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Hybrid membranes from sulphonated poly (2, 6-dimethyl-1, 4-phenylene oxide) and sulphonated nano silica for alkali recovery

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ABSTRACT

Hybrid membranes for diffusion dialysis were prepared by incorporating sulphonated nano silica particles into sulphonated poly (2, 6-dimethyl-1, 4-phenylene oxide) (SPPO) matrix. The membranes with ion exchange capacities (IECs) of 1.87–2.00 mmol/g possessed favorable thermal stability and alkali resistance. They were tested in NaOH/Na_2WO_4 feed solution via diffusion dialysis (DD) process. Results showed that as-prepared hybrid membranes exhibited better separation performance under the temperature higher than 35 °C. The highest hydroxide flux (U_{OH}) reached 0.015 m/h at 55 °C with a separation factor around 34. The pure SPPO (as control) exhibited much lower U_{OH} values at the investigated temperature range though its separation factor was higher. The structure and physico-chemical properties of the hybrid membranes were investigated to better understand the DD results. Sulfonic groups at the surface of nano silica particles were believed to enhance the transport of Na^+ and i.e., promoted the diffusion of OH^-.

1. Introductions

As a low-energy-consumption, eco-friendly and spontaneous membrane process [1], diffusion dialysis with ion exchange membrane is popular for recovering acid or alkali from industrial wastes. However, compared with anion exchange membrane diffusion dialysis (AEMDD) for acid recovery [2–6], cation exchange membrane diffusion dialysis (CEMDD) for alkali recovery is infrequently researched [7,8]. There are several reasons. Firstly, most of the polymer membrane materials are not alkali-resistant, which is disadvantageous for the long-time operation of DD process; Secondly, pure polymer materials for the membrane preparation are lack of thermal and mechanical stability; Finally, the recovery ratio and separation effect is not high enough in some cases, due to the native characteristics of the alkali solution (the paper industry waste, for instance) and the existence of high water osmosis.

Till date, many efforts have been made to improve performance of polymeric membranes [8–14] in alkali resistance, thermal and mechanical stability. Wu et al. prepared a series of PVA/SiO_2 hybrid membranes using various binary or ternary multi-silicon copolymers as crosslinking agents and the membranes possessed high flux and selectivity with favorable thermal and mechanical stability [15]. In our previous investigations, SPPO membranes were prepared by hot-pressed electrospun and the membranes indicated promoted OH- flux and selectivity than that of casting ones [16]. In addition, PVDF-poly (SSS) semi-interpenetrating membranes were also prepared and showed good thermal stability, mechanical property and alkali resistance [17].

As an engineering polymer with high glass transition temperature (T_g=210 °C), high mechanical strength, and excellent hydrolytic stability, poly (2, 6-dimethyl-1, 4-phenyleneoxide) (PPO) through bromination–quaternization or sulphonation was well used to prepare anion exchange membranes or cation exchange membranes [4,6,8]. The anion exchange membranes were commercialized and widely used in industrial acid recovery while the corresponding cation exchange membrane is a little far from the commercialization due to the low OH^- dialysis coefficient and inefficient alkali recovery yield [8]. These are mainly due to the hydrophobic nature of PPO backbone and lower water uptake [1]. Even though increasing sulphonation can increase water uptake and ion transport, there is also a limitation that swelling of membrane may enhance as the increasing of ion exchange capacity. In our previous work [14], it was demonstrated that addition of pure nano silica could provide assisted transport channel and increase the dialysis coefficient of OH^-. However, loading content

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Table 1
Ion exchange capacities (IECs) and water uptake (W_R) of the membranes.

Membrane number	Loading content of nano silica (%)	IEC (mmol/g)	W_R (%)	Thickness (μm)
A	0	2.00	70.19	76
B	2	1.96	132.25	73
C	4	1.93	168.09	69
D	6	1.90	200.00	65
E	8	1.87	222.50	72

of nano silica should keep a high level to obtain better result, which could cause particle aggregation during the membrane process. Therefore, in the current work, SPPO hybrid membranes will be prepared through blending SPPO with sulphonated nano silica (SNS). Loading of SNS not only improves the membrane hydrophility, but also provides extra ion exchange groups at the organic–inorganic interface: $-SO_3Na$ in the SPPO chain provide the main transport channel of Na^+, while $-SO_3^-$ on the surface of nano silica provide the assisted transport channel of Na^+. The membrane fundamental properties as well as the separation performance will be discussed in term of the SNS loading content. The mass transfer mechanism will also be discussed.

2. Experimental sections

2.1. Materials

SPPO in Na^+ form with an ion exchange capacity ca. 2.0 mmol/g was kindly supplied by Tianwei Membrane Co. Ltd. (Shandong, China). Nano silica powder with average particle sizes of 20–30 nm was purchased from nanosabz Co (Tehran, Iran) and it was heated at 200 °C for 2 h before use. Dimethylformamide (DMF), acetone, toluene, NaOH, HCl, Na_2WO_4 and 1, 3-propanesultone with analytical pure were purchased from Sinopharm Chemical Regent Co. Ltd. (Shanghai, China). Deionized (DI) water was utilized throughout.

2.2. Preparation of hybrid membranes

Surface of nano silica was treated with 1, 3-propanesultone as reference [18,19] reported. In a typical sulphonation process, 1 g nano silica and 4.4 g 1, 3-propanesultone were added into 300 ml toluene and the mixture was firstly dispersed under ultrasound for 10 min. Then the suspension was mechanically stirred at the temperature of 120 °C for 48 h. After that the nano silica was filtrated and soxhlet extracted by acetone for 48 h. Finally the nano silica was dried at 55 °C in vacuum and kept in glass desiccator. The IEC of SNS is 0.30 mmol g^{-1} from the result of elemental analyzer. SPPO was dissolved in dimethylformamide (DMF) to form a 20 wt% solution. Then, various amount of SNS (0, 2, 4, 6 or 8 wt% of SPPO) was dispersed in 20 mL DMF under ultrasonic condition and then the solution was dropwise added to the aforementioned SPPO solution. The obtained suspension was dispersed evenly by means of ultrasonic and cast onto clean glass plate. The glass plate was placed in a 50 °C oven for 24 h to remove solvent and the samples were designated as membrane A, B, C, D or E, respectively.

2.3. Characterization methods

Sulphonation degree of nano silica and ion exchange capacities (IECs) of hybrid membranes were measured by using a Vario EL cube elemental analyzer. Water uptake (W_R) was measured at 25 °C to investigate the hydrophilicity of the membranes. The membrane samples were dried and weighed. They were then immersed in DI water for 48 h and weighed after removing surface water. The value of W_R was calculated as the relative weight gain per gram of the dry sample.

To investigate the alkali resistance, membranes were cut into 3×3 cm^2 pieces and pre-weighed before immersing in 2 M 65 °C NaOH solutions for 60 h. The membranes were then immersed in DI water and the water was changed at 3 h interval within 12 h. After wiping out membrane surface water, the wet membrane was immediately weighed for accuracy and the dimensional stability was detected by the change rates of area. Also, membranes *C* and *E* were chosen for testing TEM images before and after the alkali treatment to confirm the stability of SNS in membrane matrix.

Thermo gravimetric analysis (TGA) was conducted on a NETZSCH 449F3 Simultaneous Thermal Analysis under air flow from room temperature to 700 °C with a heating rate of 10 °C/min. The morphology of membranes was observed by a scanning electron microscopy (S-4800, Hitachi Limited, Japan). Membrane samples were fractured in liquid nitrogen and coated with gold before tests. Dispersion of nano silica particles was observed by a

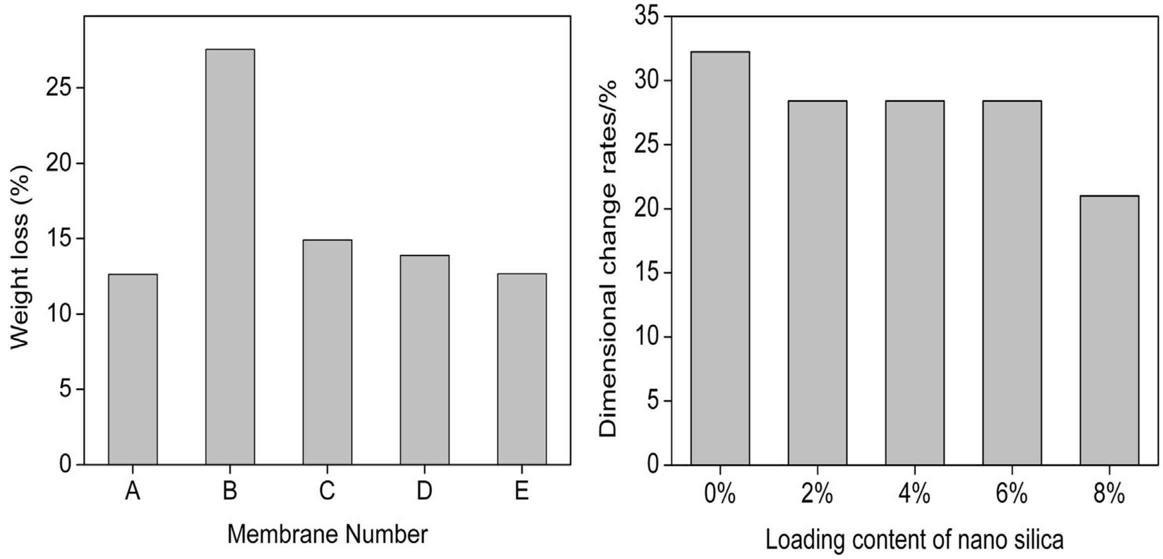

Fig. 1. Weight loss and dimensional stability of as-prepared membranes.