



Electrodialysis heterogeneous anion exchange membrane modified by PANI/MWCNT composite nanoparticles: Preparation, characterization and ionic transport property in desalination



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HIGHLIGHTS

- PVC/PANI–MWCNT nanoparticle anion exchange membranes were prepared.
- Selectivity was improved by increasing the PANI/MWCNT nanoparticle content.
- Flux was enhanced by an increase in nanoparticle concentration and then declined.
- Electrical resistance was decreased by increasing the PANI/MWCNT nanoparticle.
- Modified membranes showed superior performance compared to pristine one.

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ABSTRACT

In this research polyaniline (PANI)-co-multi walled carbon nanotubes (MWCNTs)/polyvinylchloride (PVC) nano-composite heterogeneous anion exchange membranes were prepared by solution casting technique. The effect of PANI/MWCNT nanoparticle concentration on membrane electrochemical properties was studied. Membrane water content was decreased by the increase of nanoparticle concentration. Ion exchange capacity (IEC) was improved initially by the increase of nanoparticle concentration up to 2 wt.% and then showed decreasing trend by more additive content from 2 to 4 wt.%. IEC was enhanced again with more increase in additive concentration from 4 to 16 wt.%. Fixed ionic concentration (FIC) also showed increasing trend by an increase in nanoparticle content. Membrane potential, transport number and selectivity were improved in NaCl and Na₂SO₄ ionic solutions by the increase of PANI/MWCNT nanoparticles. Also membranes exhibited lower selectivity and transport number for bivalent ions compared to monovalent type. Membrane permeability and flux were enhanced initially in both monovalent and bivalent ionic solutions by an increase in additive concentration up to 1 wt.% and then showed decreasing trends by more additive content from 1 to 16 wt.%. Prepared membranes showed lower permeability and flux for bivalent ions compared to monovalent type. Modified membranes showed better performance in comparison with pristine membrane.

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1. Introduction

Ion exchange membranes (IEMs) are one of the most advanced separation membranes which play an important role in an increasing number of processes in chemical and biochemical industry [1–3]. These membranes are widely studied and utilized as active separators in various electrically driven processes such as electrodialysis for desalting brackish waters, reconcentrating brine from seawater and

production of table salt. Additionally, IEMs are efficient tools in food and pharmacy processing as well as manufacturing of basic chemical products. IEMs also play an important part in environmental protection such as treating biological effluents and electroplating wastewater especially high toxic heavy metal ions, resource recovery and many more processes [1–15]. In such processes, the ion interactions with membrane, water and with each other occur in complex fashions. So, knowledge of the physico/chemical properties of ion exchange membrane is a major contributing factor behind decisions about their applicability in specific separation processes at different operating conditions [9, 12,16–19].

Preparing inexpensive membranes with special adapted physico-chemical characteristics may be as a vital step in future chemical and

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waste treatment application [4,12,20–22]. A lot of research has already been performed to improve the IEMs' physico-chemical properties which resulted in various modification techniques. The variation of functional groups, selection of different polymer matrices, polymer blending, use of various additives, alteration of cross-linked density, and surface modification are some important ways to achieve superior IEMs [5,6,12,16,23–33]. The homogeneous IEMs usually show good electrochemical properties but are weak in mechanical strength whereas heterogeneous types have acceptable mechanical property but with inadequate electrochemical properties. Early references on the heterogeneous ion exchange membrane revealed that these membrane can be prepared by calendering ion exchange particles into an inert plastic film or dry molding of inert film forming polymers and ion exchange particles and then milling the mold stock in another way by dispersion of resin particles in polymeric solution and casting technique [4,19,24,30–32].

Utilizing inorganic nanoparticles or fillers into polymeric materials also has been examined in many applications to enhance the mechanical, thermal and chemical stability of polymeric matrices in severe conditions such as high temperature and strongly oxidizing environment and also to improve the separation properties of membranes based on synergism between the organic–inorganic component properties [11,23,25,33–38]. In last decade a growing number of researchers worldwide have shown an interest in combination of carbon nanotube with conducting polymer to produce composite nanoparticles for different applications [39,40].

The PANI/MWCNT nanoparticle is one of the well known composite nanoparticles which have been gained a great deal of attention because of its interesting feature and capacity. PANI is one of the most important and promising intrinsically conducting polymers due to its unique features such as easy synthesis, high intrinsic ionic and electronic conductivity, simple acid–base chemistry as well as environmental and thermal stability and relatively low cost [2,40–54] which makes this polymer usable in energy storage systems, electrochemical sensors and separation processes such as gas separation, pervaporation, electro dialysis as well as water and waste water treatment [2,43,44,55–58]. Multiwalled carbon nanotube is also an important group of nanomaterials with unique structural, chemical and mechanical properties because of high aspect ratio and surface area which has been utilized widely in separation processes [39–42,59–63]. Reported researches on PANI/MWCNT composite nanoparticles reveal good interaction between both components which is due to interfacial interaction or hydrogen bonds forming between amine groups of aniline and carboxylic group of functionalized-multiwalled carbon nanotubes [39,40,59].

Currently no reports have been considered incorporating polyaniline/multiwalled carbon nanotube composite nanoparticles into IEMs and the literature is silent on the characteristic and functionality of electro dialysis heterogeneous anion exchange membrane prepared using PANI/MWCNT nanoparticles. Preparing heterogeneous anion exchange membranes with the appropriate properties for the application in electro dialysis processes related to water recovery and waste water treatment was the primary target of current research. For the purpose, (PVC/PANI–MWCNTs) mixed matrix heterogeneous anion exchange membranes were prepared by a solution casting technique using anion exchange resin powder as functional groups and tetrahydrofuran as solvent. PVC is a flexible and durable polymer with suitable biological and chemical resistance [64–66]. Polyaniline/multiwalled carbon nanotube (PANI/MWCNT) composite nanoparticle was also employed as inorganic filler additive in membrane fabrication in order to improve the IEM physico/chemical properties.

The effects of PANI/MWCNT composite nanoparticle concentration in the casting solution on electrochemical characteristics of prepared heterogeneous anion exchange membranes were studied. During this experiment, sodium chloride and sodium sulfate were employed as mono and bivalent ionic solutions for membrane

characterization. The results are valuable for electro-membrane processes especially in electro dialysis process for water recovery and treatment. Moreover, sonication was employed in membrane fabrication to achieve better homogeneity in membrane matrix and to obtain the balance between electrochemical properties and mechanical integrity.

2. Materials and methods

2.1. Materials

Polyvinylchloride (PVC, grade S-7054, density: 490 g/lit, viscosity number: 105 Cm^3/g) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as membrane matrix. Tetrahydrofuran (THF, molar mass: 72.11 g/mol, density: 0.89 g/cm^3) was employed as solvent. Polyaniline/multiwalled carbon nanotube composite nanoparticles (PANI/MWCNTs, nanopowder, 80 nm < particle size, including 10 wt.% MWCNTs and 90 wt.%) were provided from NANORADBEHAN Company, Iran. Anion exchange resin (Amberlyst® IRA-402, strongly basic anion exchanger, Cl^- form) by Merck was used in membrane preparation. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used. The chemical structure of used polymer binder and nanoparticles is shown in Table 1.

2.2. Preparation of cation exchange membranes

The heterogeneous anion exchange membranes were prepared by solution casting technique and phase inversion method. The preparation proceeded by dissolving the polymer binder (PVC) into solvent (THF) in a glass reactor equipped with a mechanical stirrer (model: Velp Scientifica Multi 6 stirrer) for more than 6 h. This was followed by dispersing resin particles (–300 + 400 mesh) as functional groups and PANI/MWCNT composite nanoparticles as an additive in polymeric solution, respectively. In addition for better dispersion of particles and breaking up their aggregates, the solution was sonicated for 1 h using an ultrasonic instrument. Then the mixing process was repeated for another 30 min using the mechanical stirrer. The mixture was then casted onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature (25 °C) and immersed in distilled water. As final step, membranes were pretreated by immersing in 0.5 M NaCl for solution 48 h. The membrane thickness was measured by a digital caliper device (Electronic Outside Micrometer, IP54 model OLR) to maintain the membrane thickness around 70 μm . The composition of casting solution is given in Table 2.

2.3. Test cell

The membrane electrochemical property measurements were carried out using the test cell (Fig. 1) [23–26,33,67]. The cell consists of two cylindrical compartments made of Pyrex glass which are separated by membrane. The membrane was fixed between rubber rings. One side of each vessel was closed by Pt electrode supported with a piece of Teflon and the other side was equipped with membrane. The top of each compartment contained two orifices for feeding and sampling purposes. In order to minimize the effect of boundary layer and during experiments and to establish the concentration polarization on the vicinity of membrane surface, both sections were stirred vigorously by magnetic stirrers.

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} gr, OHAUS Corp.) and then dried

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