



# Fabrication of mixed matrix heterogeneous cation exchange membrane modified by titanium dioxide nanoparticles: Mono/bivalent ionic transport property in desalination



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## HIGHLIGHTS

- PVC/TiO<sub>2</sub> nanoparticle mixed matrix cation exchange membranes were prepared.
- Membrane selectivity showed initially a constant behavior and then decreased.
- Membrane mechanical strength was improved by an increase of additive content.
- FTIR spectra analysis proved stronger affinity of nanoparticles for bivalent ions.
- A decrease of pH enhances membrane charge density and improves flux.

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## ABSTRACT

Polyvinylchloride-co-TiO<sub>2</sub> nanoparticle mixed matrix heterogeneous cation exchange membranes were prepared by the solution casting technique. The effect of TiO<sub>2</sub> nanoparticle concentration in casting solution on membrane physico-chemical properties was studied. SOM images showed uniform particle distribution and relatively uniform surfaces for prepared membranes. Membrane water content was decreased by an increase of additive concentration. Ion exchange capacity was improved initially by an increase of nanoparticle content and then decreased. Transport number and selectivity initially showed a nearly constant trend by an increase of additive content up to 2 wt.% and then decreased sharply by a more additive concentration. Sodium permeability was enhanced by an increase of nanoparticle concentration up to 0.5 wt.% and then decreased by a more additive content from 0.5 to 2 wt.%. Sodium permeability was increased another time by a more increase in additive concentration from 2 to 16 wt.% and then showed a decreasing trend by a more nanoparticle content. A different trend was found for barium permeability. FTIR spectra analysis decisively proved stronger affinity of TiO<sub>2</sub> nanoparticles for barium ions compared to sodium ones. A decrease of pH enhances positive charge distribution on nanoparticle surface and improves the flux. Membrane mechanical strength was also improved by an increase of nanoparticle content ratio in the membrane matrix.

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## 1. Introduction

In the field of separation science and technology, membrane has obtained much attention in diverse fields of industries such as environmental protection, wastewater treatment and food/pharmacy processing. So utilizing efficient membranes is a concern of most industries [1,2]. The ion exchange membranes are widely utilized as active separators in different electrically driven processes such as electrodialysis for desalting

brackish waters, reconcentrating brine from seawater and production of table salt. Moreover, IEMs are efficient tools in resource recovery, treating industrial and biological effluents and many more processes. Thus, the development of ion exchange membranes with acceptable physico-chemical properties is highly desired [3–12].

In ion exchange membranes charged groups are attached to polymer backbone and freely permeable to opposite sign ions under an electrical field influence [5,13–16]. In these processes, ion interactions with membrane, water, and with each other occur in complex fashions. Knowledge of the electrochemical properties of ion exchange membranes is an important factor behind decisions about their applicability in separation processes.

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Preparing IEMs with special physico/chemical characteristics may be a vital step in future chemical and waste treatment application [16–20]. Variation of functional groups, selection of different polymeric matrices, polymer blending, use of various additives, alteration of cross-link density, uniform distribution of functional groups and surface modifications are important ways to obtain superior ion exchange membranes [4, 8–10,13,14,18,21–24].

Utilizing inorganic particles or fillers especially nanomaterials into polymeric matrices has been examined in many applications to enhance the mechanical, thermal and chemical stabilities 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 the synergism between the organic–inorganic component properties [8–10,21–24].

Among this, nanometal oxide materials (NMOs) particularly showed a high adsorption characteristic because of the high proportion of surface sites at edges or corners [24,25]. Titanium dioxide ( $\text{TiO}_2$ ) nanoparticle is one of the well-known NMOs which has gained a great deal of attention because of its high hydrophilicity, high adsorption capacity, stable chemical property, low cost and safety toward both humans and the environment [22,24–30]. The reported researches revealed that titanium dioxide nanoparticles have been utilized widely in adsorbent beds and membrane processes for effluent treatment due to its unique adsorption, antibacterial and hydrophilic characteristics [1,23, 25,27,29–39].

Currently no researches have been considered incorporating titanium dioxide nanoparticles into ion exchange membranes and the literature is silent on the characteristics and functionality of electro dialysis IEMs prepared using  $\text{TiO}_2$  nanoparticles. Preparing heterogeneous cation exchange membranes with appropriate electrochemical properties for the application in electro dialysis processes related to water recovery and treatment was the primary target of the current research.

For this purpose, polyvinylchloride/titanium dioxide nanoparticle mixed matrix heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as the functional group agent and tetrahydrofuran as the solvent. PVC is a flexible and durable polymer with suitable biological and chemical resistance [13]. Titanium dioxide nanoparticle was also employed as an inorganic filler additive in membrane fabrication in order to improve the IEMs' physico/chemical properties.

The effects of  $\text{TiO}_2$  nanoparticle concentration in the casting solution on physico-chemical characteristics of prepared heterogeneous cation exchange membranes were studied. During the experiment, sodium chloride and barium chloride were employed as monovalent and bivalent ionic solutions for membrane characterization. The results are valuable for electro-membrane processes especially in electro dialysis process for water recovery and waste water treatment. Moreover, sonication was employed in the membrane fabrication technique to achieve better homogeneity in the 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  $\text{cm}^3/\text{g}$ ) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as a membrane base binder. Tetrahydrofuran (THF, molar mass: 72.11 g/mol, density: 0.89  $\text{g}/\text{cm}^3$ ) was employed as the solvent. Titanium dioxide nanoparticle ( $\text{TiO}_2$ , nano-powder, anatase crystal, and 15–25 nm particle size) was provided from US Research Nanomaterials, USA. Cation exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger,  $\text{H}^+$  form more than 1.7 meq/l) by Merck Inc., Germany, was also used in membrane preparation. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used.

### 2.2. Preparation of mixed matrix membranes

The heterogeneous cation exchange membranes were prepared by the casting solution technique/phase inversion method as described elsewhere [13]. The preparation proceeded by dissolving the PVC polymer binder into the solvent (THF) in a glass reactor equipped with a mechanical stirrer (Model: Velp Scientifica Multi 6 stirrer, Italy) for more than 6 h. This was followed by dispersing resin particles (–300 + 400 mesh) as functional groups and  $\text{TiO}_2$  nanoparticle as 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 (Parsonic11Smodel, S/N PN-88159, Iran). Sonication of solid particles increases the viscosity of casting solution by reducing aggregation and sedimentation which decreases the evaporation rate of casting solvent. This improves the polymer chain relaxation as well as its conformation with particle surfaces and promotes compatibility of particles and binder [40,41]. This also reduces the amount of cracks and fissures between the binder and particles and so improves the membrane selectivity. Moreover, excessive homogeneity and uniform distribution of resin particles on membrane surface and in the bulk of membrane provide superior conducting regions in the membrane and generate easy flow channels for counter-ion transportation. The presence of more conducting region can strengthen the intensity of uniform electrical field around the membrane and decrease the concentration polarization phenomenon [42]. Then the mixing process was repeated for another 30 min using the mechanical stirrer (Model: Velp Scientifica Multi 6 stirrer, Italy). 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 the final step, the membranes were pretreated by immersing in 0.5 M NaCl solution for 48 h. The membrane thickness was measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR, China) to maintain the membrane thickness around 60–70  $\mu\text{m}$ . The composition of casting solution is depicted in Table 1.

### 2.3. Experimental test cell

The electrochemical properties of the prepared membranes were measured using the test cell as reported elsewhere [8–10]. The cell consists of two cylindrical compartments which are separated by membrane. Both vessels were closed by a Pt electrode supported with a piece of Teflon in one side and other sides were equipped with a piece of porous medium to support the membrane. In order to minimize the effect of boundary layer and concentration polarization on the vicinity of membrane surface, both sections were stirred vigorously by magnetic stirrers.

### 2.4. Membrane characterization

#### 2.4.1. Morphological studies

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of particles in the membrane

**Table 1**

Composition of casting solution used in the preparation of mixed matrix ion exchange membranes<sup>a</sup>.

| Membrane      | Titanium dioxide nanoparticles ( $\text{TiO}_2$ nanoparticle: (PVC + resin)), (w/w) |
|---------------|---|
| Sample 1 (S1) | 0.0:100   |
| Sample 2 (S2) | 0.5:100   |
| Sample 3 (S3) | 1.0:100   |
| Sample 4 (S4) | 2.0:100   |
| Sample 5 (S5) | 4.0:100   |
| Sample 6 (S6) | 8.0:100   |
| Sample 7 (S7) | 16.0:100  |
| Sample 8 (S8) | 32.0:100  |

<sup>a</sup> Solvent to polymer binder (THF: PVC) (v/w), (20:1); resin particles (resin:polymer binder) (w/w), (1:1).

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