Hydrous zirconium (iv) oxide and zirconium polyelectrolyte membranes on porous stainless steel supports - The effect of modified substrate pore size on the flux and rejection characteristics of the membranes*

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Abstract

Porous stainless steel tubes were selected as the support medium for the preparation of hydrous zirconium (iv) oxide (Zr) and composite zirconium/polyacrylate (Zr/PAA) dynamic membranes. Large pore size and wide pore size range resulted in poor reproducibility. Treatment of such tubes with low concentration of suspensoids or colloids, such as fumed silica, resulted in suitable pore size reduction and considerable improvement in flux and ionic rejection of both types of membrane, prepared on such pretreated tubes. As an example, a pretreated tube with a composite membrane yielded a flux of between 240 to 250 $\ell/m^2 \cdot h$ at 6 000 kPa and gave a rejection of 80 % from a solution of sodium nitrate containing 2 000 mg/ℓ $NaNO_3$ at pH 7. When pretreatment was omitted, the corresponding values were, flux 87 $\ell/m^2 \cdot h$ and rejection 66 %. The pretreatment procedure is now being applied on an industrial scale.

Introduction

Dynamic membranes are formed *in situ* when a dilute colloidal suspension of one or more additives is passed over the surface of a porous support. Some of the more promising membranes which have been developed are the hydrous zirconium (iv) oxide membrane (Zr) and the hydrous zirconium (iv) oxide/polyacrylate (Zr/PAA) composite membrane (Marcinkowsky et al., 1966; Johnson et al., 1972).

The zirconium (iv) species are polymerised in aqueous solutions and the polymerisation increases with decreasing acidity. It is considered that the colloidal condition is important in the formation of a Zr membrane on a porous support by crossflow techniques and the favoured pH is 3,5.

The ability of zirconium to react strongly with oxygen-containing species is an important property leading to chelation of a polyelectrolyte, such as poly(acrylic acid), onto a preformed membrane and so producing a composite membrane (Zr/PAA). This chelation tends to occur most readily between five- and six-membered rings and transition metals since bond distortion occurs less frequently in such rings.

It has been proposed that in the formation of the hydrous zirconium (iv) oxide membrane, some zirconium (iv) particles are trapped within the porous structure of the substrate prior to the onset of cake formation. This then represents the Zr membrane which in acid solutions has anion exchange properties.

When a polyelectrolyte, like poly(acrylic acid), is then passed over the Zr membrane, it enters the pores of the membrane rather than forming a second layer. At low pH values the polyelectrolyte molecules are hyper-coiled and thus easily penetrate the Zr membrane and react (chelate) with the substrate. When the pH is raised, the polyelectrolyte molecules ionise and expand to block the pores thereby causing a rapid decrease in flux and an increase in ionic rejection. The membrane so formed represents the composite membrane, Zr/PAA, which in neutral to alkaline solutions has the properties of a cation exchanger (Freilich and Tanny, 1978a,b; Tanny and Johnson, 1978).

This class of membrane is designated "dynamically formed" or dynamic. Because these membranes can be formed and replaced or generated *in situ*, there is considerable potential for their use in the treatment of effluents with high fouling characteristics.

Selection of porous support

Early research on dynamic membranes was done on substrates such as Millipore or Acropore films with a narrow range of pore size. Nominal pore size ranges used were 0,2 µm to 0,45 µm. Early application of dynamic membranes involved the use of porous carbon or ceramic tubes for support. Work was done also on coating such porous supports thinly with various particulate or fibrous filter aids to achieve a surface favourable for dynamic formation of hyperfiltration membranes (Johnson et al., 1968).

The fragility of many of the supports limited the applicability of the research. Brandon et al.(1980) and Mott et al.(1977) used porous stainless steel as the support material for dynamic membranes (Carre Inc., 1982).

In our investigations also, porous stainless steel has been selected as the main support medium. Thus in industrial applications in the treatment of effluents by membrane techniques, very high pressure operation (6 000 kPa) becomes possible.

Experimental

Apparatus

A crossflow rig equipped with high pressure, low volume Hydra-Cell D10 pumps was used for laboratory tests. Stainless steel (316) was used wherever possible. Teflon flexible hose was used in the line between the pump outlet and the crossflow support. The equipment is shown schematically in Fig. 1.

Short length porous stainless steel tubes, representative of

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*Revised paper. Originally presented at the South African Membrane Separation Interest Group Symposium, Wilderness, November 1989.
Received 15 December 1992; accepted in revised form 27 April 1993.

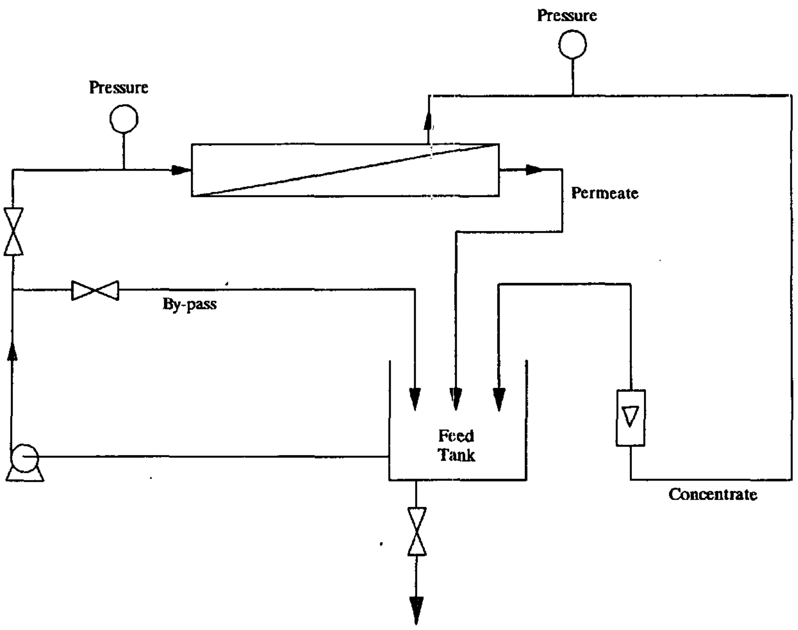

Figure 1
Flow diagram of dynamic membrane unit (feed tank equipped with pH probe and temperature control)

longer tubes used in two large-scale ultrafiltration plants were used as supports. Dimensions were : internal dia. 14 to 15 mm; external dia. 21,3 mm; effective porous length 455 mm; effective internal porous surface 0,02 m^2.

Porosity of the tubes

Porosity of the tubes was determined in terms of air pressure required to allow bubbles to emerge from the porous surface wetted with propan-1-ol (ASTM, 1983). The tubes showed the following variation : air pressure for maximum pore size, 120 to 175 mm Hg; air pressure for mean pore size, 160 to 285 mm Hg. This should be compared with pressures required in tests conducted on Millipore and Nuclepore membranes having nominal pore sizes of 0,45 µm and 1,0 µm respectively. These membranes gave values for both maximum and mean pore sizes near 560 and 440 mm Hg respectively.

The pore sizes of the porous stainless steel tubes were found to be too large and variable to enable Zr membranes and Zr/PAA membranes to be produced which exhibit consistent results with high ionic rejection and good flux values.

Pore size modification

The pore sizes of the naked stainless steel tubes were modified by treatment with either fumed silica or with precipitated hydrous zirconium (iv) oxide (Neytzell-de Wilde, 1989a). The particles were deposited from dispersions of these materials into the surface of the pores and onto the surface of the porous tube by passing such a dispersion tangentially across the surface of the porous support.

Fumed silica is produced by hydrolysis of vaporised silica tetrachloride and is manufactured by Cabot Corporation (USA) and by Degussa AG (Germany). When such material is dispersed in water, the surface hydroxyl groups can link the individual aggregates together through hydrogen bonding into intricate three-dimensional networks.

Precipitated hydrous zirconium (iv) oxide was produced by treatment of dilute solutions of zirconium nitrate with hydroxide to pH 6 to 7 under good agitation. The hydrous oxide can be regarded also as consisting of three dimensional polymers of linked tetrameric units. Increasing the pH above 4 results in the formation of increasingly large polymers of these tetrameric units (Clearfield, 1964; Hock, 1974).

Particulates such as diatomaceous earth, can also be used for pore size modification but the deposits can be dislodged readily. The three-dimensional networks produced by fumed silica or precipitated hydrous zirconium (iv) oxide when deposited in/on porous supports are not readily dislodged.

A series of tests was carried out on the crossflow filtration of suspensions of fumed silica [grade, Aerolite 200, manufactured by Degussa AG (Germany)] to demonstrate the effect of such suspensions on pore size and flux decline of porous stainless steel tubes. The initial pure water flux of the tubes used in the tests was greater than 30 000 $\ell/m^2 \cdot h$ at 1 000 kPa and 40°C.

Results : Silica membranes on porous stainless steel tubes

The results of tests carried out on deposition of silica during crossflow filtration of silica suspensions at 2 000 kPa inlet pressure are shown in Figs. 2 and 3. The flux decline is clearly related to concentration, c, of the suspension. The relation of flux versus $(1 / c)^{1/2}$ after a fixed time is shown in Figs. 3 and 4 for operation at 2 000 kPa and at 4 000 kPa respectively.

The typical behaviour of the depletion of a suspension of silica during crossflow filtration in the recycle mode is given in Fig. 5. The behaviour is similar to that of a colloidal suspension of zirconium at pH 3,5. This creation of dynamic membranes by filtering dilute inorganic colloidal solutions through porous

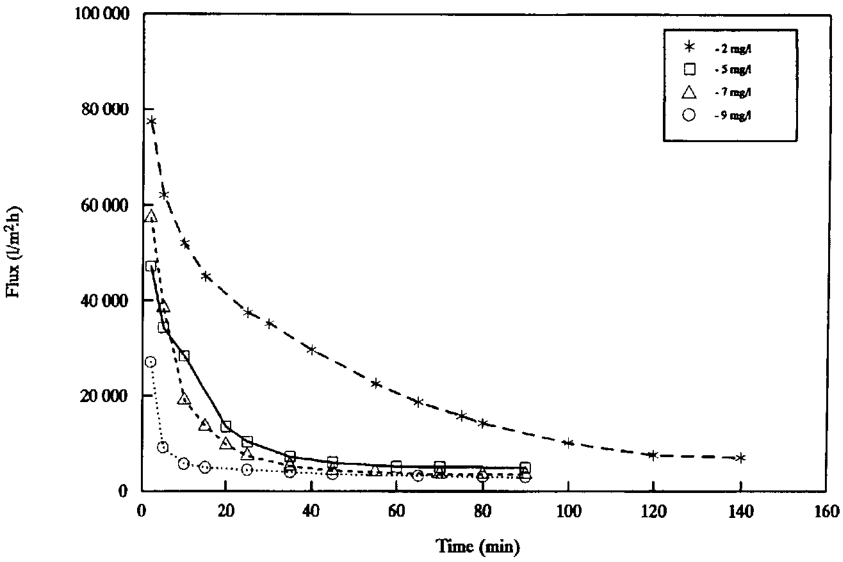

Figure 2
Flux decline during crossflow filtration of suspensions of fumed silica (recycle mode) 2 000 kPa inlet pressure at 3,1 to 3,9 m/s

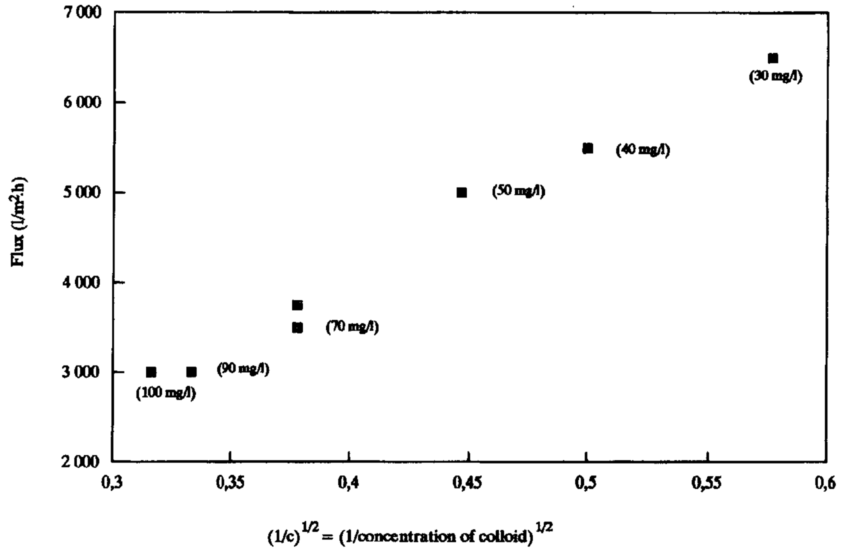

Figure 3
Effect of the concentration of fumed silica on flux decline after 80 min (crossflow velocity: 3,1 to 3,9 m/s; inlet pressure 2 000 kPa)

substrates is described in detail by Tanny (1978) and the use in particular, of dynamically formed silica membranes for ultrafiltration is also described (Tanny and Hauk, 1980; Tanny and Korin, 1981).

At low concentrations of silica 2 mg/ℓ (0,2 g/100 ℓ), effective pore size modification was achieved when such suspensions were circulated tangentially across the porous surface. At this concentration, the air pressure required for mean size estimation by bubble emergence tests on the treated tubes was similar to that for the Nuclepore membrane (440 mm Hg). This pore size is considered satisfactory for the production of Zr and Zr/PAA membranes with consistent properties.

Method of formation of Zr and Zr/PAA membranes

The method for Zr and Zr/PAA membrane formation was based on that used by Johnson et al. (1972). For Zr membrane formation a colloidal suspension near pH 3,5 containing 10 mg/ℓ Zr was used. For composite membrane formation the poly(acrylic acid) solution contained about 50 mg/ℓ poly(acrylic acid) of molecular mass near 150 000. All membranes were formed and evaluated at 40°C.

Results : Zr and Zr/PAA membranes on porous stainless steel tubes

The results of a series of tests involving the formation of Zr and Zr/PAA membranes on naked and pretreated porous stainless steel tubes are given in Table 1. Tests were carried out at different pretreatment and membrane formation pressures. The composite membranes were all evaluated up to 6 000 kPa using sodium nitrate solution of approximately 2 000 mg/ℓ at pH near 7.

The suspensions used for pore size modification were prepared from fumed silica or precipitated hydrous zirconium (iv) oxide and the maximum concentration in the suspension was 3 mg/ℓ in the tests reflected in the table. Some tests, not reported here, were carried out using suspensions as high as 5 and 7 mg/ℓ. These Zr and Zr/PAA membranes gave very high flux values. The composite membranes, however, gave rejections below 70 %. Further work at

TABLE 1
Zr AND Zr/PAA MEMBRANES ON POROUS STAINLESS STEEL TUBES (NAKED AND PRETREATED)

Zirconium membrane (Zr)			Composite membrane (Zr/PAA)								
Test	Pretreatment pressure kPa	Inlet formation pressure kPa	Test pressure kPa	Crossflow velocity m/s	Flux ℓ/m^2·h	Rejection* %	Inlet formation pressure kPa	Test pressure kPa	Crossflow velocity m/s	Flux ℓ/m^2·h	Rejection*[1] %
Naked tubes											
1025/31 T9	-	600	600	1,3	118	29	600	600	1,3	32	38
								6 000	4,0	180	67
1087/89 T10	-	2 000	2 000	3,8	168	41	2 000	2 000	3,9	30	59
								3 000	4,5	57	60
								6 000	3,9	110	55
2024 T7	-	6 000	6 000	3,8	420	47	6 000	6 000	3,8	87	66
84/86 T4*[2]	-	4 000	4 000	4,5	350	49	4 000	4 000	4,5	93	50
								2 000	4,1	30	62
								6 000		- unsatisfactory -	
Tubes pretreated with fumed silica (SiO_2) suspensions											
1073/75 T5	2 mg/ℓ SiO_2 600	600	600	1,6	201	29	600	600	1,3	56	34
								3 000	4,9	216	56
								6 000	4,3	522	56
1074/76 T3	2 mg/ℓ SiO_2 600	600	600	1,6	252	24	600	600	1,3	62	34
								3 000	4,4	237	58
								6 000	4,3	504	59
2025/27 T1	3 mg/ℓ SiO_2 1 000 - 6 000	6 000	6 000	3,9	636	45	6 000	6 000	3,9	230	72
2029/35 T2	2 mg/ℓ SiO_2 1 000 - 4 000	6 000	6 000	4,3	636	54	6 000	6 000	413	250	80
2030/36 T10	2 mg/ℓ SiO_2 1 000 - 4 000	6 000	6 000	4,3	672	41	6 000	6 000	4,3	240	81
4/6 T8	2 mg/ℓ SiO_2 2 000 - 3 500	4 000	4 000	4,5	768	45	4 000	4 000	4,7	210	73
								6 000	4,3	320	74
51/54 T4	3 mg/ℓ SiO_2 2 000	4 000	4 000	4,2	870	45	4 000	4 000	4,1	237	78
								6 000	4,3	402	78

TABLE 1 (continued)
Zr AND Zr/PAA MEMBRANES ON POROUS STAINLESS STEEL TUBES (NAKED AND PRETREATED)

Zirconium membrane (Zr)							**Composite membrane (Zr/PAA)**				
Test	**Pretreatment pressure kPa**	**Inlet formation pressure kPa**	**Test pressure kPa**	**Crossflow velocity m/s**	**Flux ℓ/m²·h**	**Rejection* %**	**Inlet formation pressure kPa**	**Test pressure kPa**	**Crossflow velocity m/s**	**Flux ℓ/m²·h**	**Rejection*1 %**
60/t64 T4	3 mg/ℓ SiO_2 2 000	4 000	4 000	4,1	915	41	4 000	4 000	4,2	180	76
								6 000	4,2	294	75
67/70 T6	3 mg/ℓ SiO_2 2 000 - 3 600	4 000	4 000	4,5	750	29	4 000	4 000	4,6	210	71
								6 000	4,5	330	74
87/90 T4*2	2 mg/ℓ SiO_2 2 000 - 3 050	4 000	4 000	4,5	885	43	4 000	4 000	4,8	225	75
								6 000	4,6	348	73
								2 000	4,0	81	68
Tubes treated with precipitated hydrous zirconium (iv) oxide (Zr) suspensions											
2013/16 T4	2 mg/ℓ Zr 600	600	600	1,3	198	21	600	6 000	3,8	366	65
2017/22 T9	2 mg/ℓ Zr 2 000	2 000	2 000	3,8	444	21	2 000	6 000	3,8	312	67
2019/21 T5	2 mg/ℓ Zr 2 000	2 000	2 000	3,8	480	26	2 000	6 000	3,8	333	68
2038/40 T6	2 mg/ℓ Zr 4 000	6 000	6 000	4,3	636	41	6 000	6 000	4,3	165	82
2041/43 T4	2 mg/ℓ Zr 4 000	6 000	6 000	4,3	588	39	6 000	6 000	4,1	195	80
2044/46 T1	2 mg/ℓ Zr 4 000	4 000	4 000	4,1	576	40	4 000	6 000	4,4	264	80

*1 Rejection from a solution containing 2 000 mg/ℓ $NaNO_3$

*2 Large pore size : bubble emergence test 136 mm Hg (max. pore size) 174 mm Hg (mean pore size)
Flux at 1 000 kPa; over 4 900 ℓ/m²·h

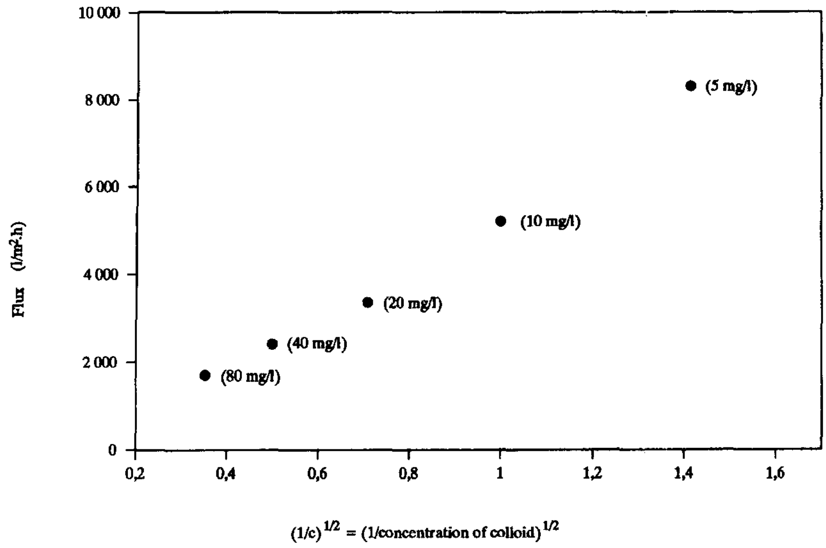

Figure 4
Effect of the concentration of fumed silica on flux after 100 min (crossflow velocity, 3,5 to 4,5 m/s; inlet pressure 4 000 kPa)

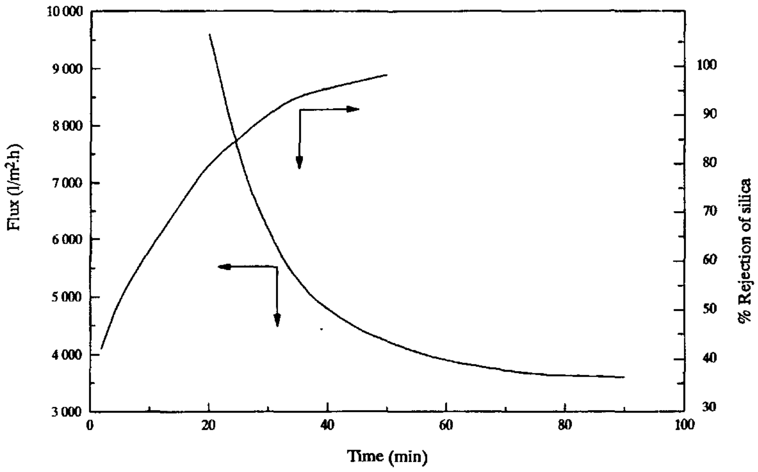

Figure 5
Crossflow filtration of suspension of fumed silica in water

these levels of pretreatment is necessary and such work needs to include storage under water.

Figure 6 shows the formation of the Zr membranes at 6 000 kPa for naked and pretreated porous stainless steel tubes. It will be seen that the Zr membrane was more readily formed on the pretreated support. This effect became more marked as formation pressures were increased from 600 to 6 000 kPa.

It can be seen from the table that the composite membranes prepared on pretreated tubes gave extremely good flux and good rejection values when compared with the composite membrane prepared on naked tubes. Figures 7 and 8 demonstrate the trend in the relation between pressure and flux for tubes treated with either 2 mg/*l* fumed silica or 2 mg/*l* precipitated hydrous zirconium (iv) oxide. Figure 9 shows the trend in the relation between flux of the Zr membrane and flux of the Zr/PAA membrane. It is evident that the pretreatment of the porous stainless steel substrate has a marked effect on the flux of both the Zr and Zr/PAA membranes. The flux of the Zr/PAA membrane, however, is directly related to the flux of the Zr membrane (Fig. 9). Many of these membraned tubes were tested for storage in water and these were found to be stable even after long periods of storage.

The pretreatment procedure was adopted in the preparation of both Zr membranes and Zr/PAA membranes in 2 industrial applications using modules with a porous area of 6,35 m^2 and a total support length of 134 m per module. The results of such trials on a desuinted wool scour plant effluent and on a textile dyehouse effluent are extremely encouraging (Neytzell-de Wilde et al., 1989b).

Conclusions

In general, in crossflow techniques involving filtration of inorganic suspensoids or colloids, the flux undergoes a rapid decline and subsequently levels off to a pseudo-steady state. Important factors which affect the rate of decline and the level of the pseudo-steady state for a given substrate are the size and morphology of the individual suspensoids/colloids, the pressures at which the suspension is passed tangentially across the porous substrate and the concentration of the suspension.

The correct treatment of porous stainless steel tubes with a dilute suspension of fumed silica or precipitated hydrous zirconium (iv) oxide to modify the substrate pore size, improved the degree of reproducibility of results obtained from membranes (Zr or Zr/PAA) prepared on such substrates. In addition, 80 % rejection and good flux values were achieved. A degree of tailoring was

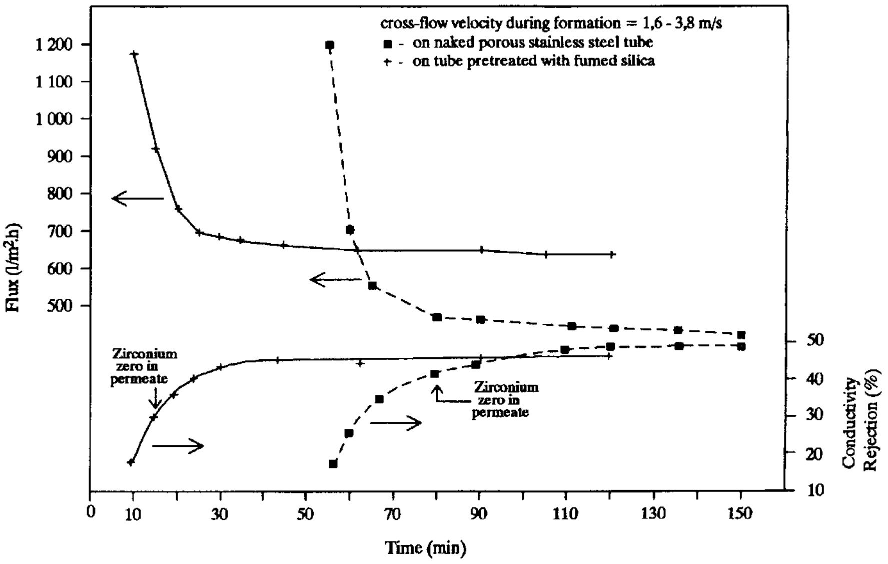

Figure 6
Hydrous zirconium (iv) oxide membrane prepared at 6 000 kPa on porous stainless steel tubes; naked and pretreated with silica

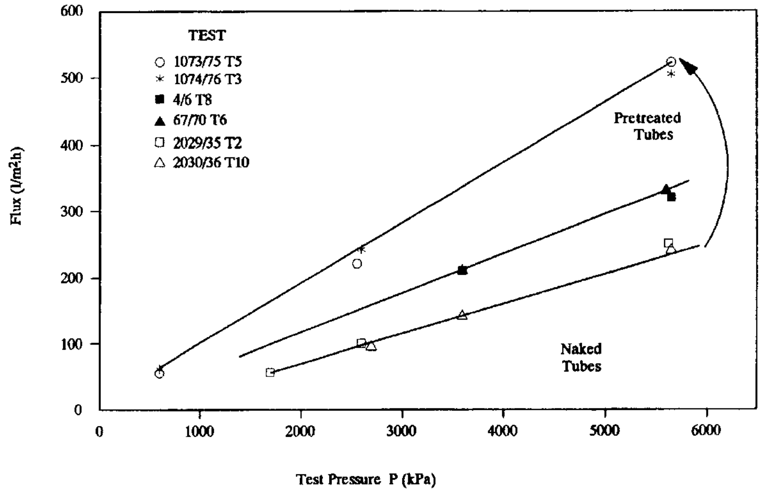

Figure 7
Trend for relation between pressure and flux for composite membranes (Zr/PAA) on treated porous stainless steel tubes (pretreatment : fumed silica, 2 mg/l)

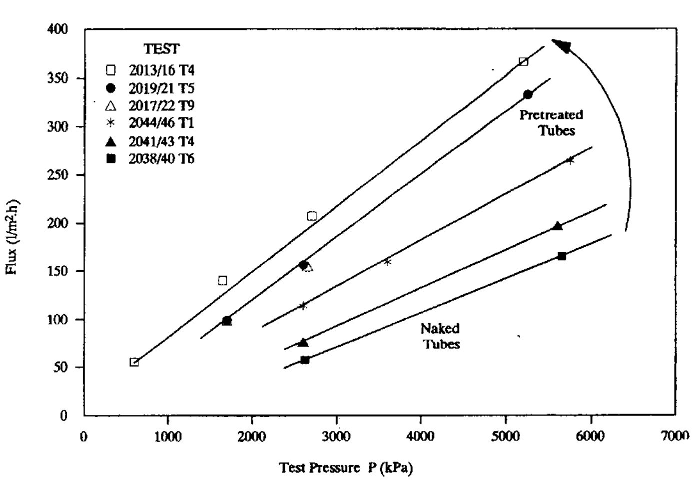

Figure 8
Trend for relation between pressure and flux for composite membranes Zr/PAA on treated porous stainless steel tubes (pretreatment : precipitated hydrous zirconium (iv) oxide, 2 mg/l)

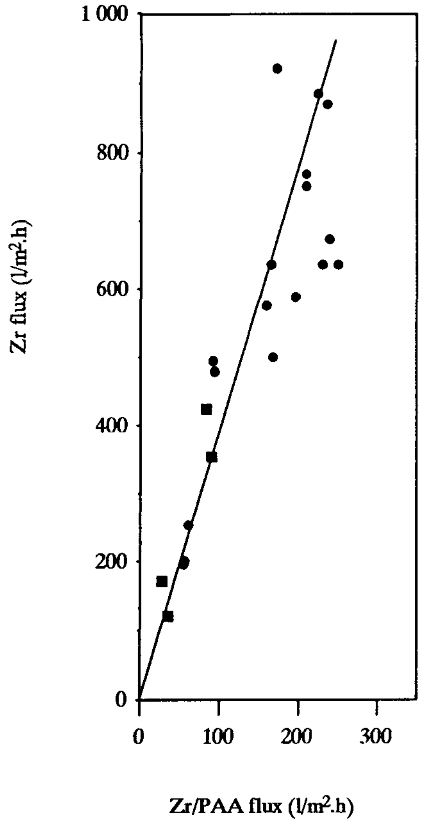

Figure 9

Trend for relation between flux of Zr membrane and Zr/PAA membrane (membranes prepared at same pressures 600 to 6 000 kPa; substrates naked or pretreated porous stainless steel. Pretreatment either fumed silica or precipitated hydrous zirconium (iv) oxide)

possible and membranes prepared at low pressures could be operated at higher pressures.

Acknowledgements

This work was carried out under a research grant from the Water Research Commission, Republic of South Africa.

References

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) (1983) Standard test method for maximum pore diameter and permeability of rigid porous filters for laboratory use, E. 128-61 (Approved 1961) in Annual Book of ASTM Standards, Section 14 Vol **14** (02) 78-81.

BRANDON, CA, GADDIS, JL and SPENCER, G (1980) Recent applications of dynamic membranes. In: *Synthetic Membranes, II.* ACS Symposium Series 154, American Chemical Society, Washington DC. 435.

CARRE INC. (1982) InfoPak No. 1 11.2.

CLEARFIELD A (1964) Structural aspects of zirconium chemistry. *Pure and Applied Chem.* **14** 91-108.

FREILICH, D and TANNY, GB (1978a) Formation mechanism of dynamic hydrous (iv) oxide membrane on microporous supports. *J. Coll. Interface Sci.* **64**(2) 362-370.

FREILICH, D and TANNY, GB (1978b) Hydrodynamics and microporous support size effects on the properties and structure of dynamically formed hydrous Zr(IV) polyacrylate membranes. *Desalination* **27** 233-251.

HOCK, AL (1974) Zirconium compounds; the industrial importance of their aqueous chemistry. *Chemistry and Industry* 864-874.

JOHNSON, JS, KRAUS, KA, FLEMING, SM, COCHRAN, HD and PERONA, JJ (1968) Hyperfiltration studies (XIV). Porous tubes precoated with filter aids as supports for dynamically formed membranes. *Desalination* **5** (3) 359-369.

JOHNSON, JS, MINTURN, RE and WADIA, FH (1972) Hyperfiltration (XXI). Dynamically formed hydrous zirconium (IV) oxide polyacrylic membranes. *Electroanalytical Chemistry and Interfacial Electrochemistry* **37** 267-281.

MARCINKOWSKY, AE, KRAUS, KA, PHILLIPS, HC, JOHNSON, JS and SHOR, AJ (1966) Hyperfiltration studies (IV). Salt rejection by dynamically formed hydrous oxide membranes. *J. Am. Chem. Soc.* **88** 5744.

MOTT, LH, BRANDON, CA and GERMAN, RM (1977) Hyperfiltration and ultrafiltration on sintered stainless steel. Paper presented at Membrane Separation Technology Seminar, Clemson University, Clemson.

NEYTZELL-DE WILDE, FG (1989a) Investigations related to treatment of effluent produced at Supacryl (Pty) Ltd. using membrane/microfilter techniques operated in the cross-flow mode. Report (Appendix A and Appendix B) submitted to Water Research Commission, September.

NEYTZELL-DE WILDE, FG, TOWNSEND, RB and BUCKLEY, CA (1989b) Hydrous zirconium (IV) oxide and zirconium polyelectrolyte membranes on porous stainless steel supports. Paper presented at First International Conference on Inorganic Membranes. Montpellier, France. 3-6 July.

TANNY, GB (1978) Dynamic membranes in ultrafiltration and reverse osmosis. *Sep. Pur. Methods* **7**(2) 185-220.

TANNY, GB and HAUK, D (1980) Filtration of particulates and emulsions with a pleated, thin channel, cross-flow module. *Sep. Sci. Technol.* **15**(3) 317-337.

TANNY, GB and JOHNSON, JS (1978) The structure of hydrous Zr(IV) oxide and polyacrylate membranes : Poly(acrylic acid) deposition. *J. Appl. Polym. Sci.* **22** 284-297.

TANNY, GB and KORIN, A (1981) A novel membrane system for the ultrafiltration of oil emulsions in synthetic membranes. In: Turbank, AF (ed.) *Synthetic Membranes. Vol II: Hyper- and Ultrafiltration Uses.* ACS Symposium Series 154.