a pilot plant.

2. PRINCIPLES OF ELECTRODIALYSIS (ED)

Electrodialysis is an electrochemical separation process in which ions are transferred through membranes, from a less concentrated to a more concentrated solution. This transfer results from the flow of direct electric current. The basic building block of the ED system is the membrane stack. These stacks consist of repeated cation and anion transfer membranes. The spaces between the membranes represent the flow paths of the demineralised and concentrated streams respectively. These flow paths are formed by plastic separators between each cation and anion membrane (figure 1). In the membrane stack, spacers are arranged so that all the individual demineralised and the concentrated streams are manifolded together respectively. A repeating section is called a cell pair and consists of the following:

- Cation transfer membrane
- Demineralised water flow spacer
- Anion transfer membrane
- Concentrated water flow spacer

A typical industrial membrane stack may have from 300 to 500 cell pairs. As water flows across the membrane surfaces, ions are electrically transferred through the membrane from the demineralised stream, to the concentrated stream, due to a direct current potential. Top and bottom steel plates are used, with tie rods, to compress the stack and seal the membranes and spacers. Thus, discrete concentrated and demineralised flow paths are formed and leakage from the sides of the membrane stack is prevented [4].

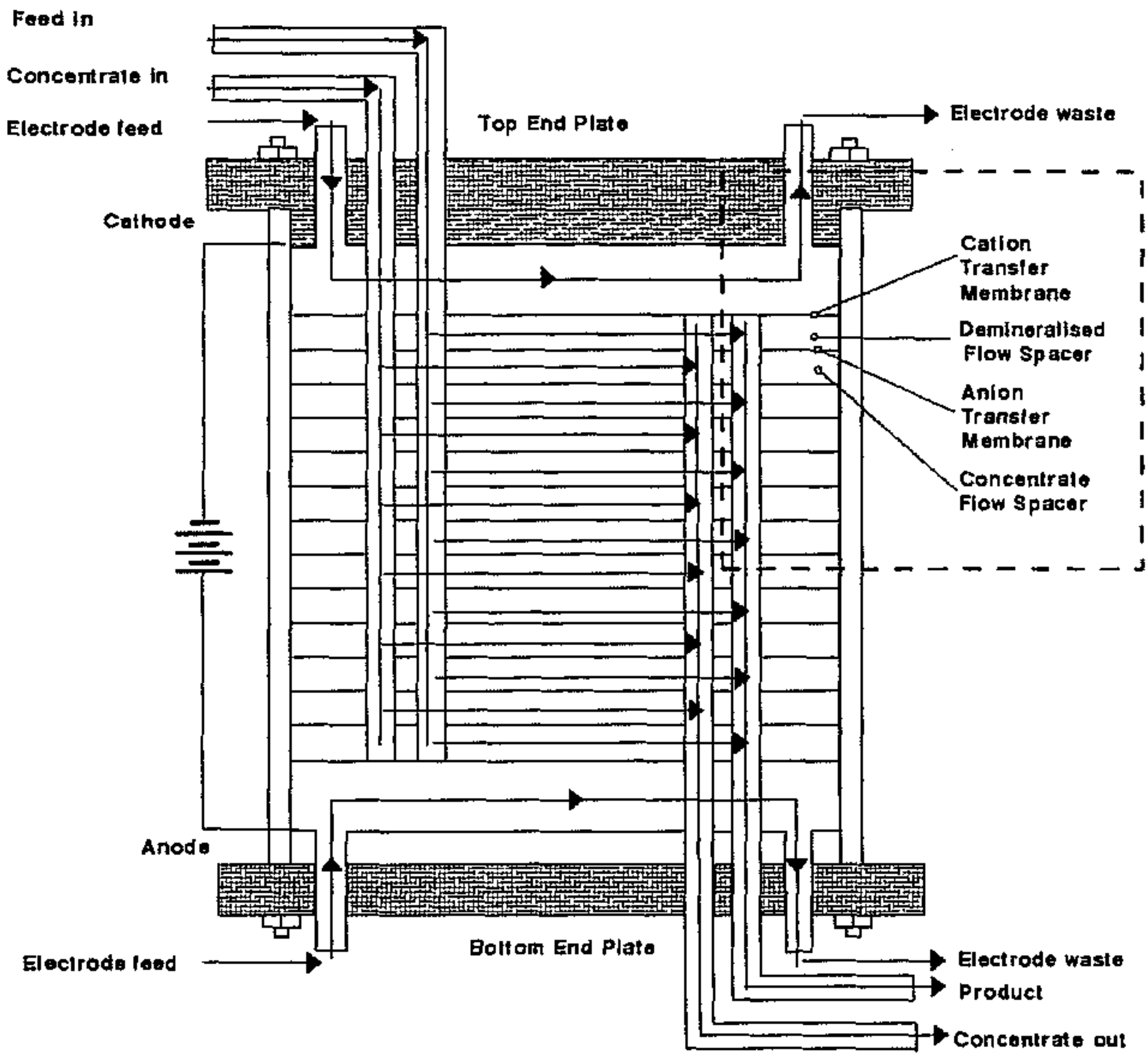

FIGURE 1

Illustration of the flow of the concentrated and demineralised streams through the membrane stack

2.1 Membranes

Two types of membranes are utilised in the ED process, namely anion and cation transfer membranes. The physical appearance of a membrane is that of a plastic sheet. The membrane is reinforced with a synthetic fibre cloth. The surfaces are uniformly flat, with a smooth texture.

2.1.1 Anion Transfer Membranes

Anion transfer membranes are manufactured from a styrene divinylbenzene copolymer. During the production of these membranes, positively charged ions are affixed to sites throughout the membrane matrix. These fixed ionic charges are quaternary ammonium ions and therefore repel positively charged ions, allowing only negatively charged ions to transfer through the membrane. Figure 2 shows the chemical structure of a typical anion transfer membrane [4].

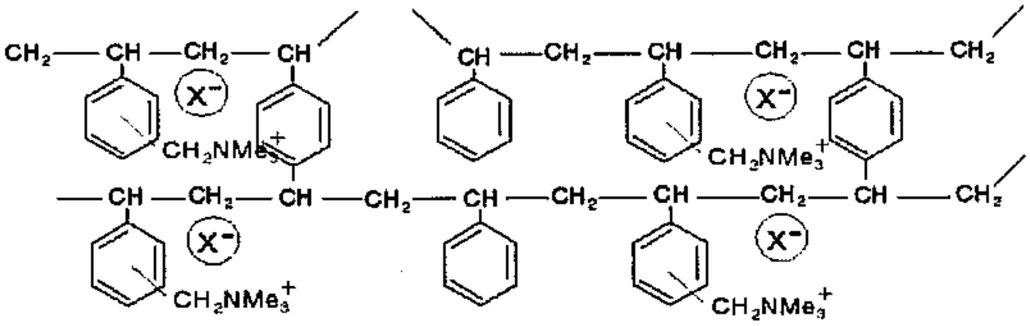

FIGURE 2
Structure of a typical anion transfer membrane

2.1.2 Cation Transfer Membranes

Cation transfer membranes are manufactured from the same base polymer as anion transfer membranes. During production, negatively charged ions are affixed to sites throughout the membrane matrix. These fixed charges are sulfonate groups which repel negatively charged ions, and allow positively charged ions to transfer through the membrane. Figure 3 shows the chemical structure of a typical cation transfer membrane [4].

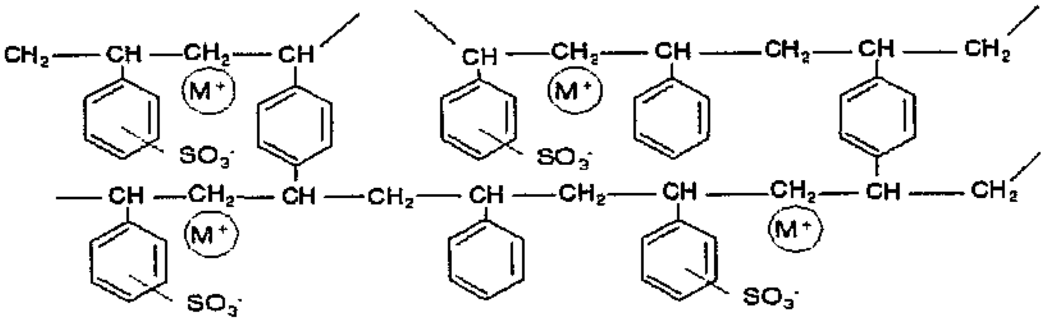

FIGURE 3

Structure of a typical cation transfer membrane

2.1.3 Membrane Properties

Properties which are characteristic of both cation and anion transfer membranes, are listed below:

- Insoluble in aqeous solutions
- Resistant to changes in pH values from 1 to 10
- Impermeable to water under pressure
- Exhibits low inherent electrical resistance
- Excellent long-term stability at temperatures of up to 65°C
- Resistant to osmotic swelling (volume expansion due of water uptake) when cycled between salt concentrations of 220 mgl^{-1} and 30 000 mgl^{-1}
- Semi-rigid for ease of handling during stack assembly
- Long life expectancy when in service

2.1.4 Spacers

Spacers are manufactured from low density polyethylene sheets, and form the concentrated and demineralised flow paths within the membrane stack. Two sheets of plastic are die-cut and glued together to provide a turbulant, "tortuous path" (figure 4). Cross-straps present in the spacer are only one-ply thick. Water is thus forced to flow in an over and under manner. This type of flow creates turbulence in the stream and allows a higher electric current flow per unit area. This aids in mixing, which in turn aids in the transfer of ions to the surface of the membranes. Turbulence also breaks up boundary layers caused by contaminants and slime at the membrane surface [4].

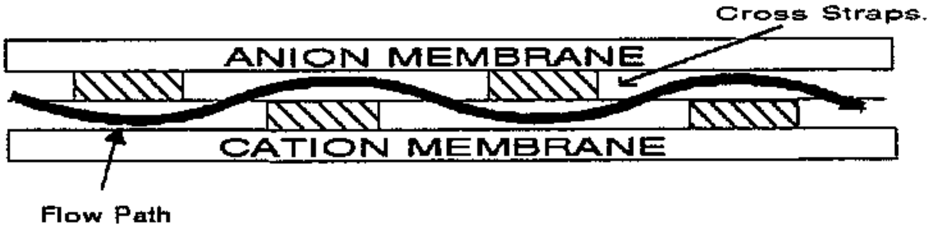

FIGURE 4

Schematic diagram of a spacer sandwiched between two membranes to form a flow compartment

3. MEMBRANE COATINGS

3.1 Zonyl Fluorosurfactant Coatings.

The principle features of fluorochemical surfactants (surface active agents) may be summarised as their ability to reduce surface tensions to extremely low levels, their chemical and thermal stability, and the effectiveness of the surfactants in use at low concentrations. It has been found that these substances repel dust, water and organic pollutants. If applied to a surface of an object, they may extend its operating life.

Generally, a surfactant consists of an organic compound having an insoluble moiety, combined with a solubilising group. Figure 5 represents the chemical structure of a typical fluorochemical surfactant:

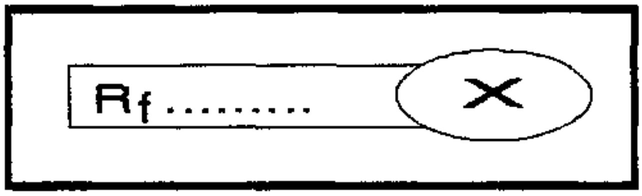

FIGURE 5

Structure of a typical fluorochemical surfactant

The R_f... portion is the stable flourocarbon "tail", and X represents a solubilising group. It is this unique flourochemical "tail", modified in length and structure to meet end use needs, which provides exceptional resistance to thermal and chemical attack. This resistance is characteristic of fluorochemical surfactants. The fluorochemical portion is responsible for dramatically reduced surface tensions. The solubilising group, X, is commonly water soluble [5, 6].

Due to the propriety nature and branding of some of the products on the market, limited information about these surfactants is available. The chemical and physical properties of the Zonyl fluorosurfactants utilised in this study, are summarised in Table 1.

TABLE 1

Chemical and Physical Properties of Zonyl Fluorosurfactants

COMMERCIAL PRODUCT NAME	ZONYL TC	ZONYL 6700	ZONYL 7040	ZONYL FSA	ZONYL FSE	ZONYL FSK
CHEMICAL STRUCTURES $R_f = F(CF_2CF_2)_{3-8}$	(NOT AVAILABLE) A: PERFLUOROALKYL ESTER B: FLUOROCARBAMATE	(NOT AVAILABLE) PERFLUOROALKYL ACRYLIC COPOLYMER	(NOT AVAILABLE) PERFLUOROALKYL ACRYLIC COPOLYMER	$R_fCH_2CH_2S-CH_2CH_2CO_2Li$	$(R_fCH_2CH_2O)_2-P(O)(ONH_4)$	$R_fCH_2CH-(OCOCH_3)-CH_2N^+(CH_3)_2-CH_2CO_2^-$
PHYSICAL FORM	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
DENSITY AT 25°C ($g\ ml^{-1}$)	1,04	1,08	1,08	1,03	1,12	1,25
PERCENT SOLIDS (weight %)	A: 8 - 13 B: 18 - 23	15 - 20	15 - 20	25	14	47
DILUENT (weight %)	WATER 65 - 70	WATER 75 - 80 ETHYLENE GLYCOL NJ TRADE SECRET REGISTRY 008502 01001-5284P 1 - 2	WATER 70 - 75 POLYETHYLENE MONOSTEARATE ETHYLENE GLYCOL 3 - 5	WATER 37,5 ISOPROPYL ALCOHOL 37,5	WATER 62 ETHYLENE GLYCOL 24	ACETIC ACID 53
IONIC TYPE	CATIONIC	CATIONIC	NON-IONIC	ANIONIC	ANIONIC	AMPHOTERIC

3.2 Polyvinyl Alcohol Coatings

A polyvinyl alcohol (PVOH) solution was obtained from the Institute for Polymer Science, University of Stellenbosch. This solution was utilised in a research programme, the aim of which was to provide composite reverse osmosis membranes containing a PVOH gel layer, with the following properties:

- chlorine resistant
- resistant to microbial attack
- stable over a wide pH range
- stable over a wide temperature range
- of high mechanical strength,
- able to withstand wet / dry cycles

Polyvinyl alcohol is highly hydrophyllic. In the unmodified form, it would be highly permeable to both water and salts. Potassium persulphate ($K_2S_2O_8$) was used as a free radical source for the crosslinking of PVOH membranes, to achieve improved performance. The effect of such coatings on the performance of anion permeable ED membranes, with regard to anti-fouling properties, was also investigated during this study.

4. ELECTRICAL RESISTANCE OF MEMBRANES

The properties of major concern with respect to ED membranes, are ion selectivity (ion-exchange capacity) and electrical conductivity. Membranes having low electrical resistance, consume less energy, thus increasing the efficiency of the ED system. In general, the resistance of membranes decreases as the concentration of the solution undergoing desalination increases. In addition, the change in the electrical resistance of membrane systems with temperature has been found to be similar to the change in membrane resistance with increasing solution concentration.

A distinction must be made between the actual membrane resistance, measured with alternating current, in a separate cell, and the apparent resistance obtained by measuring the voltage between two probes in an ED cell. The latter generally includes a polarisation component, which is mainly due to diffusion over-voltage on the diluate (less concentrated solution) side of the membrane. This polarisation component is dependant on the rate of stirring and therefore should not be included in the membrane resistance [7, 8, 9].

5. THE INFLUENCE OF MEMBRANE FOULING ON THE ED PROCESS

As previously mentioned, fouling has thus far been one of the most serious problems encountered in the electrodialytic desalination of brackish water. Fouling causes an increase in membrane resistance, which in turn causes an increase in power consumption and adversely affects process economics.

Furthermore, even at a low current density, water splitting occurs on the surface of anion transfer membranes. The transfer number of hydroxide ions at higher current densities is markedly increased. This results in a pH change of the water, and causes formation of scale on the membrane surface.

Several cells for measuring membrane fouling by synthetic foulants are described in the literature [1, 2, 10]. These fouling cells were used to compare the fouling behaviour of different membranes under different conditions, or to study the mechanism of fouling. During such studies, fouling was defined as the increase in voltage across anion transfer membranes, due to fouling agents.

6. EXPERIMENTAL METHODS

6.1 Drying of Membranes

To ensure the gradual shrinkage of membranes from the wet to the dry state, and to prevent cracking of the base polymer on a micro scale, membranes were inserted in each of the following solvents for 30 minutes:

10% MeOH / 90% H2O   MeOH = Methanol
25% MeOH / 75% H2O H_2O = Water
50% MeOH / 50% H2O
75% MeOH / 25% H2O
100 % MeOH
10% THF / 90% MeOH   THF = Tetrahydrofurane
25% THF / 75% MeOH
50% THF / 50% MeOH
75% THF / 25% MeOH
100% THF
10% Hex / 90% THF   Hex = Hexane
25% Hex / 75% THF
50% Hex / 50% THF
75% Hex / 25% THF
100% THF

Membranes were then dry stored until they were coated.

6.2 Coating of Membranes

6.2.1 Zonyl Fluorosurfactant Coatings

Aqueous coating solutions of 1%, 0,1% and 0,01% (% m/m) were prepared and the anion permeable membranes (IONICS 204 SXZL) were coated by inserting them into the desired solution for ten minutes. Coated membranes were then dried at 80°C for ten minutes. This procedure was carried out in triplicate. The membranes were then mechanically cleaned by washing in a 0,1M NaOH solution, and then stored in water.

6.2.2 Polyvinyl Alcohol Coatings

Aqeous solutions of 1%, 0,1% and 0,01% (% m/m) polyvinyl alcohol were prepared from a 2% PVOH, 1% $K_2S_2O_8$ solution. Membranes were coated by inserting them into the solutions for ten minutes, after which they were cured above a open steam bath for 30 minutes. The procedure was carried out in triplicate. After the final coating and curing, membranes were washed and stored in water.

6.3 Determination of Ion Exchange Capacities of the Coated Membranes

Ion exchange capacities were determined by volumetric titrations according to an IONICS Specification [11]. Tests were performed on three samples of each coating, and results compared with the values obtained from an uncoated, anion permeable membrane (IONICS anion 204 SXZL), hereafter refered to as the reference membrane.

6.4 Determination of the Electrical Resistance of the Coated Membranes

The test rig consisted of a cell with two platinum electrodes. Two chambers containing the electrolyte were separated by the membrane to be tested. The exposed area of the membrane was 3 cm^2. The inherent electrical resistance of the reference and coated membranes were determined in 0,1 M and 0,5 M NaCl solutions.

6.5 Accelerated Fouling Studies

A four cell flow-through apparatus, containing three ion-exchange membranes, was used. The effect of the feed stream on the centre membrane was investigated. The other two membranes were cation exchange membranes, which were utilised to isolate the anion exchange membrane being tested, from electrode reactions. Figure 6 shows a simplified diagram of the fouling cell with tangential flows.

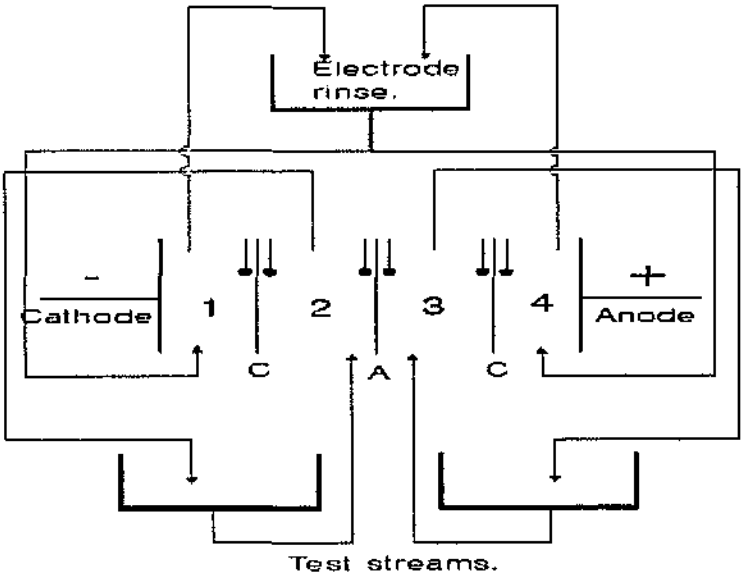

FIGURE 6

Schematic diagram of fouling apparatus

The membrane was placed between cells 2 and 3. The test stream, namely 0,1 M NaCl and 200 mgl^{-1} Dodecyl=benzenesulfonate (DBS) was passed through these cells. The electrode rinse stream, 0,1 M NaCl, was passed through cells 1 and 4, and both streams passed through the electrode rinse tank. By mixing these two streams, changes in pH, brought about by electrode reactions, were eliminated. The conductivity in the system was kept constant to eliminate potential drops. Furthermore, the mixing of the electrode rinse streams assisted in keeping the sodium concentration in the system constant.

The cathode and anode were constructed from platinum to prevent corrosion. Platinum reference electrodes were placed on either side of the central membrane. A high resistance voltmeter recorded the potential drop across the membrane. An increase in this potential indicated fouling.

Three electrolyte tanks, each of 50 liters in volume, were used. Three peristaltic pumps supplied stream flows of 0,2 liters per minute. A regulated DC supply delivered a current density of 200 mA mm^{-2} (200 mA), as the motive force for ion migration.

After fouling, the membrane was removed from the cell and mechanically cleaned by washing it in a aqueous 0,1 M NaOH solution. Cleaning by electrode polarity reversal was also investigated.

6.6 Desalination/Flux Studies

A laboratory model ED stack containing 5 cell pairs of cation and anion exchange membranes, each having an effective area of 16,75 cm^2, was used to study the desalination of a 0,1 M NaCl solution.

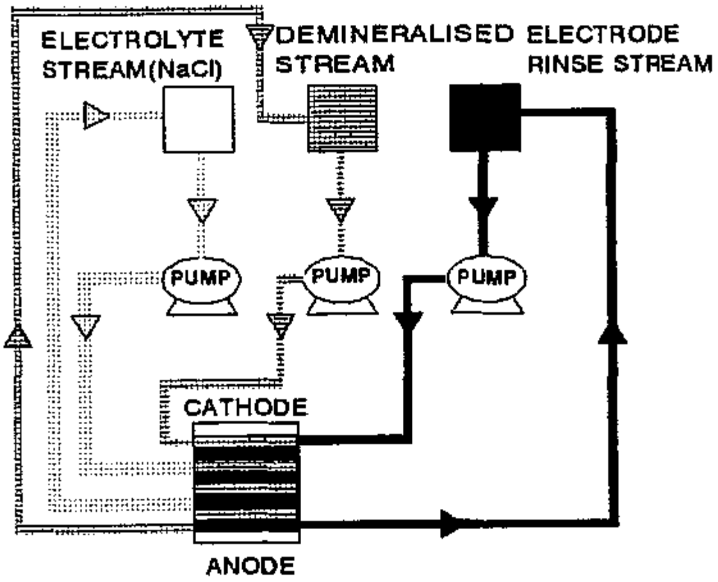

FIGURE 7

Schematic Diagram of ED Test Stack

A 10 volt direct current was applied to the stack. All the streams were recirculated. Two 160W centrifugal pumps were used to feed the concentrate and demineralised streams through the stack. A 45W centrifugal pump recirculated the electrode rinse solution. All the pumps were set to maintain flows at 1,2 litres per minute.

The salt contents of the streams were monitored by measuring the conductivities of the electrolyte and demineralised streams every 10 minutes, for a period of one hour. The decrease in the conductivity of the electrolyte stream, and the corresponding increase in the conductivity of the demineralised stream provided an indication of desalination [12].

7. RESULTS AND DISCUSSION

7.1 Determination of Ion-Exchange Capacities of the Coated Membranes

The results of ion-exchange capacities (expressed in meq g^{-1} of dry resin) for the coated and uncoated membranes are detailed in table 2.

TABLE 2

Ion-Exchange Capacities
(Milli-equivalent per gram of dry resin)

COATED SAMPLE	ION-EXCHANGE CAPACITY (meq g^{-1})
REFERENCE MEMBRANE	2,2
1% PVOH	2,02
0,1% PVOH	2,07
0,01% PVOH	2,11
1% ZONYL TC	2,11
0,1% ZONYL TC	2,14
0,01% ZONYL TC	2,18
1% ZONYL 6700	1,81
0,1% ZONYL 6700	1,83
0,01% ZONYL 6700	1,90
1% ZONYL 7040	2,02
0,1% ZONYL 7040	2,13
0,01% ZONYL 7040	2,17
1% ZONYL FSA	1,71
0,1% ZONYL FSA	1,81
0,01% ZONYL FSA	1,86
1% ZONYL FSE	2,06
0,1% ZONYL FSE	2,10
0,01 ZONYL FSE	2,23
1% ZONYL FSK	1,96
0,1% ZONYL FSK	1,93
0,01% ZONYL FSK	1,94

The ion-exchange capacities decreased with increasing coating concentration, resulting from a decrease in the available number of ion-exchange sites on and within the membrane. Values of below 2 meq g^{-1} (dry gram resin) were found for tests performed on membranes coated with Zonyl 6700, Zonyl FSA and Zonyl FSK [12]. A value of 2,2 is the minimum allowed, according to the quality control tests performed by IONICS Inc, during membrane manufacture. Based on these results, only PVOH, Zonyl TC, Zonyl 7040 and Zonyl FSK were used as coating materials for fouling and desalination studies.

7.2 Determination of the Electrical Resistance of the Coated Membranes

Results obtained are presented in table 3.

TABLE 3

Electrical Resistances of Coated Membranes

COATED SAMPLE	Test Solution	
	0,1M NaCl ohm cm^{-2}	0,5 M NaCl ohm cm^{-2}
Reference Membrane	24,62	12,80
1% ZONYL FSK	39,39	13,79
0,1% ZONYL FSK	57,12	19,70
0,01% ZONYL FSK	71,89	20,68
1% ZONYL FSE	44,32	14,77
0,1% ZONYL FSE	60,07	20,68
0,01% ZONYL FSE	77,80	23,64
1% ZONYL TC	63,03	27,57
0,1% ZONYL TC	70,91	21,66
0,01% ZONYL TC	81,74	24,62
1% ZONYL FSA	56,13	17,73
0,1% ZONYL FSA	59,09	22,65
0,01% ZONYL FSA	87,65	25,60
1% ZONYL 7040	65,00	20,68
0,1% ZONYL 7040	65,98	26,59
0,01% ZONYL 7040	81,74	23,64
1% ZONYL 6700	53,18	25,60
0,1% ZONYL 6700	66,97	26,59
0,01% ZONYL 6700	84,69	25,61
1% PVOH	53,18	25,60
0,1% PVOH	66,97	26,59
0,01% PVOH	84,69	25,60

The results of the analysis performed in the 0,1M NaCl test solution, show that an increase occured in the electrical resistance of the membranes, with decreasing coating concentration. It appears that the coating material increases the electrical conductivity of the membrane (decreasing the electrical resistance), as the coating concentration increases. An example of this is the electrical resistance value of 39,39 ohm cm^{-2} for the membrane coated with 1% Zonyl FSK, and a corresponding value of 71,89 ohm cm^{-2} for the membrane coated with 0,01% Zonyl FSK. A decrease in the electrical resistance of the membrane, indicates an increase in its electrical conductivity.

An average variation of 28 ohm cm^{-2} in electrical resistance was noted between the 1% and 0,01% coatings. Therefore, the changes in electrical resistance appear to be directly related to coating concentration. However, when the 0,5 M NaCl test solution was used, the same changes in electrical resistance did not occur. As mentioned in section 4.4, membrane resistance decreases, as the concentration of the test solution increases. The test method and apparatus proved to be inaccurate and insensitive at high concentrations of test solution. This would account for the absence of large variations in the second test series.

7.3 Accelerated Fouling Studies

The results of the fouling studies on the reference and coated membranes are summarised in table 4, expressed as the percentage increase in potential across the membrane being tested.

TABLE 4

Results of Fouling Studies

COATED SAMPLE	POTENTIAL ACROSS ANION PERMEABLE MEMBRANE (VOLTS)											PERCENTAGE INCREASE IN MEASURED POTENTIAL AS AN INDICATION OF FOULING
	0HRS	1HR	2 HRS	3HRS	4 HRS	5HRS	6HRS	7HRS	8HRS	9HRS	10HRS	
REFERENCE MEMBRANE	3,63	4,68	5,71	6,77	7,76	10,15	11,13	11,93	12,70	13,38	13,93	384
1% PVOH	3,26	4,32	5,12	6,21	7,14	8,02	10,23	11,26	11,90	13,65	13,96	428
0,1% PVOH	2,65	4,29	6,20	7,01	7,68	8,51	9,00	9,90	10,28	10,80	11,40	430
0,01% PVOH	3,17	–	5,72	6,84	7,99	12,66	13,90	14,99	15,97	16,81	17,04	538
1% ZONYL FSE	2,72	3,21	3,56	3,93	4,33	4,69	5,31	5,67	6,08	6,50	6,96	255
0,1% ZONYL FSE	4,16	5,34	6,35	7,21	8,00	8,71	9,44	10,24	10,97	11,74	12,33	296
0,01% ZONYL FSE	2,74	3,18	3,74	4,47	4,86	5,62	6,29	7,12	7,62	8,38	9,55	348
1% ZONYL TC	3,48	4,19	4,75	5,36	5,86	6,36	7,49	8,56	9,74	11,44	12,31	353
0,1% ZONYL TC	4,12	4,77	5,85	6,58	7,85	8,17	10,06	11,34	12,85	13,97	15,17	368
0,01% ZONYL TC	2,54	3,16	3,73	4,26	5,37	6,73	7,85	10,19	11,15	11,32	11,43	450
1% ZONYL 7040	2,90	3,71	4,94	6,12	7,41	8,83	10,09	11,01	11,50	12,73	13,29	353
0,1% ZONYL 7040	2,59	3,82	5,29	5,40	7,45	12,67	14,14	15,61	16,51	17,42	17,77	686
0,01% ZONYL 7040	2,02	2,99	3,99	5,01	6,12	7,16	8,31	9,56	10,84	11,94	13,91	692

In all cases, the potential across the membrane increased as fouling occurred. The anionic fluorosurfactant Zonyl FSE showed the greater resistance to fouling when compared to the other coatings. A decrease in coating strength from 1% to 0,01% resulted in a 36,5% increase in fouling as measured by the potential across the membrane for this coating series.

Similarly, decreased coating strengths from 1% to 0,01% of PVOH, Zonyl TC and Zonyl 7040, resulted in increased fouling of 25,7%, 27,5% and 96%, for each coating series respectively. However, at 1% concentrations of the coatings used all Zonyl fluorosurfactants showed greater resistance to fouling, than the uncoated reference membrane (table 4).

Furthermore it should be noted that for the cationic surfactant Zonyl TC, 1% and 0,1% coating concentrations showed greater resistance to fouling than the reference membrane. This was not the case for the 0,1% coating concentration of the non-ionic fluorosurfactant, Zonyl 7040.

In all instances where PVOH was used as coating material, the membranes fouled to an appreciably greater extent, than the reference membrane.

A graphical representation of comparative fouling is shown in figure 8.

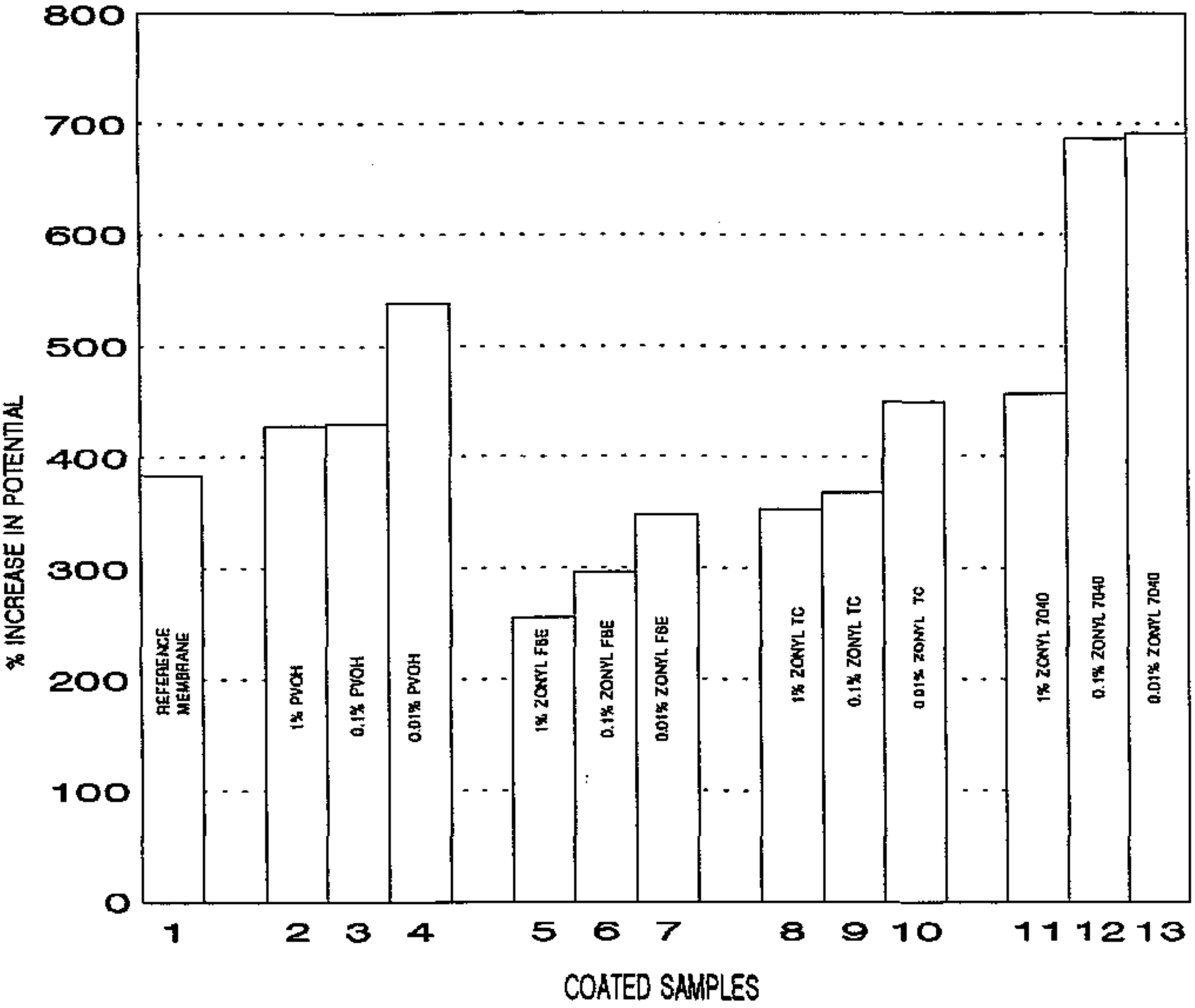

FIGURE 8

Comparitive Fouling of Coated Membranes

Graphical representations of each individual fouling study are included in appendix A.

Mechanical cleaning (ie washing of membrane) using 0,1 M NaOH showed only a temporary improvement, as the potential across the membrane could not be restored to its original value. After cleaning, an average decrease of 1,5V in potential was noted, yet the voltages steadily increased to original values recorded prior to mechanical cleaning.

Cleaning by electrode polarity reversal proved to be successful, as the reduction in voltage across the membranes tested, returned to near original values. This indicated an effective removal of foulants that had accumulated on the membrane surface.

7.4 Desalination/Flux Studies

Results are presented in table 5, and expressed as the percentage decrease in conductivity of the solution undergoing desalination, over a specific time period.

TABLE 5

Desalination Studies

COATED SAMPLE	CONDUCTIVITY OF THE CONCENTRATE SOLUTION (mS cm^{-1})		DECREASE IN CONDUCTIVITY OF THE CONCENTRATE SOLUTION (PERCENTAGE OF ORIGINAL VALUE)
	ORIGINAL VALUE	FINAL VALUE	
Reference Membrane	10,23	0,199	1,95%
1% PVOH	10,37	1,275	12,30%
0,1% PVOH	10,33	1,440	13,90%
0,01% PVOH	10,42	0,873	8,37%
1% ZONYL 7040	10,42	1,002	9,62%
0,1% ZONYL 7040	10,44	1,217	11,63%
0,01% ZONYL 7040	10,51	1,199	11,41%
1% ZONYL TC	10,36	1,480	14,29%
0,1% ZONYL TC	10,32	0,852	8,26%
0,01% ZONYL TC	10,34	1,200	11,61%
1% ZONYL FSE	10,72	1,650	15,39%
0,1% ZONYL FSE	10,36	1,019	9,84%
0,01% ZONYL FSE	10,30	1,217	11,82%

A decrease in desalination properties of the coated membranes was found, when the values are compared with those of the uncoated, reference membrane. This test method proved to be insensitive, preventing the variance in desalination properties of membranes coated with 1%, 0,1% and 0,01%, of a specific solution, to be established.

However, the results of ion exchange capacity determinations (section 7.1) indicate a definite decrease of capacities with increasing coating concentration. This indicates a decrease in desalination properties of the membrane, with increasing coating concentration, and therefore coating layer thickness. Whereas tests conducted on the reference membrane indicated a reduction in conductivity of the test solution to 1.95% of the original value, tests performed on coated membranes indicated values of between 15,39% to 8,26%.

8. CONCLUSIONS

From the results obtained the following can be concluded:

- Upon application of the fluorosurfactants and PVOH as surface coatings, membrane ion-exchange capacities, and therefore permselectivities decreased below the required limit.
- In all cases, desalination properties decreased upon application of surface coatings. An increase in coating layer thickness resulted in a decrease in flux or desalination properties.
- Membrane electrical resistance decreased with increasing fluorocarbon layer thickness (coating concentration).
- Only in certain cases, was a greater resistance to fouling exhibited, when compared to the uncoated reference membrane.
- The application of coatings to membranes did not provide the desired enhancement of mechanical cleaning requirements.

9. RECOMMENDATIONS

It is recommended that more emphasis be placed on pretreatment of feed water to the ED system, to alleviate the problem of membrane fouling.

If membrane fouling did not occur, organic foulants would pass through the ED system. The presence of organics in cooling water would aid the growth of bacteria, thereby increasing biocide dosage requirements.

The effect of the reduction in membrane electrical resistance with increasing coating concentration on the current efficiency of the ED system should be investigated. A financial feasibility study will have to be undertaken, to establish if the decrease in desalination or flux, warrants the increase in current efficiency of the ED process, and the increase in anti-fouling properties of the membranes.

10. ACKNOWLEDGEMENTS

The WRC and Eskom are hereby acknowledged for funding this project. The technical support and assistance from the Institute for Polymer Science, University of Stellenbosch, is appreciated.

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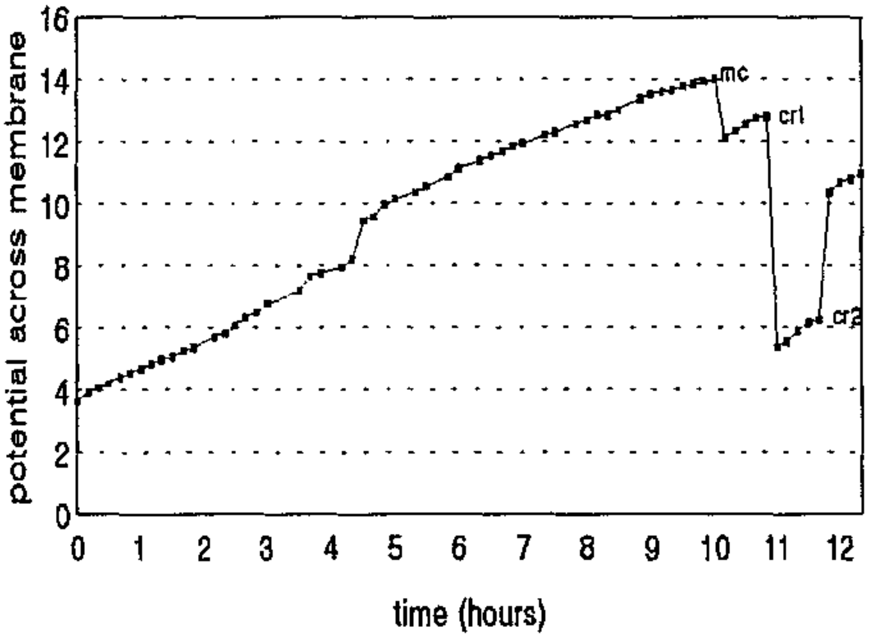
APPENDIX A

FOULING OF REFERENCE MEMBRANE

FOULANT: 200 PPM DBS



mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 8
Fouling Study of Reference Membrane

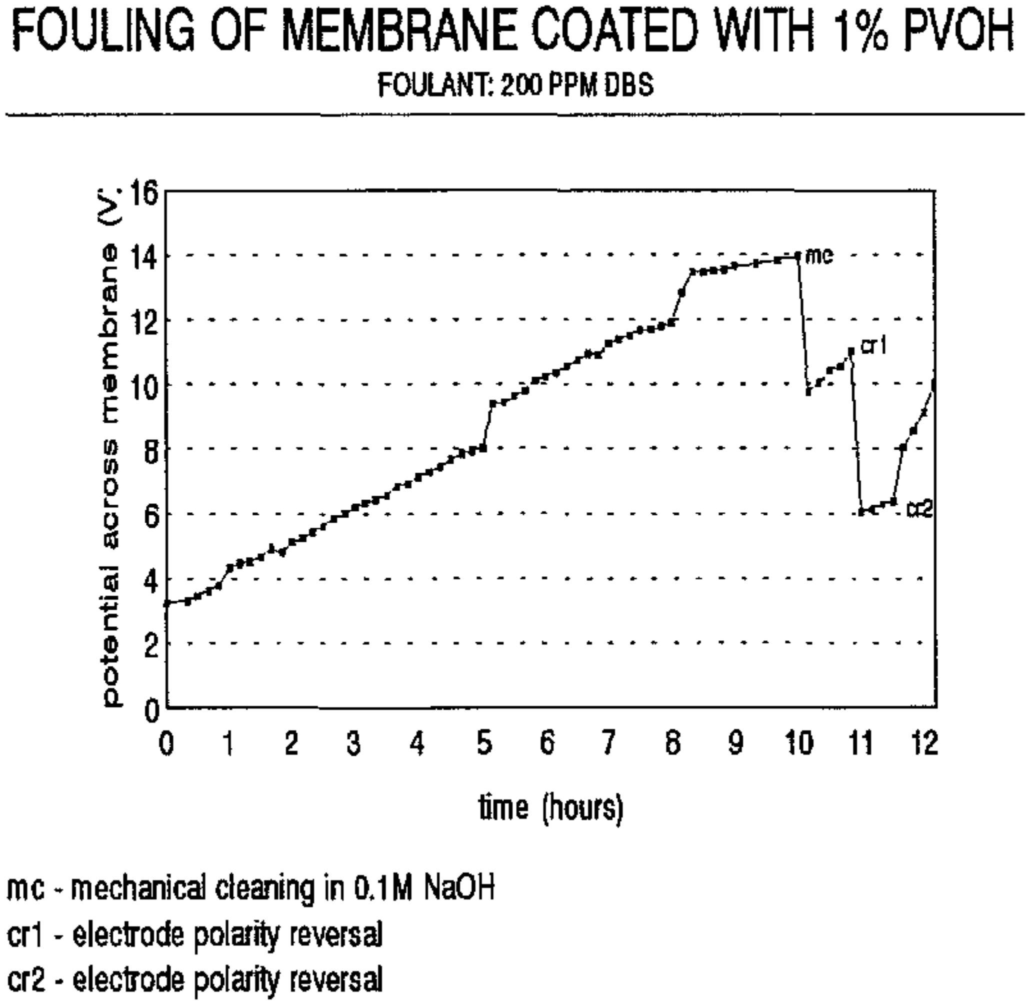
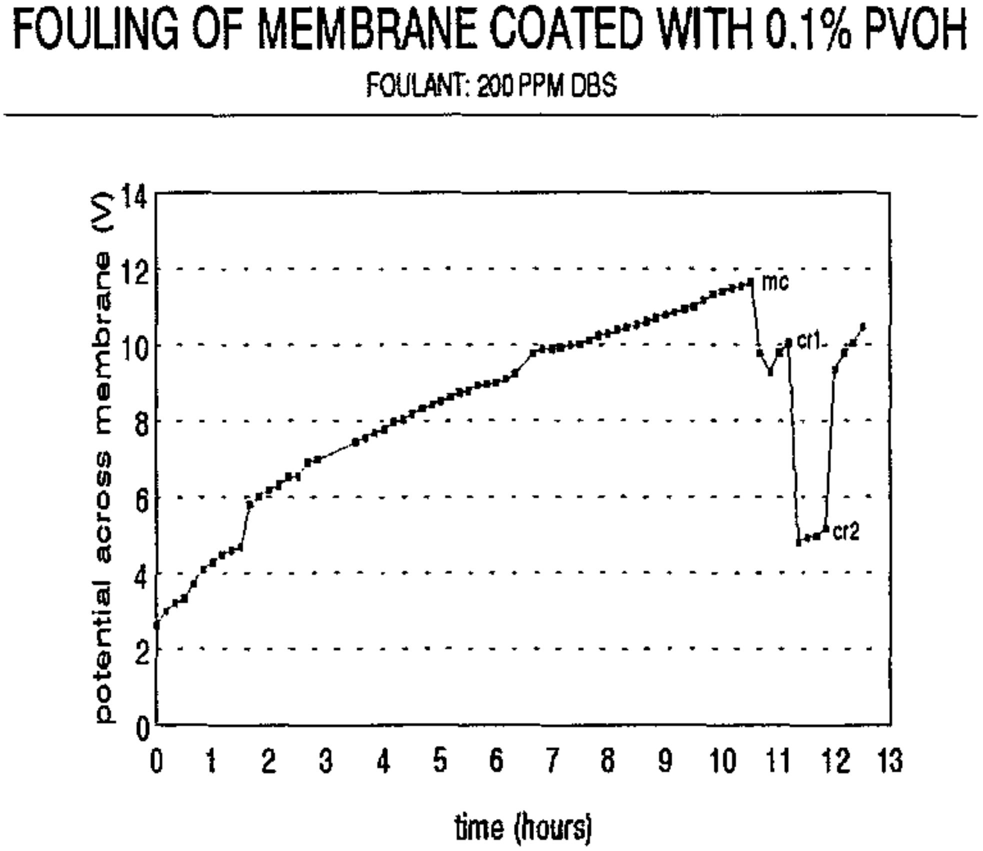


FIGURE 9
Fouling Study of Membrane Coated with 1% PVOH



mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 10
Fouling Study of Membrane Coated with 0,1% PVOH

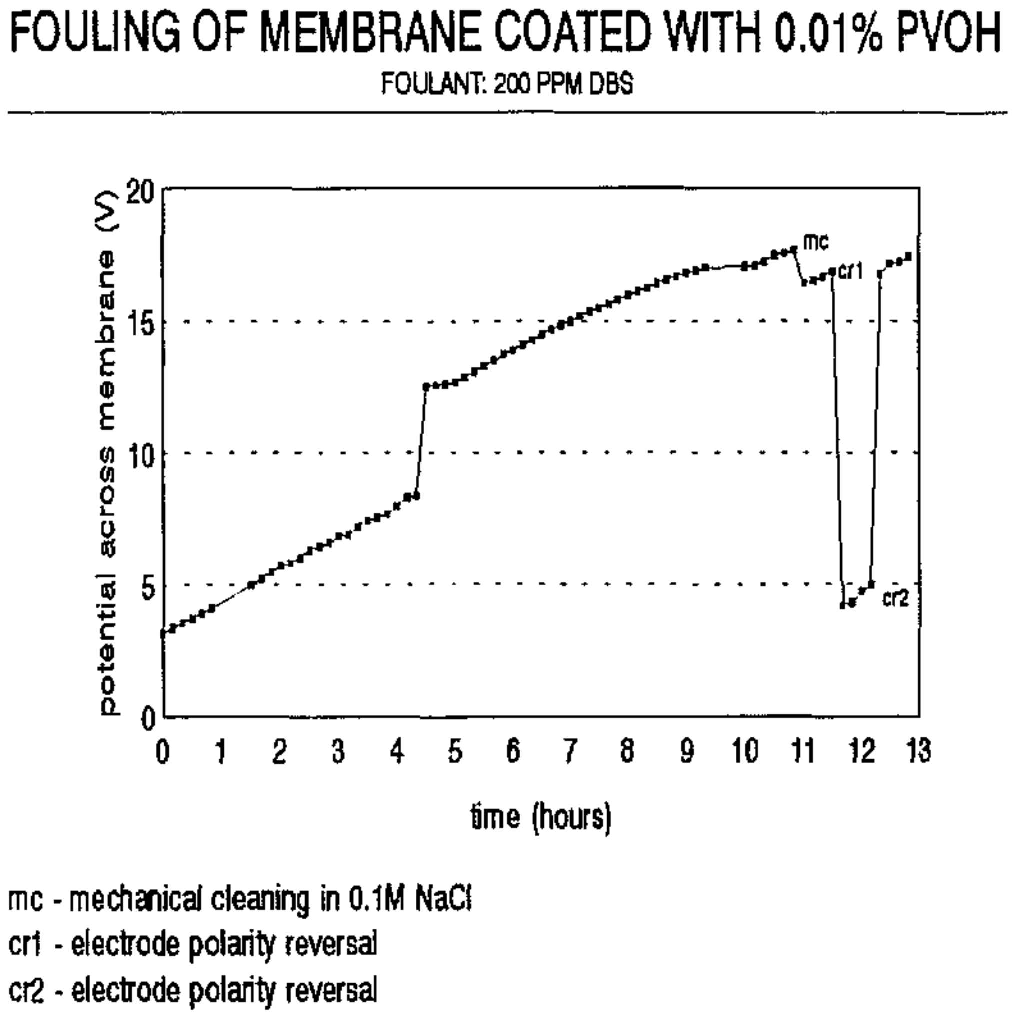
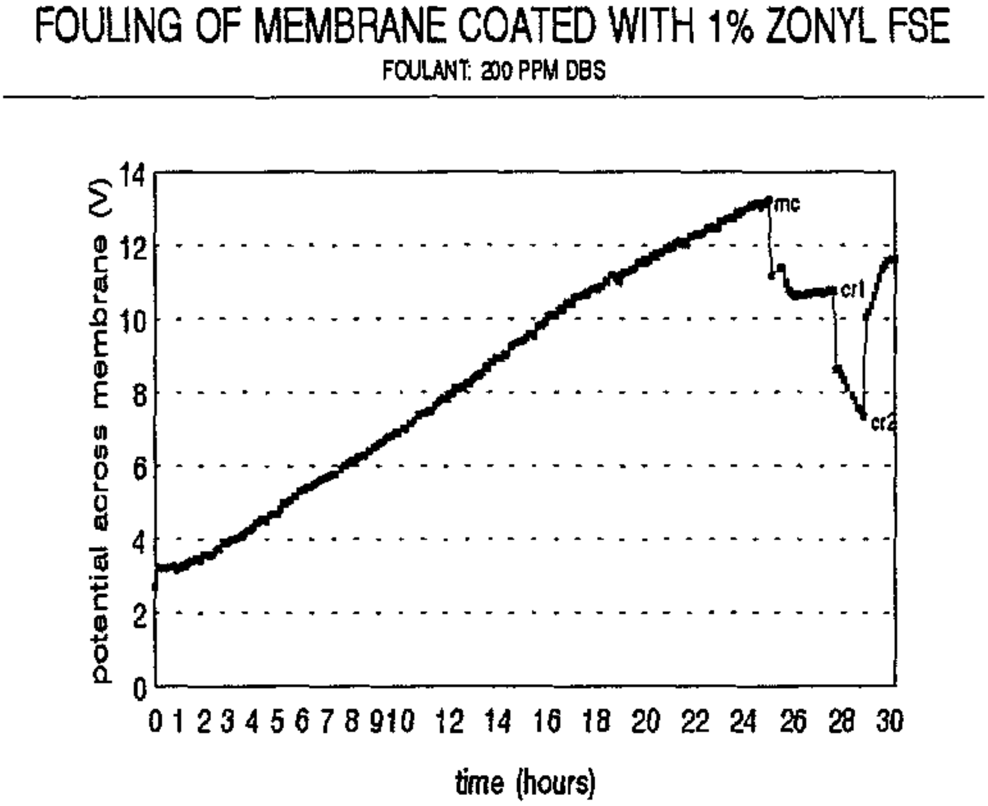
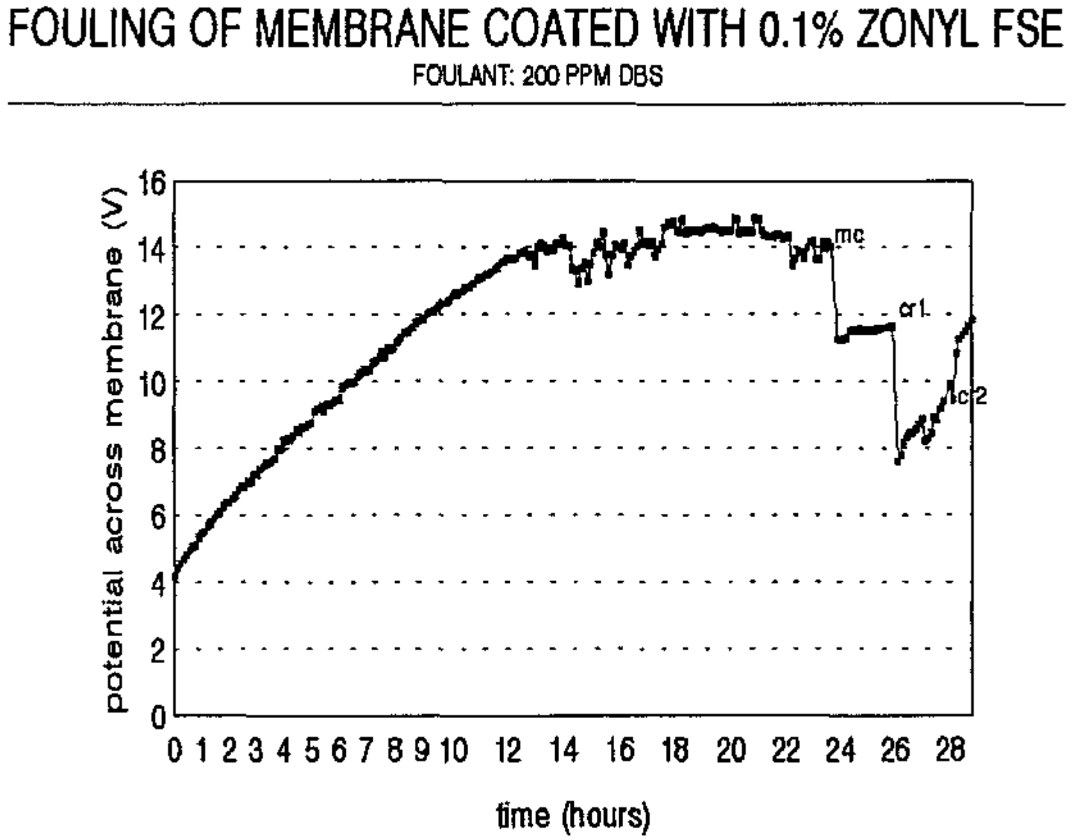


FIGURE 11
Fouling Study of Membrane Coated with 0,01% PVOH



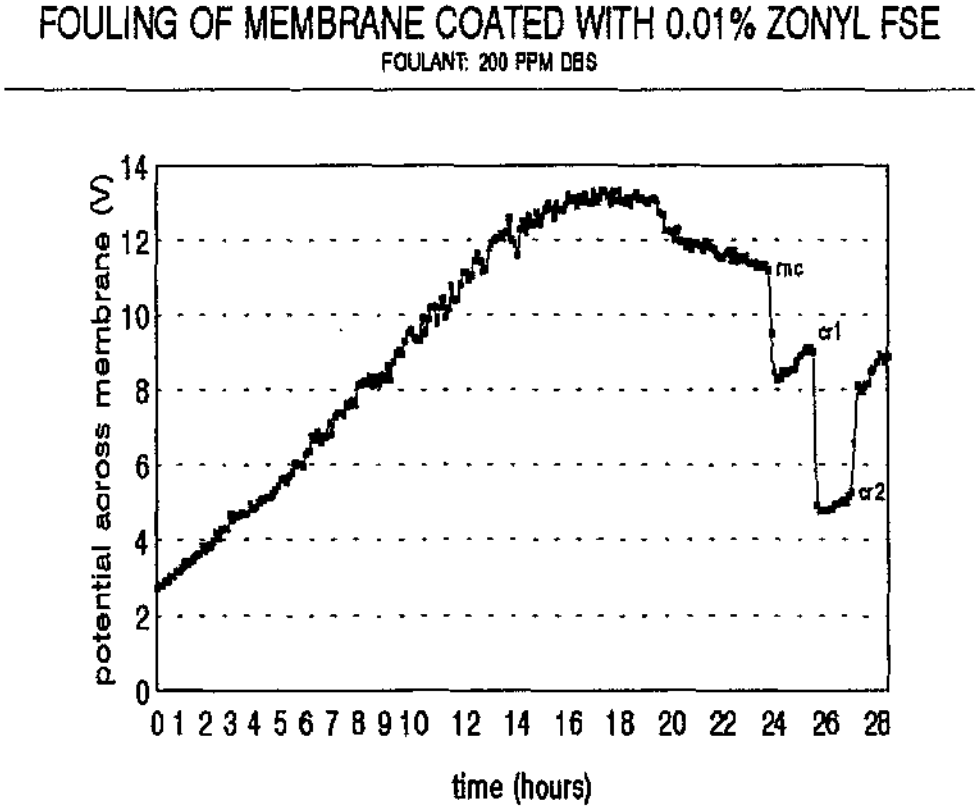
mc - mechanical cleaning in 0.1M NaCl
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 12
Fouling Study of Membrane Coated with 1% ZONYL FSE



mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 13
Fouling Study of Membrane Coated with 0,1% ZONYL FSE



mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 14
Fouling Study of Membrane Coated with 0,01% ZONYL FSE

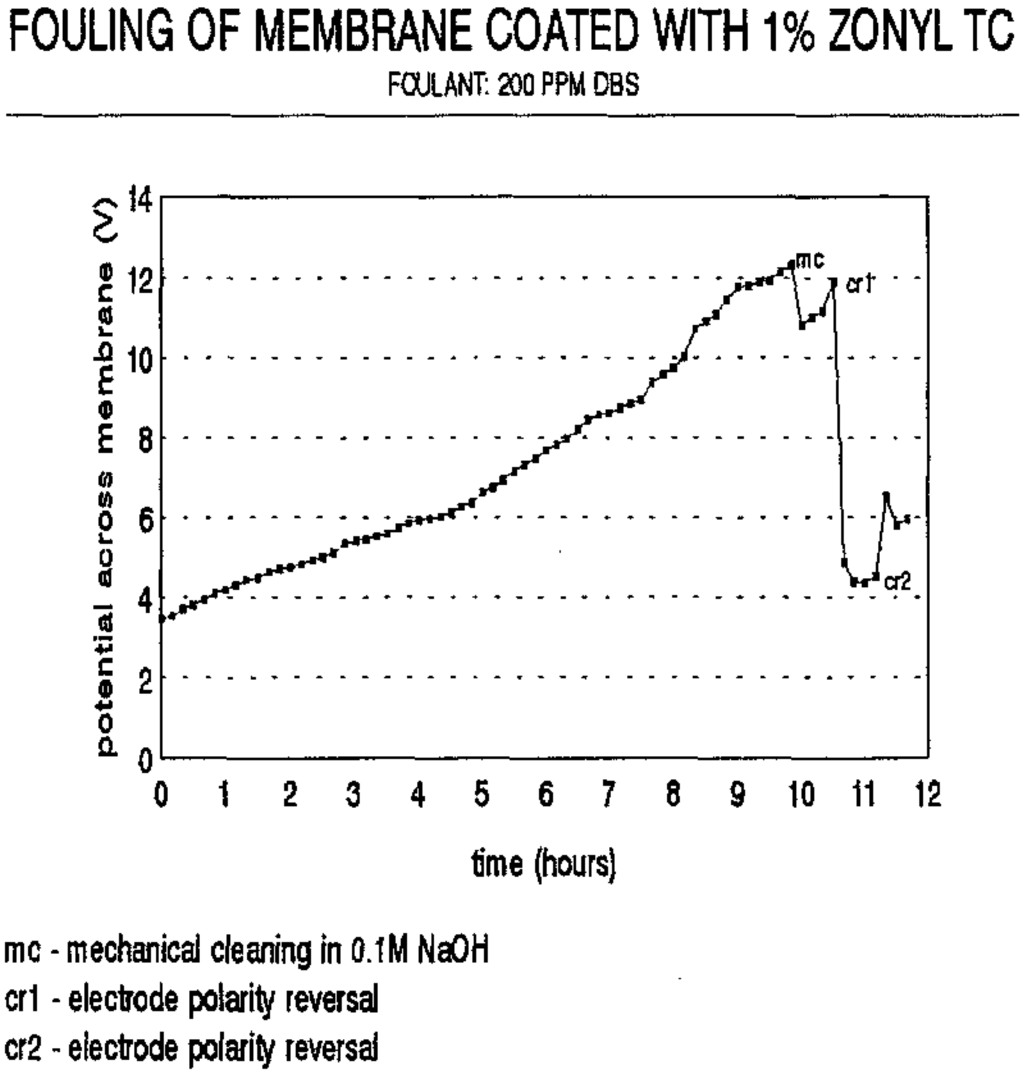
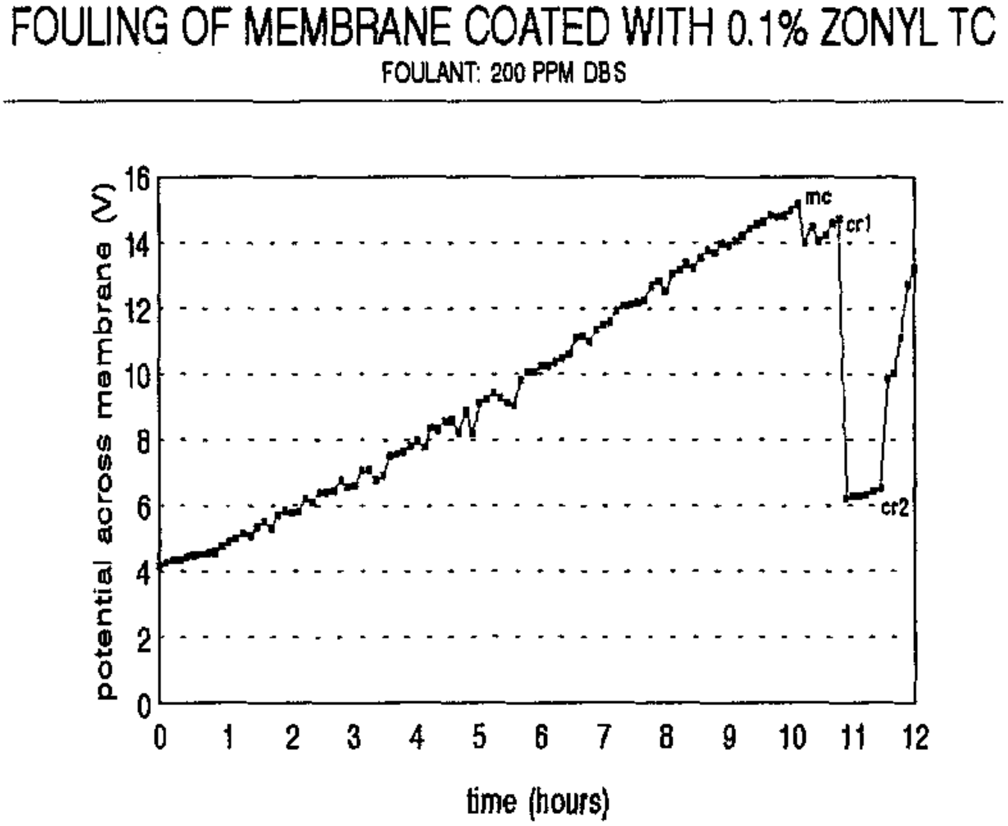
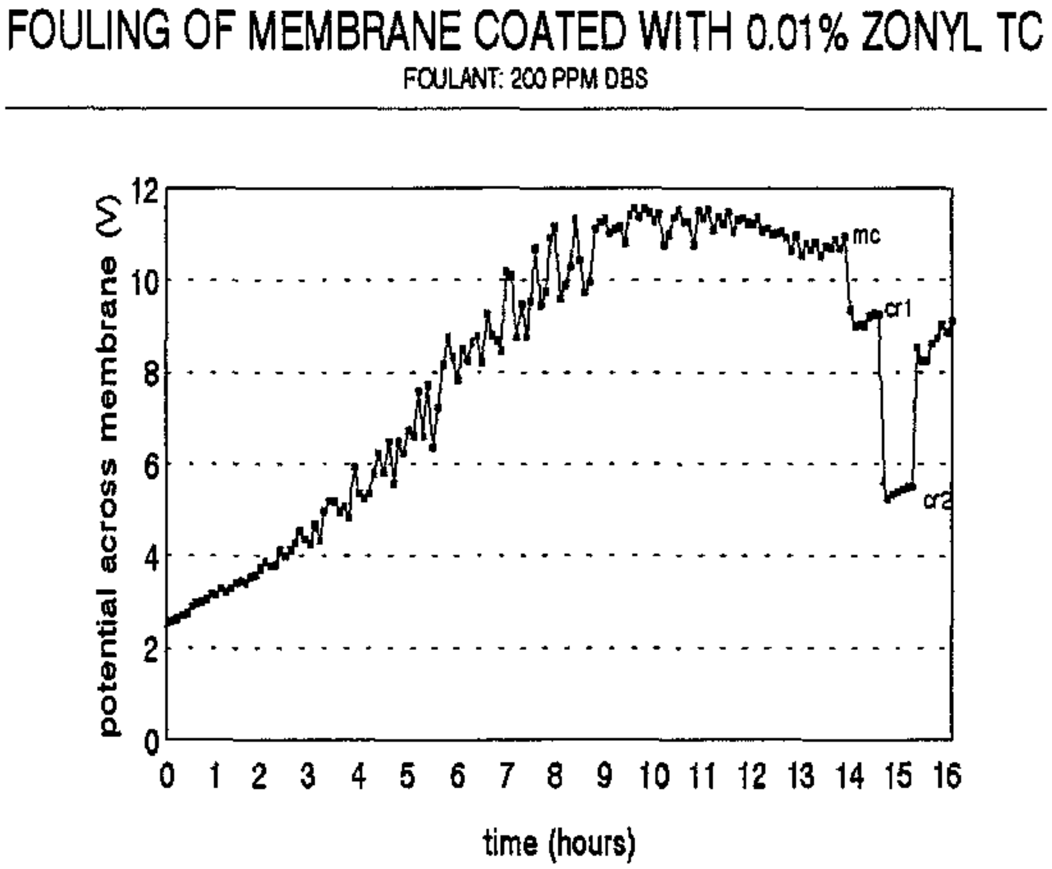


FIGURE 15
Fouling Study of Membrane Coated with 1% ZONYL TC



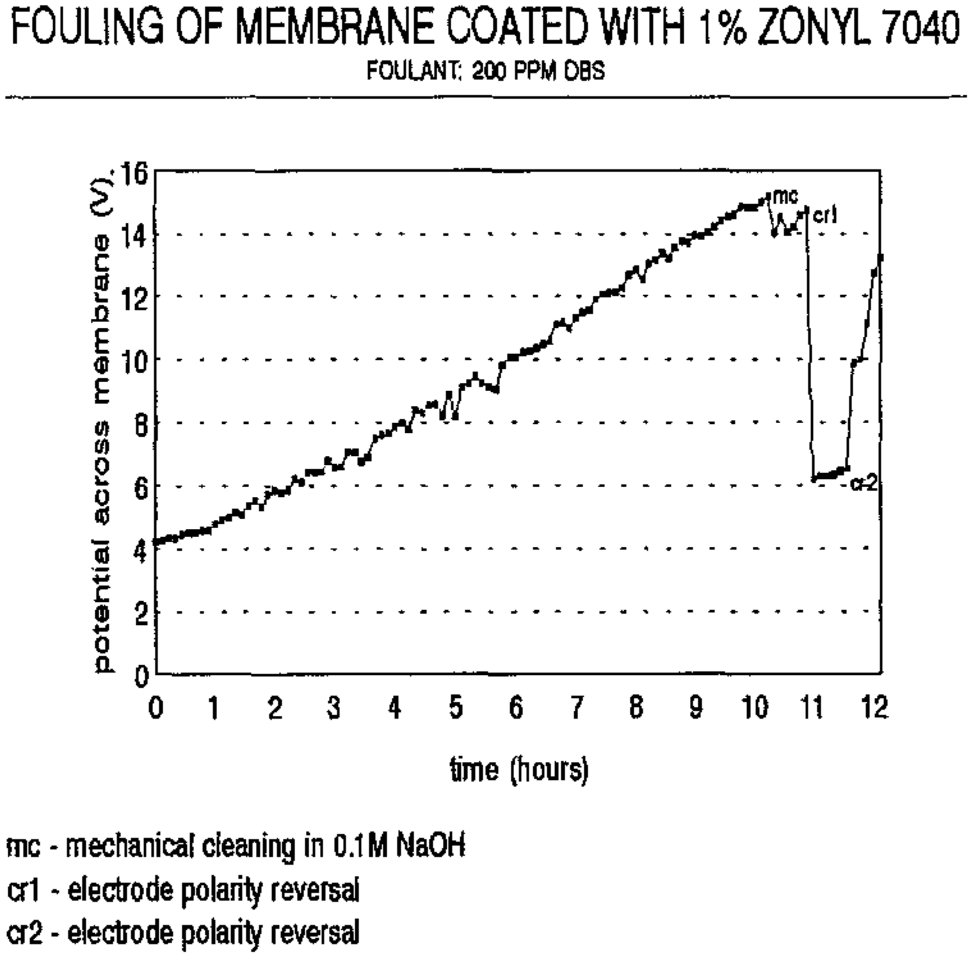
mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 16
Fouling Study of Membrane Coated with 0,1% ZONYL TC



mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 17
Fouling Study of Membrane Coated with 0,01% ZONYL TC



mc - mechanical cleaning in 0.1M NaOH
cr1 - electrode polarity reversal
cr2 - electrode polarity reversal

FIGURE 18
Fouling Study of Membrane Coated with 1% ZONYL 7040

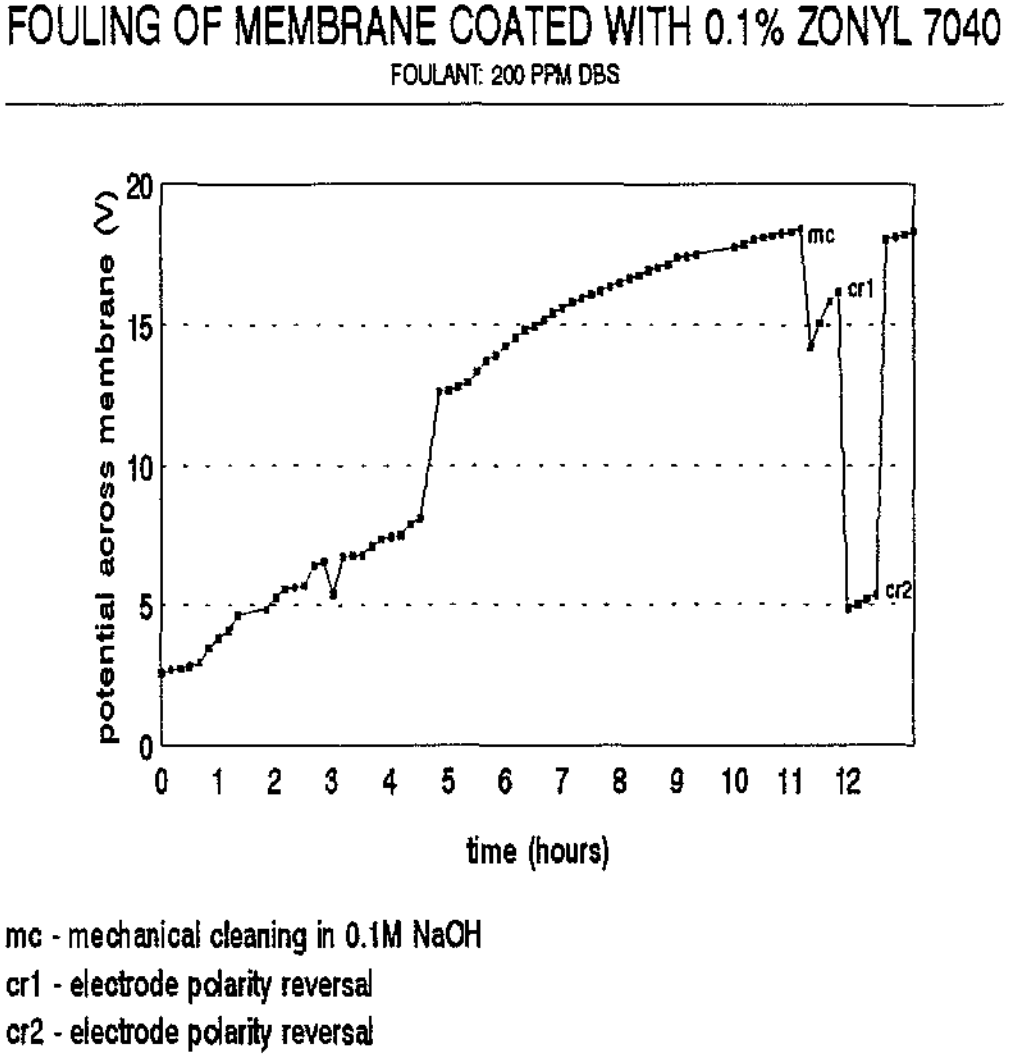


FIGURE 19
Fouling Study of Membrane Coated with 0,1% ZONYL 7040

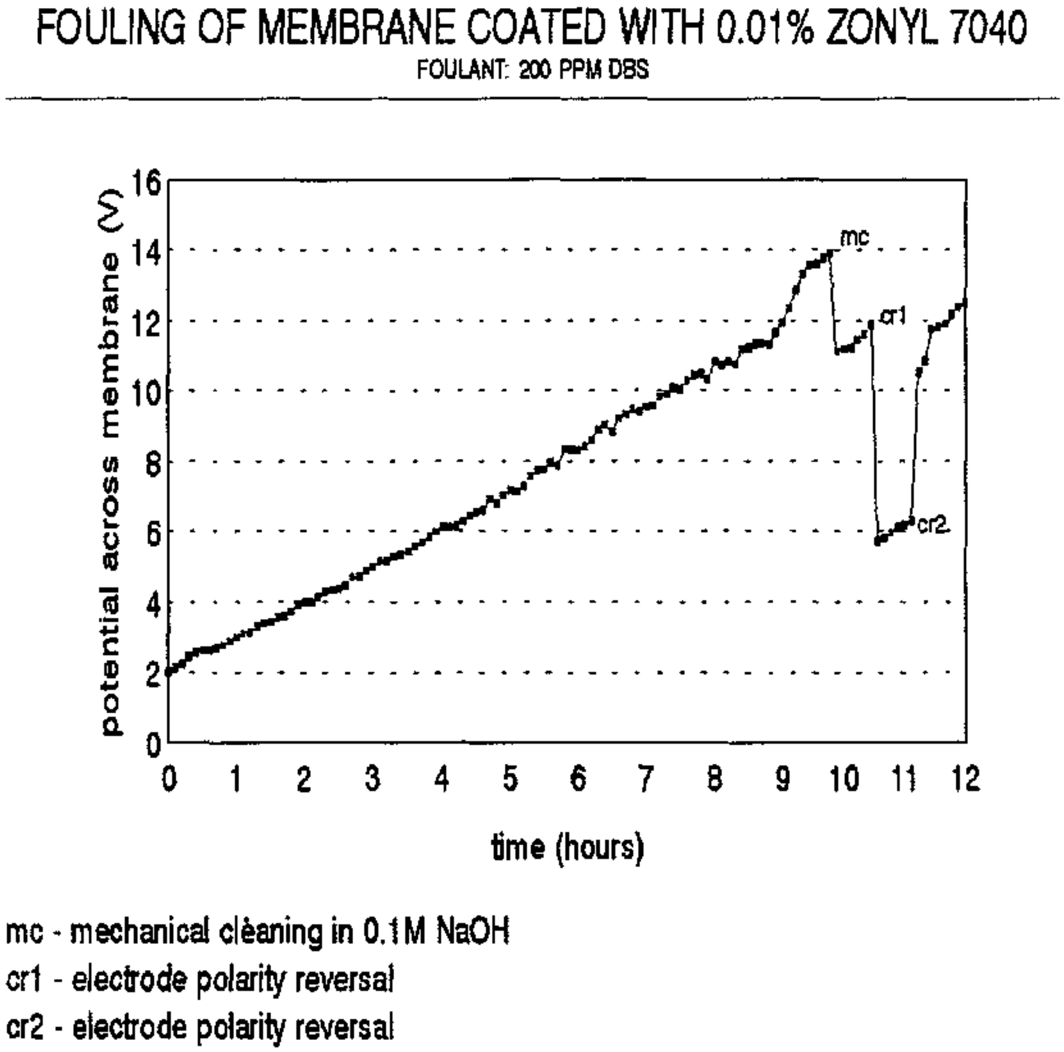


FIGURE 20
Fouling Study of Membrane Coated with 0,01% ZONYL 7040