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Preparation and electrochemical characterization of mixed matrix heterogeneous cation exchange membranes filled with zeolite nanoparticles: Ionic transport property in desalination

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HIGHLIGHTS

- PVC/zeolite nanoparticles heterogeneous cation exchange membranes were prepared.
- Selectivity was enhanced by increase of additive content and then decreased.
- E-conductivity/flux was obviously increased by increase of additive concentration.
- Membrane selectivity was improved by increase of electrolyte concentration.
- Membranes showed high transport number, selectivity and E-conductivity at pH 7.

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ABSTRACT

In the current research mixed matrix PVC based-co-zeolite nanoparticles heterogeneous cation exchange membranes were prepared by solution casting technique. The effect of used additives and also electrolyte's concentration and pH variations on membrane electrochemical properties was studied. Results showed that membrane water content, membrane potential, transport number and selectivity were improved initially by use of zeolite nanoparticles up to 8 %wt. in the casting solution and then began to decrease by more increase in additive concentration from 8 to 16 %wt. Utilizing zeolite nanoparticles in the casting solution also led to increase in membrane electrical conductivity and ionic flux obviously. Membrane transport number, selectivity and membrane electrical conductivity were all enhanced by increase of electrolyte concentration. Moreover, membranes showed higher transport number/selectivity and lower electrical resistance at pH 7 compared to other pH values. Among the prepared membranes, modified membrane containing 8 %wt. zeolite nanoparticles showed more suitable electrochemical properties compared to others. Also obtained results revealed that modified membranes in this study are comparable with that of other commercial ones. The obtained results are valuable for electromembrane processes especially electrodialysis for water recovery and treatment.

1. Introduction

In the field of separation science and technology, membranes have obtained much attention in diverse industries and human life. Nowadays, ion exchange membranes have been utilized widely as active separators in electrically driven processes such as electrodialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt. Ion exchange membranes are also efficient tools in resource recovery, food and pharmacy processing and environmental protection such as treating industrial and biological effluents as well as manufacturing of basic chemical products [1–5]. In IEMs charged groups attached to polymer backbone are freely permeable to opposite sign ions under an electrical field influence [6].

In such processes, ion interactions with membrane, water, and with each other occur in complex fashions. Knowledge of the electro kinetic properties of ion exchange membranes is major contributing factor behind decisions about their applicability in specific separation processes and energy storage devices [2,7,8].

Preparing IEMs with special physico-chemical characteristics may be as vital step in future application [2,4]. A lot of research has already been carried out to improve the IEMs physico-chemical properties. Variation of functional groups type, selection of different polymeric matrices, polymers blending, using of inorganic additives/filler, alteration of

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cross-link density and surface modification are the important techniques to obtain superior IEMs [1,2,9,10].

Utilizing inorganic particles or fillers especially nanomaterials into polymeric materials has been examined in many applications to enhance the physico-chemical characteristics and separation properties based on the synergism between the organic–inorganic components [2,5]. Zeolite nanoparticles are well known inorganic materials with very interesting features and capacity such as high adsorption capacity, ion exchange property, sieving characteristic, stable chemical property and safety toward the environment which provides unique physico-chemical properties [11–15].

Currently no reports have considered incorporating zeolite nanoparticles into ion exchange membranes and the literature is silent on characteristics and functionality of electrodialysis IEMs.

Preparing heterogeneous cation exchange membranes with special adapted physico-chemical properties for application in electrodialysis processes related to water recovery and water treatment was the primary target of current research. For the purpose, mixed matrix (polyvinylchloride/zeolite nanoparticles) heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. PVC is a flexible and durable polymer with suitable biological and chemical resistance [16,17]. Zeolite nanoparticles were also employed as inorganic filler additive in membrane fabrication. Moreover, investigation of IEMs electrochemical properties at different electrolytes concentrations and pH values is necessary due to polarization phenomenon and also difference in functional groups dissociations.

The effect of used additives' concentration in the casting solution and also electrolyte's concentration and pH variations on membrane electrochemical properties was studied.

During the experiments, sodium chloride was employed as ionic solution for the membrane characterization. The results are valuable for electro-membrane processes especially electrodialysis process for water recovery and water treatment.

2. Materials and methods

2.1. Materials

Polyvinylchloride (PVC, grade 7054, Density: 490 g/l, viscosity: 105 cm^3/g) supplied by BIPC Company, Iran, was used as binder. Tetrahydrofuran (THF, Merck Inc., Germany) was employed as solvent. Zeolite nanoparticles (white powder, average particle size <100 nm, Germany) were used as inorganic filler additive. Cation exchange resin (ion exchanger Amberlyst® 15, strongly acidic cation exchanger, H^+ form — more than 1.7 milli equivalent/g dry, density: 0.6 g/cm^3, particle size (0.355–1.18 mm) ≥ 90%) by Merck Inc., Germany, was also utilized in membrane fabrication. All other chemicals were supplied by Merck. Distilled water was utilized during the experiments.

2.2. Preparation of mixed matrix ion exchange membrane

In order to undertake the membranes preparation, resin particles were dried in oven at 30 °C for 48 h and then pulverized into fine particles in a ball mill and sieved to the desired mesh size. The ion exchange resin with desired particles size (−325 + 400 mesh) was used in membranes fabrication. The preparation proceeded by dissolving the polymer binder into THF solvent in a glass reactor equipped with a mechanical stirrer for more than 5 h. This was followed by dispersing a specific quantity of grinded resin particle as functional groups agents and zeolite nanoparticles as additive in polymeric solution, respectively. The mixture was mixed vigorously at 25 °C to obtain uniform particle distribution in polymeric solution. In addition, for better dispersion of particles and breaking up their aggregates, the polymeric solution was sonicated for 1 h using of ultrasonic instrument. Excessive homogeneity and uniform distribution of particles (resin, additive) in membrane matrix provide superior conducting regions for the membranes and generate easy flow channels for counter ions transportation. Presence of more conducting region on membrane surface also can strengthen the intensity of uniform electrical field around the membrane and decreases the polarization phenomenon [18]. Furthermore, uniform distribution of particles in polymeric solution increases the viscosity of solution and reduces the evaporation rate of solvent. This makes better the polymer chains conformation with particles surfaces and improves the membrane selectivity [19]. Then, mixing process was repeated for another 30 min by the mechanical stirrer. The mixture was then cast onto a clean and dry glass plate at 25 °C. The membranes were dried at 25 °C for 10 min and immersed in distilled water. As final stage, membranes were pretreated by immersing in NaCl solution. The membrane thickness was measured by a digital caliper device around 60–70 μm. The composition of casting solution is depicted in Table 1.

2.3. Test cell

The membranes' electrochemical properties measurements were carried out using the test cell (Fig. 1). The cell consists of two cylindrical compartments made of Pyrex glass which are separated by membrane. One side of each vessel was closed by Pt electrode supported with Teflon and the other side was equipped with membrane. The membrane area was 19.63 cm^2.

2.4. Membrane characterization

2.4.1. Water content

The water content was measured as the weight difference between the dried and swollen membranes. The wet membrane was weighed (OHAUS, Pioneer™, Readability: 10^{-4} g, OHAUS Corp.) and then dried in oven until the constant weight was obtained. The following equation [20–22] can be used in water content calculations:

$$\text{Water content}\% = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100 \quad (1)$$

2.4.2. Membrane potential, transport number and permselectivity

The membrane potential is algebraic sum of Donnan and diffusion potentials determined by the partition of ions into the pores as well as the mobilities of ions within the membrane phase compared with the external phase [23]. This parameter was evaluated for the equilibrated membrane with unequal concentrations ($C_1 = 0.1$ M/$C_2 = 0.01$ M) of electrolyte solution at ambient temperature on either sides of membrane. During the experiment, both sections were stirred vigorously to minimize the effect of boundary layers. The developed potential across the membrane was measured by connecting both compartments and using saturated calomel electrode (through KCl bridges) and digital auto multi-meter (DEC, Model: DEC 330FC, Digital Multimeter, China).

Table 1
Compositions of casting solution used in preparation of homemade mixed matrix nanocomposite heterogeneous cation exchange membranes [a].

Membrane	(Additive — zeolite nanoparticles) (%wt.)
Sample 1 (S1)	0.0 %wt./Unmodified membrane
Sample 2 (S2)	0.5 %wt.
Sample 3 (S3)	1.0 %wt.
Sample 4 (S4)	2.0 %wt.
Sample 5 (S5)	4.0 %wt.
Sample 6 (S6)	8.0 %wt.
Sample 7 (S7)	16.0 %wt.

[a] Polymer binder (PVC):solvent (THF)) (w/v), (1:20); ((resin particle:polymer binder) (w/w), (1:1).