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APPLICATION OF CERAMIC MEMBRANES TO REVERSE OSMOSIS

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ABSTRACT

Colloidal TiO_2 sols which contain stable particles that are ca. 50 Å in diameter have been produced. Scanning electron photomicrographs indicate that supported membranes which are free from flaws can be fabricated from these TiO_2 sols. These photomicrographs indicate that the membranes thus formed are approximately 1 micron thick. Furthermore, these photomicrographs indicate that total coverage of the support has been obtained.

In order to assess potential uses of ceramic membranes, it is necessary to determine if they are capable of achieving separations of industrial significance. A surface-force pore-flow model has been employed to predict the rejections expected for these TiO_2 membranes when used to process solutions containing polyethylene glycols of different molecular weights. These results were then used to predict the expected performance of these membranes when used to concentrate the permeate from the ultrafiltration of cheese whey.

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INTRODUCTION

Prior to 1959 no membranes were commercially available for ultrafiltration and reverse osmosis applications. Since that time, the synthetic membrane industry has grown by leaps and bounds. By 1988, the worldwide market for synthetic membranes had reached $1.2 billion/year (1). Consumer pressure and political attitudes over the next decade will force a variety of industries to decrease the amounts of pollutants that they discharge to the environment. This decrease will necessitate the removal of waste materials from a variety of process streams at minimal cost. An attractive solution to many of these waste treatment problems involves the use of permselective membrane technology.

The appeal of membrane technology is based on its ability to process large volumes of waste streams with minimal energy input relative to alternative technologies. However, in order to meet the increasingly stringent demands of these waste treatment applications, it will be necessary to develop membranes that are capable of operating at high temperatures and in harsh chemical environments. Ceramic membranes can meet these requirements. Typical ceramic membranes maintain their integrity at temperatures in excess of 200 °C (2). Furthermore, these membranes are stable in a wide variety of harsh chemical environments. Finally, these membranes are thoroughly resistant to many of the organic solutes and solvents which cause failure of polymeric membranes. These properties make ceramic membranes ideal for processing a variety of waste streams, including those which contain organic solvents.

Attempts to fabricate inorganic membranes date back to 1928 (3). In recent years, investigations of inorganic membranes have focused on the use of sol-gel techniques for the fabrication of ceramic membranes (4,5,6). Our research program is directed toward producing ceramic membranes for adaptation to industrial processes involving very low molecular weight solutes. The tasks in this

Table 1. Compositions of Sweet and Acid Wheys

COMPONENT	SWEET WHEY	ACID WHEY
Water	93.0	93.5
Total Solids	7.0	6.5
Lactose	4.9	4.4
Protein	0.8	0.7
Minerals/ash	0.5	0.8
Lactic acid	0.2	0.5
Fat	0.2	0.04
Other	0.4	0.06

process involve: 1) the development of stable colloidal gels; 2) the fabrication of supported ceramic membranes that are free from flaws; and 3) the characterization of the supported membrane.

Our earlier efforts in this area focused on the development of ceramic membranes of gamma-Al_2O_3 for adaption to industrial ultrafiltration processes (7,8). These studies indicated that these membranes have pores which have a mean pore radius of approximately 20 Å. Permselective characterization studies indicated that these membranes have a molecular weight cut-off of 2000. It was also demonstrated that these membranes could be effectively modelled using a surface force-pore flow model.

Our earlier studies also involved the use of these alumina membranes to process a typical industrial feedstock, viz. cheese whey. For every pound of cheese that is manufactured, typically 8 to 10 pounds of cheese whey are produced (9). The entries in Table 1 indicate the compositions of typical whey streams (10). These cheese wheys can be processed by ultrafiltration to yield whey protein concentrates which are commercially valuable products.

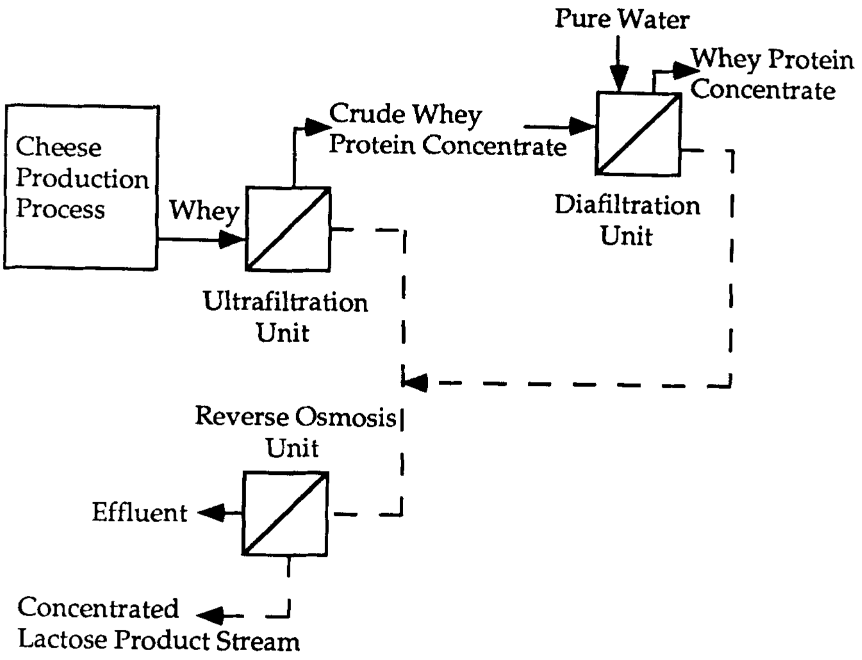

Figure 1. Schematic diagram of a typical cheese whey filtration process.

Figure 1 is a schematic diagram of a process for the production of whey protein concentrates. The first step involves separating the protein and other high molecular weight species from the remainder of the cheese whey. This step is carried out in an ultrafiltration unit. The second step involves diafiltration of the retentate solution to further enrich the protein content of the final product. This enrichment is accomplished using a second ultrafiltration step in which additional water is added to the feed stream. The product from this process is a whey protein concentrate which can be used in a variety of food processing applications. An additional step can be added to this process in order to minimize the amount of waste that is produced. This final step involves the concentration of the two permeate streams from steps one and two. This final concentration is performed by removing most of the water from these two streams to produce a concentrated solution of lactose and salts. The concentration is accomplished using a reverse osmosis unit. The water produced by this final step is essentially pure water that can be reused. The lactose concentrate can serve as a carbohydrate source in the production of animal feed.

The overall process shown in Figure 1 requires that one have available two distinct types of membranes. Both ultrafiltration (diafiltration) and reverse osmosis membranes are required.

Experiments were performed to determine if our alumina membranes would meet the requirements necessary for use in the ultrafiltration stage. These membranes had the necessary selectivity characteristics (essentially 100% rejection of the protein) . Our experiments also demonstrated that these membranes could be operated and regenerated over the extended operation times necessary for industrial applications.

The next logical step in the development of ceramic membrane technology is the production of membranes capable of reverse osmosis. The work presented here represents an extension of our previous work into the area of reverse osmosis. Previously we demonstrated the ability to produce colloidal sols which contain stable particles that were ca. 50 Å in diameter. Unsupported ceramic membranes fabricated from these sols possess the selectivity properties necessary for use in reverse osmosis. BET measurements indicate that unsupported TiO_2 membranes produced from these sols are characterized by mean pore diameters of less than 15Å (11). However, in order to employ this technology in a reverse osmosis application, it will be necessary to fabricate supported membranes which are free from flaws.

The work presented here involves the fabrication and preliminary characterization of supported nanoparticulate TiO_2 membranes. The data that are available will also be used in

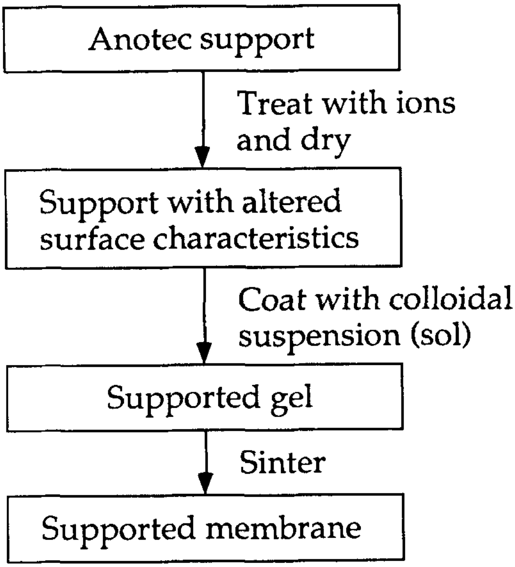

Figure 2. Flow diagram of the procedure used for deposition of nanoparticles on an Anotec support.

conjunction with a model to predict the performance of these membranes as reverse osmosis separation devices.

EXPERIMENTAL

Materials

Titanium iso-propoxide, tertiary amyl alcohol, and benzene were all obtained from Aldrich Chemical Company. All chemicals were used without further purification.

The supports used were 0.02 μ Anodisc™ filter membranes obtained from Anotec Separations.

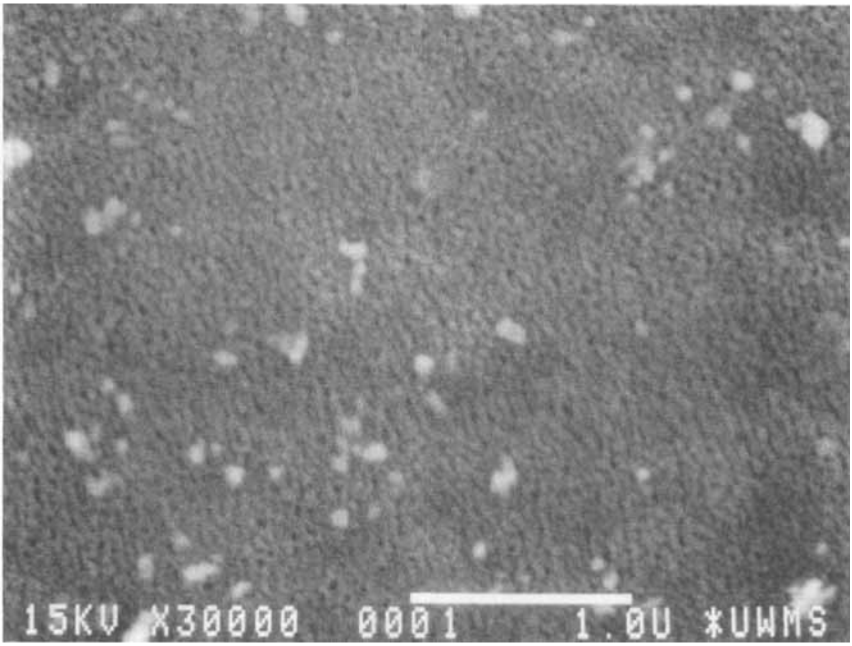

Figure 3. Electron photomicrograph of an Anotec Anodisc™.

Methods for Production of Membranes

The TiO_2 sols were prepared using the the technique described in a previous paper (2). The experimental protocol for depositing the sols on a support in order to obtain a supported membrane is described below and summarized in Figure 2. First the the supports were placed in an ionic solution to adjust the charge characteristic of the surface of the support. Next the supports were placed in tertiary amyl alcohol for 30 minutes. Immediately upon removal from the alcohol, the supports were immersed in a 0.05 M TiO_2 sol. After 20 seconds, the supports were slowly removed from the sol and any excess sol was shaken from the surface of the supports. The

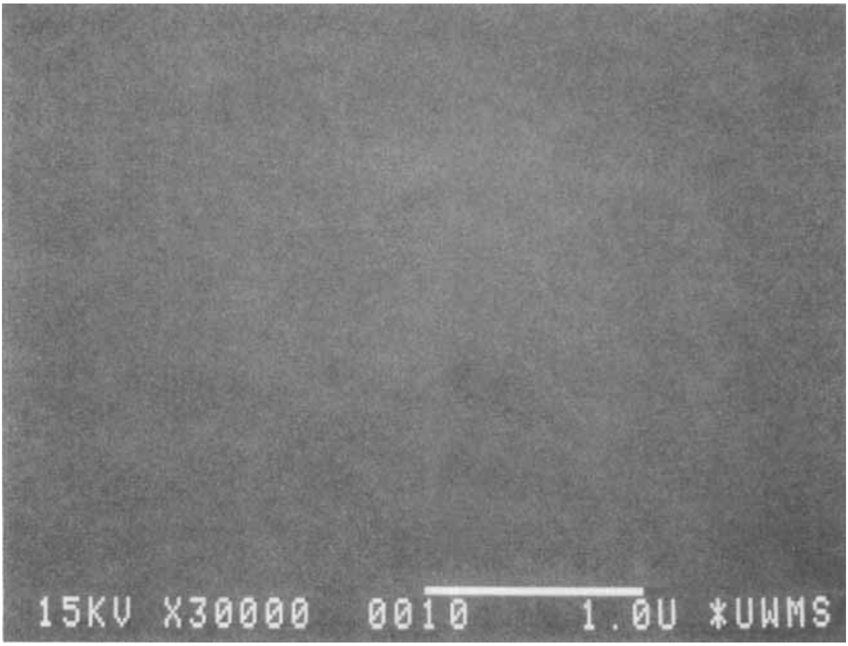

Figure 4. Electron photomicrograph of an Anotec Anodisc™ that has been coated with a 0.05M titania sol of 50 Å particles.

supported membranes were allowed to dry in ambient air for 1 hour. The supported membranes were then fired to 200 °C at a ramp rate of 1°C/ minute. The membranes were held at 200 °C for 1 hour and then were cooled to ambient temperature at a ramp rate of 1°C/minute.

Analytical Methods

The structures of the membrane surfaces were determined using a scanning electron microscope Model JOEL-JSM-35C.

RESULTS AND DISCUSSION

Electron Microscopy Studies

A scanning electron photomicrograph of the top surface of an Anotec Anodisc™ support is shown in Figure 3. This micrograph indicates that pores on the top surface of the Anodisc™ are approximately 0.02 mm in diameter. This value is in good agreement with the information provided by Anotec. Furthermore, the pores are uniformly distributed across the surface of the membrane.

Figure 4 is an electron photomicrograph of the top surface of an Anodisc™ that has been coated with a 0.05 M titania sol using the procedure described above. Inspection of Figure 4 indicates that a membrane has been successfully deposited and that this membrane is free from flaws. In addition, this inspection also indicates that coverage of the surface of the support is complete. Comparison of Figures 3 and 4 indicates that the pores that were evident in the uncoated support have been totally covered by the membrane. The result is an extremely smooth surface that is free of such flaws as pinholes and cracks.

Other investigators have suggested that the stresses that develop during drying are highly dependent on the thickness of the membrane. Therefore, information about the thickness of the membrane is extremely important in understanding and limiting the stresses that develop during the fabrication process. Figure 5 is an electron photomicrograph of a fracture edge of the same membrane shown in Figure 4 . From this micrograph, an estimate of the membrane thickness can be made. Inspection of Figure 5 indicates that this preparation protocol produces a membrane no more than 1 μm thick. Combination of this information with the fact that the membrane depicted is free from flaws indicates that membranes less than 1 μm in thickness are thin enough that stresses developed in

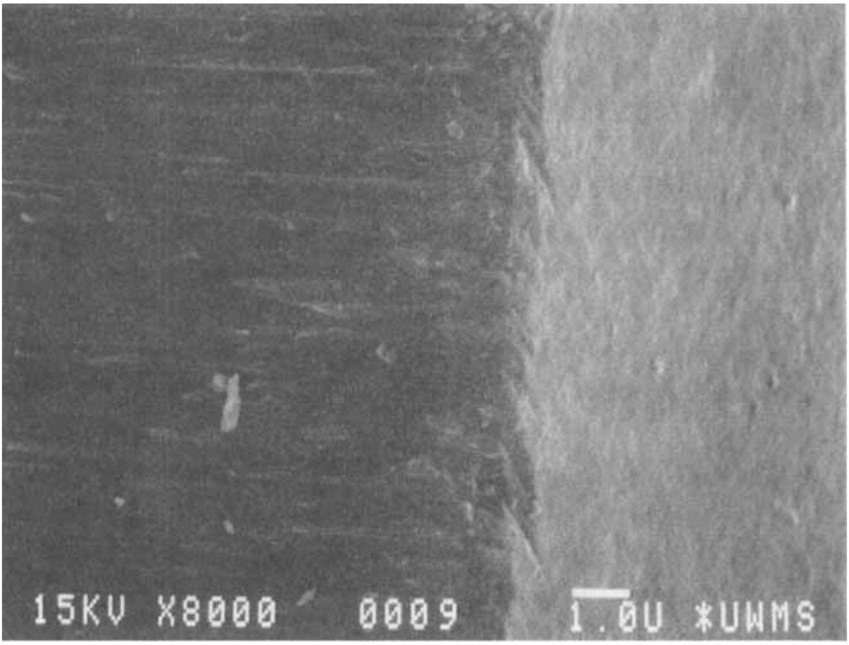

Figure 5. Electron photomicrograph of a fracture edge of an Anotec Anodisc™ that has been coated with a 0.05M titania sol of 50 Å particles

the plane of the membrane during the gelation process are limited to sufficiently low values to prevent cracking.

Others have suggested that the strength of the attraction between the membrane and the support material plays an important role in the fabrication of flaw-free membranes. We also attribute our success in preparing a flaw-free membrane to the alteration of the charge on the surface of the support during the experimental protocol. By treating the surface of the alumina support, we were able to decrease the positive charge on the surface, thereby decreasing the electrostatic repulsion forces between the sol particles and the surface of the support. Hence we were able to enhance the nature of the process by which sol particles are deposited on the support. Furthermore, once the sol particles have been deposited on the support, the particles are more strongly held to the surface whose charge has been altered. This increased interaction between the membrane and the support material also causes a decrease in the stresses that develop during gelation.

Modelling Studies

Flaw-free supported membranes have been fabricated from sols containing 50 Å particles. Unsupported membranes fabricated from these same sols have pores that are 15 Å in diameter. It is possible using this information, and information obtained in previous studies, to predict the expected performance of these supported membranes.

The model employed in this work is the surface force-pore flow model of Mehdizadeh and Dickson (12). This model predicts that the observed rejection will be dependent on the transmembrane pressure, the solute radius, the pore radius, and a potential function that describes the force exerted on a solute molecule inside the pore by the pore wall. This potential function is of the form:

$$\ln \Phi(\rho) = \ln(\theta_1/R_w) + \theta_2\rho^2 \qquad (1)$$

where θ_1 and θ_2 are adjustable parameters that are characteristic of the materials involved (including the solute), R_w is the radius of an average pore and ρ is a dimensionless radial distance from the center of the pore (i.e., r/R_w). However, θ_1 and θ_2 are highly correlated and θ_2 was therefore arbitrarily set to 0.5. Early indications are that θ_1 is dependent on the mass of a solute molecule, and therefore on its radius. The variables to be studied in our assessment of the ability of this model to predict membrane performance are the solute radius, pore radius, transmembrane pressure drop and θ_1.

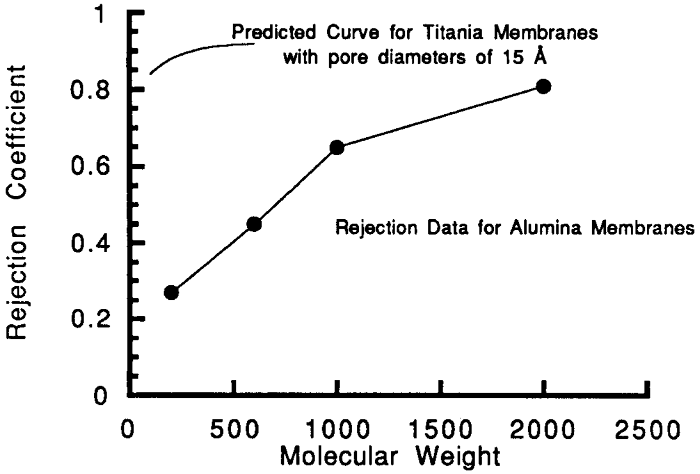

Figure 6. Rejection as a function of the molecular weight of the PEG solute present in an aqueous solution subjected to a pressure of 700 kPa.

To employ this model it is necessary to determine values of the potential function as a function of solute size. Consequently the following assumptions were made: (1) the potential function is independent of membrane material (as long as the membrane is a metal oxide); (2) the potential function is independent of pore radius. The validity of these assumptions will be tested when experimental rejection data become available.

Values of the potential function have been determined for polyethylene glycol (PEG) solutes of different molecular weights. These values are based on experimental rejection data obtained for these solutes using alumina membranes (see Figure 6). Furthermore, the solute radii for the solutes in question have been previously reported (13). Thus values of the potential functions are known as a function of solute radius.

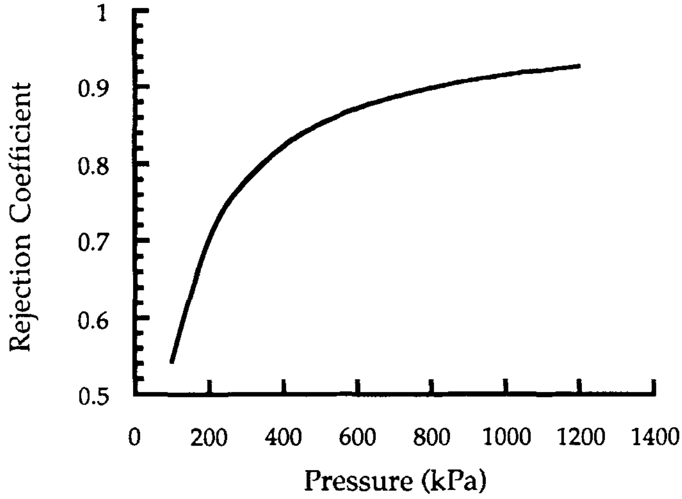

Figure 7. Rejection as a function of pressure drop for PEG with a molecular weight of 200.

The mean pore radius of the titania membranes is 7.5 Å and the solute radius is a known function of molecular weight (13). These variables and the values of the potential function that were previously determined were then inserted into the model calculations. Figure 6 contains a plot of the resultant theoretical predictions, together with the experimental data for the rejection of PEG obtained using the alumina membranes. The model is valid only over the range of molecular weights from 100 to 600. The lower limit is established by the commercial availability of PEG solutes with average molecular weights of less than 100. The upper limit arises because solutes with molecular weights greater than 600 have an effective solute radius which is greater than that of the pore radius. Thus a model of membrane performance would predict a step change in the rejection at such a point to 100% rejection based on mechanical sieving considerations alone. Inspection of Figure 6 indicates that for titania membranes with an average pore diameter of 15 Å one can expect to achieve rejections of greater than 80% for PEG solutes with molecular weights greater than 100.

As noted above, pressure plays an important role in determining the rejection coefficients which will be obtained using the indicated titania membranes. The curve in Figure 7 indicates the variation of the rejection coefficients with pressure for PEG with a molecular weight of 200. Rejection increases dramatically from 0% rejection at low pressures and approaches values in excess of 95% as the pressure is increased to 1000 kPa. These results are typical of pressure effects predicted by the model. They indicate that in order to obtain optimum rejection, it will be necessary to operate these titania membranes at high pressures.

Consider the use of reverse osmosis to concentrate the permeate stream produced by ultrafiltration of cheese whey (see Figure 1). Use of the aforementioned model permits one to predict the rejection of lactose that will be obtained with the nanoparticulate TiO_2 membranes if the following assumptions are made: (1) the potential function for lactose is the same as that for PEG of the same molecular weight; (2) lactose and PEG molecules of the same molecular weight have essentially the same radii. Using this information, one predicts a rejection coefficient of 91% for lactose. If such rejections are observed experimentally, these membranes would be adequate for use in the industrial concentration of the lactose contained in permeate streams produced by the ultrafiltration of whey.

CONCLUSIONS

Colloidal sols containing 50 Å titania particles have been prepared. Unsupported membranes fabricated from these sols have been characterized as having mean pore diameters of 15 Å. Supported membranes have also been fabricated from these sols.

Scanning electron micrographs indicate that these supported membranes both provide complete coverage of the support and are free from flaws. Predictions of the performance expected of these membranes indicate that they should be able to function effectively in reverse osmosis applications.

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