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Natural zeolite clinoptilolite-phosphate composite Membranes for water desalination by pervaporation



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ABSTRACT

Natural zeolite membranes, directly sectioned from mineral deposits, have been previously reported to show molecular sieve characteristics in selective separation of water and hydrated cations. Although a high removal of cations was observed, the low water flux was a limitation for any potential industrial applications. In this study novel clinoptilolite-based phosphate composite membranes were prepared by dry pressing of mixed powder materials followed by high temperature autoclave steaming and characterized by XRD, SEM-EDX. Their performance for pervaporative water desalination was examined using different levels of salinity in a temperature range of 25–95 °C and feed side pressure of 1 atm. At 1400 ppm Na feed salinity and 95 °C, a water flux of 15 kg/m² h and over 95% removal of Na⁺ were obtained. The water flux achieved was about 10 times higher than the flux obtained using natural zeolite rock membranes. Introducing phosphate into the composite membranes appears to provide not only mechanical strength, through the possible chemical bonding between zeolite particles and the in-situ phosphate cement, but also to create a chemically favorable interface between zeolite crystals. Such interface might facilitate the desalination process bypassing the technical difficulties of ion leakage/diffusion through the inter-crystal spaces commonly associated with synthetic zeolite membranes.

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1. Introduction

Water scarcity has become both a reality and a major problem in search of a solution. One practical approach is to recover and reuse the contaminated wastewater produced by industrial operations such as oil and oil sands industries [1,2]. In Alberta, Canada, 80% (135 billion barrels) of oil sands are located deep underground requiring in-situ oil sands bitumen extraction technologies [3]. Steam assisted gravity drainage (SAGD) is a thermal in-situ oil sands bitumen recovery process. High temperature steam is injected into a steam chamber to heat bitumen that causes the low viscosity bitumen to flow into production chamber by gravity [3,4]. Obviously a sustainable SAGD process relies heavily on water resources and quality for the boiler to produce high temperature steam. One of the challenges in the SAGD process is to efficiently recycle the produced water for reuse in steam generation. Processing or produced water from SAGD contains high salinity and various dissolved organics [3]. Water desalination by polymeric membranes through reverse osmosis is a well-established process;

however, the high hydrocarbon contents and operating temperatures that are often required can destroy the membranes [5,6].

Recently the use of molecular sieve membranes for water desalination has attracted attention both from academia and industry [7,8]. Water desalination by zeolite membranes operated in both RO (Reverse Osmosis) mode and pervaporation mode has been reported [8–11]. Molecular sieving/ion-sieving, competitive ion adsorption and charge exclusion are general mechanisms for these separations [11,12]. The intrinsic molecular sieving/ion-sieving characteristics and the well-known ion exchange property of zeolite molecular sieves as well as their relatively high thermal and chemical stabilities have positioned them as promising alternatives for water desalination and de-oiling at high temperatures. Currently, almost all synthetic zeolite membranes are synthesized as a thin crystal layer supported on various porous substrates [10,11,13]. In order to reduce the defects (cracks) and provide enough flux, the pore size and porosity of the support materials have to be strictly specified. This combined with the need for chemical and physical compatibility dramatically increase the cost for suitable support materials. In addition, there are technical challenges associated with the synthesis of a defect-free two dimensional thin layer from three dimensional crystal particles. The intercrystalline spaces created during the synthesis of zeolite crystals naturally form non-selective passages for both water

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molecules and ions, which inevitably reduces the efficiency of the membranes [14,15].

Previously, we reported that natural zeolite, clinoptilolite, sheet membranes sectioned directly from rock deposits (British Columbia, Canada) demonstrated molecular sieve characteristics during water desalination [16,17]. Clinoptilolite is one of the most abundant and ubiquitous natural zeolite deposits in the world. Clinoptilolite deposits of high phase purity and crystal sizes as large as 20 μm can be found [18,19] making them a valuable, low-cost material for molecular sieve related separations, including water desalination. Using these clinoptilolite membranes over 99% removal of cations (such as Na^+ , Ca^{2+} , Mg^{2+} and K^+) was observed, but the water permeate flux was relatively low (less than 1 $\text{kg}/\text{m}^2\text{h}$). One difficulty with using natural zeolite rocks is the deposit-dependent variability. However, the low cost, and the promising results of the previous study have encouraged us to manufacture natural zeolite based membranes that are scalable and property tuneable. Phosphate cement is a widely recognized ceramic material used in dental treatments and synthetic bones [20–22]. The well-known chemical bonding ability of phosphate with many other materials have been used to seal/lock radioactive hazardous materials for environment remedy applications [22]. The tetrahedron molecular structure of phosphate is very similar to silicate, which has the property, under certain conditions, to form polyphosphate structures resembling the aluminosilicate framework [23,24]. In this study we mimicked the structure of the natural zeolite membrane, which is a closely packed natural zeolite crystals with dense inorganic fillers around them. We developed a clinoptilolite-phosphate composite membrane where the unique chemical bonding property of phosphate was used as dense inorganic matrix. Instead of using natural zeolite membranes sectioned from rock deposits, the new clinoptilolite-phosphate composite membranes were prepared by the combination of natural zeolite which can be quality controlled by a commercialized purification process with phosphate ceramics. Finally the performance of clinoptilolite-phosphate composite membranes was evaluated in pervaporative water desalination. To the best of our knowledge, this is the first report of a clinoptilolite-phosphate composite membrane prepared and used for pervaporative water desalination.

2. Experimental

2.1. Materials

Natural zeolite, clinoptilolite was supplied (St. Cloud, New Mexico) as powders with a particle size of through 320 mesh. The specifications from the supplier are listed in Table 1. Monopotassium phosphate (MKP) was purchased from Rotem Amfert Negev Ltd. MgO powder (surface area < 0.3 m^2/g) was purchased from Martin Marietta, USA. Fumed SiO_2 was obtained from Elkton Products Inc, Canada. All the above materials were directly used in membrane preparation without further treatment/purification. 10 L of saline water stock solution (1400 ppm Na) used in the

Table 1
Chemical composition of commercial natural zeolite clinoptilolite (Ca, Na₂, K₂) ($\text{Al}_6\text{SiO})_{24}\text{H}_2\text{O}$ (St. Cloud Mining Company).

Major Oxides	Wt%	Major oxides	Wt%
SiO_2	70	MgO	1.5
Al_2O_3	12.1	Na_2O	0.3
CaO	3.4	Fe_2O_3	1.6
K_2O	3.0	P_2O_5	0.05

membrane water desalination tests was prepared by dissolving NaCl (Fisher Scientific Canada) in distilled water.

2.2. Membrane preparation

Clinoptilolite-phosphate composite membranes were prepared by dry powder pressing followed by high temperature steaming. Monopotassium phosphate (MKP) and MgO powder (1:2 M ratio) were thoroughly mixed with a pestle and mortar. Clinoptilolite powder (through 320 mesh) was mixed with the phosphate mixture in a 1:1 weight ratio. The composite powder of zeolite and phosphate was placed in a stainless steel pressing mold with a die of 2 in. diameter and pressed under a total force of 20 t for 20 s using a hydraulic presser (Carver, Inc.). The resulted green disk of 2 in. diameter with a thickness of about 1.3–1.5 mm was mounted on a ceramic support inside an autoclave that had 1/3 of its volume filled with de-ionized water. The membrane support was designed so that the green disk stood vertically with both faces perpendicular to the water surface of the autoclave. The autoclave with the membrane disk was then placed overnight (around 12 h) in a conventional oven pre-heated at 100 °C. After this first steaming the composite membrane surface was hardened and easy to handle and was cut to a 3.1 × 2.3 cm rectangular shape (to fit the testing cell) using an operating knife. The cut rectangular membrane was placed back in the autoclave for a secondary steaming at 150 °C for three days. After this secondary steaming the membrane was washed with distillate water and dried on a paper towel at room temperature.

Phosphate only membranes were prepared with MgO and MKP powders at a 2:1 M ratio following the same procedures as zeolite-phosphate composite membrane with no addition of zeolite.

SiO_2 -phosphate composite membranes were prepared following the same procedures as above, except that the zeolite portion was replaced with the same weight ratio of fumed SiO_2 .

2.3. Membrane characterization

The prepared membranes were characterized by XRD and SEM-EDX analysis. XRD patterns were collected by Rigaku Geigerflex Model 2173 diffractometer with a Co tube and a graphite monochromator. Surface morphologies of the membranes were examined by SEM (Zeiss EVO MA 15) equipped with a Bruker Silicon Drift Detector for Energy Dispersive X-Ray analysis to identify the elemental composition of different morphological regions on the membranes.

2.4. Water desalination

The performance of the clinoptilolite-phosphate membranes in pervaporative water desalination was evaluated in a lab made cross-flow stainless steel membrane testing system shown in Fig. 1. The membrane cell was designed to hold two rectangular membranes with a dimension of 2.5 × 3.5 cm^2 and allow simultaneous testing. Membranes were sealed to the frame of the cell by a commercial high temperature Epoxy resin (working temperature 150 °C, Tri-Tex co Inc.). Nano-powder of fumed SiO_2 (CAB-O-SIL, Cabot.) was used as a sealant filler to adjust the consistency of the sealant for best result. Two different salt levels of feed streams were used. The low salt feed was Edmonton city tap water containing ~50 ppm of Na. The high salt saline water (1400 ppm Na) was prepared by mixing NaCl and distilled water. Sodium concentration of 1400 ppm was used because typical oil sands SAGD produced water contains about 1400 ppm of sodium [25]. Saline water was fed to the membrane feed side by a circulating pump at a flow rate of 1 L/min. Permeate water samples were collected through an alcohol-dry ice-cold trap connected to a

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