Desalination 352 (2014) 142–149

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

$BaCO_3$ nanoparticles embedded retentive and cation selective membrane for separation/recovery of Mg^{2+} from natural water sources

Niharika Srivastava [a,1], Kuldeep V. Joshi [b], Amit K. Thakur [a,1], Shobhana K. Menon [b], Vinod K. Shahi [a,*]

[a] Electro-Membrane Processes Division, CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364002 (Gujarat), India
[b] Department of Chemistry, Gujarat University, Ahmedabad-380 009 (Gujarat), India

HIGHLIGHTS

- $BaCO_3$ nanoparticles embedded Mg^{2+} retentive membranes
- Electro-membrane process for recovery of Mg^{2+} from natural water sources
- Cation-exchange membrane with Mg^{2+} retention property
- Stable and selective membrane with good conductivity and ion-exchange capacity

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form 24 July 2014
Accepted 14 August 2014
Available online 7 September 2014

Keywords:
$BaCO_3$ nanoparticles
Retentive membrane
Ion-exchange membranes
Nanoparticles embedded membrane
Mg^{2+} separation

ABSTRACT

$BaCO_3$ nanoparticles (NPs) (20 and 100 nm) were prepared using poly(vinyl pyrrolidone) (PVP) as stabilizer. The prepared NPs showed high adsorption capacity for Mg^{2+} in presence of other cations (Na^+, Ca^{2+} etc.). $BaCO_3$ nanoparticles embedded sulphonated poly(ether sulfone) (SPS) membranes were prepared, which showed Mg^{2+} retentive and cation selective properties. These membranes exhibited good thermal, mechanical, and chemical stabilities along with conductivity and ion-exchange capacity due to SPS matrix. Mg^{2+} retentive nature of these membranes was attributed to the embedded $BaCO_3$ NPs. Further, SPS-NPE membrane was assessed suitable for electro-separation process. Electrodialytic studies confirmed very high retention values for Mg^{2+} in comparison with Na^+ and Ca^{2+}. The energy consumption of proposed process suggested suitability of these membranes for separation/recovery of Mg^{2+} from natural water resources.

1. Introduction

Seawater contains high Mg^{2+} concentration (~1300–1400 mg/l) along with 400–500 mg/l Ca^{2+} [1,2]. In the United States, electrolysis of fused magnesium chloride, obtained from brines, well and sea water, is the primary source for magnesium. At the cathode, Mg^{2+} ions reduced to magnesium metal, however at the anode each pair of Cl^- oxidized to Cl_2. Presence of ~20,000 mg/l Cl^- and ~11,000 mg/l Na^+ along with other monovalent and bivalent ions diminished the chances for selective recovery of Mg^{2+}, and emerged as a great challenge.

Advanced membrane technologies provide a variety of economically feasible applications for water/waste water treatment, chemical processing, energy production and pharmaceutical manufacturing [3,4]. Specific nano-filter membranes are reported for the selective separation of Mg^{2+} from seawater [2]. However, recovery of Mg^{2+} with high purity in presence of other ions is desirable. Donnan dialysis (membrane-based equilibrium process) also has been proposed for the removal of Ca^{2+} and Mg^{2+} from water resources [5,6]. No report is available regarding Mg^{2+} retentive membrane for its separation or recovery from natural water sources. Because of modularity and profitability, electro-membrane separation techniques are well suited for the separation of inorganic salts of varied molality [7–9].

Ion-exchange membrane based electro-membrane process offers many advantages related to resources and energy management for the separation/recovery of Mg^{2+} from natural water resources (multi-ionic system). Ion exchange membranes contain charged functional groups attached with polymer backbone and showed selectivity for oppositely charged ions (counter-ions) under electrical potential gradient [10–12]. Demands for the specific ion selective membranes are increased for the removal/recovery of valuable ions from waste solutions. Several types of ion-exchange membranes were reported for the separation of ions with the same charge from mixed electrolyte solutions by electrodialysis [13–20]. However, due to inability of cation-exchange membrane to discriminate between bivalent cations, selective separation/recovery of $Mg^{2+}$from multi-ionic natural resources

---

[*] Corresponding author. Tel.: +91 278 2569445; fax: +91 278 2567562/2566970.
E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).
[1] Tel.: +91 278 2569445; fax: +91 278 2567562/2566970.

http://dx.doi.org/10.1016/j.desal.2014.08.014
0011-9164/

is challenging. The idea for developing Mg^{2+} retentive and cation selective membrane based electro-separation seems to be a useful option for its selective separation/recovery from natural water resources.

Various types of retentive membranes were reported for retention of bacteria and virus [21,22]. Herein, we report a novel $BaCO_3$ NPS embedded SPS membrane (SPS-NPE) based electro-separation process for selective separation/recovery of Mg^{2+} from natural water resources (ground and sea water).

2. Experimental

2.1. Materials

Poly(ether sulfone) (PES) (Udel P-3500) was received from Solvay Advanced Polymers. Poly(vinyl pyrrolidone) (PVP), $BaCl_2$, Na_2CO_3, H_2SO_4, NaCl, $MgCl_2$, $CaCl_2$ etc. of AR grade, were obtained from S.D. fine Chemicals, India. All chemicals were used without any further purification. Deionized (DI) water was used in all experiments.

2.2. Sulfonation of PES and synthesis of PVP stabilized $BaCO_3$ NPs

Detailed procedures for sulfonation of PES and preparation of SPS membranes have been described in Section S1 (Supplementary data) [23]. SPS membranes were conditioned in HCl and NaOH solutions (0.10 M) alternatively, and washed with distilled water.

For the preparation of $BaCO_3$ NPs, 5 ml of Na_2CO_3 solution (0.1 M) was mixed with 10 ml of PVP (1 mg/ml) aqueous solution in a beaker. After vigorous stirring (30 min) the pH of the solution was adjusted to 9.0 using 2.0 M HCl. Subsequently, 5 ml of $BaCl_2$ solution (0.2 M) was drop-wise added to the above mixture under continuous stirring. White precipitate was collected and washed with distilled water followed by methanol and dried in a vacuum (60 °C) for further characterization.

For preparing NPs embedded membranes, the desired quantity of SPS was dissolved in dimethylacetamide (20% w/v) to obtain a homogeneous solution and $BaCO_3$ NPs (2.5–10.0% w/v) were added with constant stirring and continued stirring for 12 h. The resultant viscous solution was cast in the form of thin film of the desired thickness on a clean glass plate after proper degassing and dried under IR lamp followed at 70 °C for 12 h. Uniform distribution of NPs (active sites) on the membrane surface was confirmed by SEM images. NPs embedded membranes with different loading of $BaCO_3$ (wt.%) were prepared and designated as SPS-NPE-*x*%, where *x* denotes weight percentage of $BaCO_3$ NPs (2.5–10.0), while pristine membrane was named as SPS.

2.3. Instrumental analysis

Detailed instrumental analysis is included in Section S2 (Supplementary data).

2.4. Physicochemical and stability analysis of SPS-NPE nanocomposite membranes

The detailed procedures for water uptake, and ion uptake capacity (IUC) measurements are included in Section S3 (Supplementary data) [24–26]. Membrane stabilities were also assessed in harsh oxidative, hot aqueous and acidic and basic environments. The oxidative stability of SPS-NPE membranes was evaluated in Fenton's reagent at 80 °C for 3 h. It served as an accelerated test to simulate the strong oxidative water splitting conditions and membrane degradation by oxy active radicals [27]. For the hydrolytic stability test, small pieces of membranes were boiled in water for 24 h at 120 °C in a pressurized closed vial. The oxidative and hydrolytic stabilities were evaluated by loss in weight, ion-exchange capacity and physical appearance of the test samples [28]. Membrane stability was also assessed in HCl and NaOH solutions (5.0 M) for a fixed time period (48 h) by recording weight loss [29,30].

2.5. Electrochemical characterizations

The Mg^{2+} transport number in the membrane phase was obtained by Hittorf method as reported earlier [20,29]. Conductivity of SPS-NPE membranes was measured in equilibrium with different electrolytic environments (0.02–0.10 M) using a potentiostat/galvanostat frequency response analyzer (Auto Lab, Model PGSTAT 30, Eco Chemie, B.V. Utrecht, The Netherlands). The membranes were sandwiched between two in-house made circular electrodes ($4.0\ cm^2$) of stainless steel. Direct current (dc) and sinusoidal alternating currents (ac) were supplied to the respective electrodes for recording the frequency at a scanning rate of 1 μA/s within a frequency range of 10^6 to 1 Hz. The membrane resistance was obtained from Nyquist plots [31].

The chronopotentiometric responses (described in Section S4 (Supplementary data)) for SPS-NPE-10% and SPS-NPE-2.5% membranes were recorded in equilibrium with different electrolyte solutions (NaCl, $CaCl_2$ and $MgCl_2$) of known concentrations [32].

2.6. Adsorption studies for Mg^{2+} and Ca^{2+}

Stock solutions of Ca^{+2} and Mg^{+2} (1000 mg/L) were prepared. The Mg^{2+} and Ca^{2+} removal experiments in aqueous media were carried out using $BaCO_3$ NPs in absence of any other competing ions. The experiments were carried out by adding 0.01–0.10 g of $BaCO_3$ nanoparticles in 100 ml of 100 mg/L Ca^{+2} and Mg^{+2} solutions in 250 ml PVC flask. All the experiments were carried out at ambient temperature (25 ± 1 °C). After continuous stirring for a 12 h the solid was separated by centrifugation (model no. R-4C, Remi laboratory centrifuge) (3000 rpm) and filtered through IC Millex-LG filter (Millipore) and the unremoved Ca^{+2} and Mg^{+2} were estimated by Dionex ion chromatography system ICS 1000. Operating conditions for Ca^{+2} and Mg^{+2} were as follows: column, IonPac® SCS-1 (4 × 250 mm); eluent, 3 mM methanesulfonic acid (MSA) (Sigma-Aldrich); column temperature, 30 ± 2 °C; flow rate, 1.0 ml min^{-1}; injection volume, 25 μl; system back pressure, 1920 psi.

2.7. Electrochemical recovery of Mg^{2+} in membrane cell

An electrodialytic cell for recovery of Mg^{2+} (Fig. 1) was fabricated by acrylic sheet. Membrane cell was divided into four compartments viz., catholyte, anolyte, feed and permeate compartments using anion-exchange, cation-exchange, and SPS-NPE membranes. All streams were connected through separate tanks under recirculation mode using peristaltic pumps. A DC power supply (model L 1285, Aplab, Mumbai, India) was used to apply constant current, while the potential was measured using digital multimeter (model 435, Systronics, India) connected in a series mode. Distance between both electrodes and effective membrane area was kept at 0.50×10^{-2} m and $8.0 \times 10^{-3}\ m^2$, respectively. Electrodes were made of expanded TiO_2 sheets coated with a triple precious metal oxide (titanium–ruthenium–platinum) (6-μm thickness), with 1.5 mm thickness, and obtained from Titanium Tantalum Products (TITAN, Chennai, India). All four storage tanks and pumps were used to feed the different compartments, separately with $6.0 \times 10^{-3}\ m^3/h$ constant flow rate in batch mode operation. The whole set up was placed at room temperature (30 °C) without any additional temperature control. Under the influence of applied voltage, Na^+ or Ca^{2+} was migrated from feed to permeate compartments, while Mg^{2+} was retained in feed compartment through SPS-NPE membrane. Experiments were carried out for the desired time and samples were collected from the initial feed and output for estimation of cations by AA-680 Shimadzu atomic absorption/flame emission spectrophotometer in the case of mixed metal transport.