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Abstract

Porous cellulose acetate membranes obtained from Osmonics Inc. were characterized in terms of pure water permeability constant, solute transport parameter, and mass transfer coefficient with aqueous sodium chloride solution as the reference system. Reverse osmosis separation behavior of radium-226 as nitrate, chloride, and sulfate salts was studied. Reverse osmosis method of removing radium-226 from aqueous solutions has been compared with other methods, and it has been shown to be one of the best methods for alleviating radium contamination problems.

INTRODUCTION

The radioactivity in water and wastewater originates from natural and artificial or man-made sources. Among the unstable isotopes of naturally occuring radionuclides, the most predominant are potassium-40, rubidium-87, and the decay series of thorium-232, uranium-235, and uranium-238. The three decay series together comprise over 36 unstable radionuclides which are found in significant quantities in the aquatic environment, particularly in deep well water supplies, private wells in the general vicinity of uranium deposits, and all the industrial uranium facilities including mines and mills. These unstable radionuclides emit alpha, beta, and gamma radiations ranging in energy from 0.05 to 9.0 MeV. Exposure to such intense radioactivity poses a severe health hazard and is a possible cause of radiation-induced bone cancer, lung cancer, nonspecific malignant neoplasms, and in general any type of cellular aberration.

One of the most detrimental decay products derived from the decay series of uranium-238 is radium-226. There are various unstable isotopes of radium, but each radium isotope decays into a relatively short-lived daughter which emits hazardous high-energy alpha particles. As a result, the United States Public Health Service Advisory Committee on the 1962 Drinking Water Standards recommended a limit of 3 pCi/L for radium-226. The standard specified radium-226 in particular, because other radium isotopes are much less important in causing internal radium exposure. Recently, the United States Environmental Protection Agency has revised this value to 5 pCi/L. Such low tolerance limits call for removal of radioactive contamination by adequate treatment of wastewater.

The types of wastewater treatment methods which have been used to alleviate aqueous radium-226 contamination problems are directly related to the source of pollution, the mode of final water use, and the endogenous level of this nuclide. The methods presently in use for the removal of dissolved radium on an industrial level are selective membrane mineral extraction, reverse osmosis, barium sulfate coprecipitation, and both inorganic and macroreticular cationic resin ion exchange. The presently available radium removal technology used in nonindustrial or municipal facilities consists of zeolite ion exchange, reverse osmosis, manganese impregnated acrylic fibers, lime-soda softening, aeration, greensand filtration, and sandfiltration.

Reverse osmosis in a promising method for desalinization and concentration of aqueous salt solutions, and the process does not involve any phase transformation of the liquid. Some of the attractive features of reverse osmosis are low expenditure of energy, simplicity of processing technology, and the operation of the process at ambient temperatures. High-pressure reverse osmosis suffers from the disadvantages of high capital investment and severe membrane compaction problems. On the other hand, low-pressure reverse osmosis involves lower capital investment and an insignificant amount of membrane compaction. The work done so far on the low-pressure reverse osmosis treatment of mining and metallurgical waste effluents (*1–8*) has been very encouraging in that both valuable metal ions and product water of good quality could be recovered at the same time. As part of the program of low-pressure reverse osmosis and its application in the treatment of waste effluents, a detailed study of the reverse osmosis treatment of radium-bearing effluents under a variety of conditions was undertaken and the results are reported in this paper.

EXPERIMENTAL

Static Cell

The stainless steel static cell consisted of a detachable upper part and a lower part. The membrane was supported on a stainless steel porous plate embedded in the lower part of the cell. The lower part of the cell was provided with an outlet through which the membrane-permeated product solution was collected at atmospheric pressure. The upper part of the cell contained the feed solution of interest in contact with the membrane under pressure. The two parts of the static cell were fitted and sealed with the aid of two rubber O-rings. The effective surface area of the membrane in the cell was 13.4 cm^2. The desired pressure was achieved by compressed nitrogen gas from a gas cylinder. A magnetic stirrer fitted in the upper part of the cell, located about 0.64 cm above the membrane, was used in the uniform stirring of the feed solution, thereby minimizing the concentration polarization. The schematic diagram of the whole experimental arrangement is similar to the one reported earlier (*4*). Cellulose acetate membranes obtained from Osmonies Inc. were used in the present studies.

PROCEDURE

All the experiments were conducted at laboratory temperature (23 to 25°C). The membranes were pressurized with pure water at 400 psig for 2 hr before subsequent use in the experiments at the operating pressure of 300 psig. The pure water permeation rate (PWP), the membrane permeated product rate (PR) for a given area of the membrane, and the solute separation (f) were determined in all the experiments at preset operating conditions. A feed solution containing 2750 mg/L of sodium chloride was used to obtain data on membrane specification and to specify the mass transfer coefficient (k) on the high-pressure side of the membrane. The feed and the product solutions containing sodium chloride were analyzed by specific resistance measurements. The product rate data were corrected with respect to viscosity and the temperature (25°C). Because low concentrations were used in the experiments, solute separation (f) data were calculated using the relation

$$f = \frac{\text{solute concentration in feed} - \text{solute concentration in product}}{\text{solute concentration in feed}}$$

The feed and the membrane-permeated product solutions were analyzed for Ra-226 as follows: transfer an aliquot of the solution containing Ra-

226, add 5 mL concentrated HCl and 200 mL of distilled water, and boil for 5 min. To the hot solution add 5 mL of 1 *M* citric acid solution and then adjust the pH between 8 and 9 with ammonium hydroxide solution. To the ammoniacal solution add 40 mg of lead and 0.5 mg of barium nitrate solution. Place the beaker on a magnetic stirring plate, insert the magnetic stirring bar, add 0.5 g of ammonium sulfate as a solution, and adjust the pH to 1.0 with 1 : 1 sulfuric acid. Stir the solution for half an hour. Filter the combined sulfate precipitate of lead, barium, and radium on millipore HABP04700, wash the precipitates with 1% sulfuric acid, and discard the filtrate. Transfer the millipore filter into the original beaker, wash off the precipitate with a fine jet of water, then adjust the solution pH between 8 and 9 with ammonium hydroxide and add 5 mL of 0.25 *M* EDTA solution. Rinse the filter with water, discard the filter, and boil the solution. Place the beaker on a magnetic stirring plate, add 0.5 g of ammonium sulfate in the form of a solution, and while stirring add glacial acetic acid and adjust the pH to 4.0 using a pH meter. Continue stirring for 30 min. Filter the precipitate of barium and radium sulfates on a millipore HABP02500 filter disk and discard the filtrate. Dry the filter and mount on a circle of gummed label and determine radium-226 by alpha spectrometry.

RESULTS AND DISCUSSION

Membrane Specifications

The cellulose acetate membranes used can be specified in terms of parameters such as the pure water permiability constant, A, and the solute transport parameter, D_{AM}/K_δ, at a particular operating pressure. The product rate and the solute separation obtained with a membrane so specified are functions of the mass transfer coefficient, k, on the high-pressure side of the membrane, which is governed by the feed flow rate and the feed concentration used in the experiment. A computer program (*9*) using experimental data on pure water permeation rate, membrane-permeated product rate, and solute separation at preset operating conditions for the aqueous sodium chloride feed solution containing 2750 ppm salt was used in the calculation of A, D_{AM}/K_δ, and k. The data presented in Table 1 on the values of A and D_{AM}/K_δ for sodium chloride at 300 psig specify the membrane used in the present studies. The feed flow conditions used in all the experiments done in the present investigation are specified in terms of the corresponding value of k obtained with the reference system of sodium chloride solution containing 2750 ppm of salt. To enable comparison of the

TABLE 1

Membrane Specification Data[a]

Film no.	$A \times 10^6$ g mole H_2O (cm^{-2} sec^{-1} atm^{-1})	D_{AM}/K_δ for NaCl (10^4 cm/sec)	Feed concentration = 2750 mg/L NaCl, $k = 13.1 \times 10^{-4}$ cm/sec	
			Solute separation (%)	Product rate (g/hr)
1	2.74	1.87	58.3	31.4
1	2.64	3.66	60.7	31.7

[a] Membrane area 13.4 cm^2; pressure 300 psig.

TABLE 2

List of Solutes Used with Some Physicochemical Data

No.	Solute	λ_+°	λ_-°	$D_{AB} \times 10^5$ (cm^2/sec)	$k \times 10^4$ (cm/sec)
1	$Ra(NO_3)_2$	66.8	71.42	1.378	11.81
2	$RaCl_2$	66.8	76.35	1.422	12.06
3	$RaSO_4$	66.8	80.8	0.9754	9.38

relative performance of the membrane for feed solutions for which physicochemical data such as osmotic pressure and other pertinent data are not readily available, it is useful to provide such specifications for the membrane in terms of easily obtainable prarameters for a convenient and well-studied reference feed solution system such as the sodium chloride solution.

Solute Transport Parameter

In Table 2 the solutes used in the present studies together with the relevant physicochemical data such as the limiting ionic conductances (λ_+, λ_-), the calculated diffusivities (D_{AB}), and the mass transfer coefficient (k) values are given. The analysis of the data and the relations used in the calculations are the same as reported before (5). Using the data on product rates (PR), solute separation (f), the effective membrane area(s), the density of the solution (d), and the mass transfer coefficient (k) values, the solute transport parameter (D_{AM}/K_δ) for the various salts studied were calculated. The data on D_{AM}/K_δ and k, together with solute separation and product rates, are presented in Table 3.

TABLE 3

Data on Solute Transport Parameters

Salt	Solute separation	Product rate (g/hr)	k (cm/sec)	D_{AM}/K_δ (cm/sec)
$Ra(NO_3)_2$	0.8200	11.30	11.81×10^{-4}	4.78×10^{-5}
$RaCl_2$	0.8400	11.50	12.06×10^{-4}	4.22×10^{-5}
$RaSO_4$	0.8620	12.10	9.38×10^{-4}	3.74×10^{-5}

Separation of Radium Salts

The uranium mine tailings were leached with dilute nitric acid, dilute hydrochloric acid, and dilute sulfuric acid to obtain solutions containing $Ra(NO_3)_2$, $RaCl_2$, and $RaSO_4$, respectively, and these solutions were subjected to reverse osmosis. The solute separation data (Table 3) of the radium salts studied show an increase in the separation (86.2%) as compared to a solute separation of 59.5% in the case of sodium chloride. This is in keeping with the fact that divalent metal ion salts are better separated than monovalent metal salts. It is to be noted that the solute transport parameter (D_{AM}/K_δ) decreased with an increase in the solute separation. It is also interesting to compare the solute separation data of radium associated with different anions. Radium sulfate separation is higher than radium chloride which in turn is greater than radium nitrate. This trend in separation has been documented in the case of other metal salts in earlier studies (*5*, *7*, *8*). The observed increase in solute separation in the case of radium sulfate as compared to that of radium nitrate may be attributed to the presence of radium sulfate ion-pairs in solution. The experimental fact the ion-pairs are in general better separated than bare hydrated metal ions in reverse osmosis has been well documented in earlier studies (*5*, *7*, *8*).

Ion-pair formation in the case of metal ion sulfate solutions and the resulting increase in solute separation is of significance in practical situations. In the case of solutions containing metal ions associated with either nitrate or chloride anion, it is possible to increase the solute separation by the addition of sodium sulfate and at the same time obtain high product water recovery by using more porous cellulose acetate membranes. Ion-pair formation and the consequent increase in solute separation can be considered significant for the practical industrial treatment of barren mining and metallurgical waste effluents containing traces of metal ions associated with nitrate or chloride anion.

Data on the separation of radium-226 from solutions obtained on leaching uranium mine tailings are presented in Table 4. The cellulose acetate

TABLE 4

Separation of Radium-226

^{226}Ra (pCi/L)	Pressure (psig)	Product rate (g/hr)	Separation (%)
910	300	13.2	83.5
390	300	14.4	92.3
380	300	10.1	86.8
390	300	10.6	82.1

TABLE 5
Methods for the Removal of Radium

Method	Maximum feed concentration (pCi/L)	Efficiency of removal (%)
Selective membrane mineral extraction	1500	99.7
Reverse osmosis	750	99.4
Barium sulfate coprecipitation	300	Variable
Ion exchange	100	95.0
Manganese-impregnated acrylic fibers	125	96.0
Lime-soda softening	35	85.0
Aeration	5	18.0
Greensand filtration	10	50.0
Sand filtration	—	Variable

membranes which gave sodium chloride separation of the order of 60% resulted in separating radium to the extent of 86%. Based on the present and previous studies (*3–8*), one can conclude that membranes which can give 70% sodium chloride separation should yield separation of radium to the extent of 99% or more. From these results it is reasonable to conclude that reverse osmosis treatment of radium-bearing waste effluents could result in producing product water of suitable quality for either recycle operations or for discharge into nearby streams.

The different methods employed in the radium removal technology both in industrial and municipal water treatment along with the efficiency of removal of radium ore are presented in Table 5. From this it is reasonable to conclude that reverse osmosis is one of the best methods for alleviating aqueous radium contamination problems.

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