

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 l/m²-h at 6 000 kPa and gave a rejection of 80 % from a solution of sodium nitrate containing 2 000 mg/(NaNO₃ at pH 7. When pretreatment was omitted, the corresponding values were, flux 87 l/m²-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 μ m to 0,45 μ m. 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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