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# Electrochemical characterization of mixed matrix nanocomposite ion exchange membrane modified by ZnO nanoparticles at different electrolyte conditions “pH/concentration”

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ABSTRACT

In this research, novel PVC based nanocomposite ion exchange membrane was prepared by casting technique. ZnO nanoparticles were employed as semiconductor additive in membrane fabrication. The effect of nanoparticles concentration on properties of home-made membranes was studied. A relatively uniform surface for the membranes and uniform particles distribution were observed in SOM images. The membranes were characterized in different electrolyte conditions “concentrations/pH”. Results revealed that membrane water content, membrane potential, transport number and selectivity were enhanced initially by increase of additive concentration up to 10 wt% in membrane matrix and then showed decreasing trend by more additive loading. The ionic permeability and flux were also decreased initially by increase in additive content up to 5 wt%. The permeability and flux were increased another time by more increase in additive content. An opposite trend was observed for membrane electrical resistance. Moreover, membranes showed higher transport number and selectivity at pH 7 compared to other pH values. Membrane electrical conductivity was decreased by increase of pH value. Also membrane transport number and selectivity were initially enhanced by increase of electrolyte concentration and then began to decrease slightly at high electrolyte concentration.

## 1. Introduction

Nowadays, easy scaling-up and low energy consumption of membrane separation in comparison with other caused to expand industrial applications of membranes. Thus, various membranes have developed for the use in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, pervaporation separation and electrodialysis [1]. Ion exchange membranes (IEMs) are used in various electrically driven processes such as desalination of saline water by electro dialysis, reconcentrating brine from seawater, salt production, fuel cells, recovery of valuable metals from effluents industries, *etc.* [2–16]. The Donnan membrane equilibrium principle is the base of ion exchange membrane separation [1].

Ion-exchange membranes can be divided into two major categories of homogeneous or heterogeneous according to structure and preparation procedure. Also there are two types of IEMs based on different functional groups, *i.e.* anionic (bearing $-CH_2N^+R_3$ groups) and cationic (bearing $-SO_3^-$ groups) ones [17]. Anion exchange membranes pass anions and repel cations. While cation exchange membranes allow passing cations but reject anions [18].

There are several approaches to improve selectivity and ionic flux of ion exchange membranes. Many research have reported various methods to modify ion exchange membranes features. Change in functional groups or cross-link density, polymers blending, surface modification and use of various additives, are important ways to gain superior IEMs [5,14,18–25]. The latest initiative is development of composite ion exchange membranes using inorganic materials in polymeric matrix [26].

Composite ion exchange membranes besides improvement of efficiency, show remarkable changes in IEMs properties, such as mechanical strength, thermal stability, electrical, magnetic and *etc.*, compared to pure organic polymeric membranes [4,27–32].

In the past decade, semiconductor materials such as metal oxide nanoparticles have been widely studied in various areas because of their unique properties. Among metal oxide materials, ZnO has remarkable physical and chemical properties such as wide

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band gap, good chemical stability, low dielectric constant and represents antibacterial properties [33–42]. Also, Zinc oxide is considerable because of its lower prices, lightness and ease of accessibility and is nontoxic [43,44].

There are a few studies about development of Zinc Oxide composite membranes and the literature is silent on IEMs comprising ZnO nanoparticle.

The primary target of current research was preparing the novel nanocomposite cation exchange membranes with appropriate physico-chemical properties for the application in electro-dialysis processes related to water recovery and treatment. For this purpose, Polyvinyl chloride (PVC) based heterogeneous cation exchange membranes were prepared by solution casting techniques using tetrahydrofuran as solvent, cation exchange resin powder as functional groups agent, and ZnO nanoparticle as additive. PVC was chosen because of its low cost, excellent resistance to erosion, acids, alkaline and its stiffness [45–48].

Besides dependency of IEMs' behavior on their physico-chemical properties, the nature of electrolyte solution also affects on their performance [49]. Few researches have reported the effect of environmental conditions on IEMs properties despite they can have significant influences [24,50–52]. This investigation can be important because of the formation of boundary layers on the membranes surface and the occurrence of concentration polarization phenomena and also change in membranes functional groups dissociations under different conditions.

Therefore at the next step of this research, the modified ion exchange membranes were characterized in different electrolytic environment to evaluate their potential performance under various conditions. The variations of membrane resistance, ionic selectivity and transport number were studied in NaCl solution with concentration range of 0.001–0.1 M and pH of 2, 7 and 12.

The obtained results could be of particular importance for various electro-membrane processes especially the electrodialysis and further improvement of separation efficiency in wastewater treatment.

## 2. Material and method

### 2.1. Materials

Polyvinyl chloride (PVC, grade S-7054, high porosity, bulk density (DI N-53466): 490 g/l, viscosity number (DIN-53726): 105 cm$^3$/g) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as binders. Tetrahydrofuran (THF) as solvent and cation exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger, H$^+$ form-more than 1.7 meq/g dry, spec. density 0.6 g/cm$^3$, particlesize (0.355–1.18 mm) ≥90%) as functional groups agent by Merck Inc., Germany, were used in membrane fabrication. ZnO nanoparticle (ZnO nano-white-powder, average particle size 20 nm, BET area 50 m$^2$/g) was also used as inorganic additive. Distilled water was used for all experiments. The other chemical components were purchased by Merck.

### 2.2. Preparation of nanocomposite membranes

The heterogeneous cation exchange membranes were prepared by solution casting technique and phase inversion method described in the literature [26]. The resin particles were firstly dried in oven (SANEE. V. S. Co.) at 30 °C for 48 h and then pulverized into fine particles in a ball mill (Pulverisette 5, Fritisch Co.). Then the ion exchange resin sieved to desired size (37–44 μm) for membrane fabrication. Casting solutions were prepared by dissolving the PVC as base polymer in the THF solvent in a glass reactor equipped with a mechanical stirrer (Mode l: VelpSientifica Multi 6 stirrer). Afterward a specific quantity of grinded resin particle as functional groups agents and various amounts of ZnO nanoparticle as additive were dispersed in polymeric solutions, respectively (Table 1). The polymeric solution was mixed severely for more than 6 h to achieve uniform particles distribution. To avoid particles' aggregation the solution was sonicated for 1 h using an ultrasonic instrument and then the mixture was stirred again for another 30 min using the mechanical stirrer. The prepared solution was casted onto a clean and dry glass plate with 400 μm casting knife at 25 °C. After 60 s air exposure, the membranes were dried at ambient temperature and immersed in distilled water. The membranes were then soaked in NaCl solution. Table 2 represents a brief description of membrane preparation procedure steps. A digital caliper device was used to measure the membrane thickness and ensure its value was around 70 μm.

### 2.3. Experimental test cell

The electrochemical properties of the prepared membranes were evaluated through a series of experiments in a test cell (Fig. 1) as reported earlier [3,26,29]. The sample membrane disk was fixed between rubber rings and separate two cylindrical compartments (each 180 cm$^3$) of cell which made of Pyrexglass. The two ends of each compartment were equipped with Pt electrodes supported with pieces of Teflon. Two openings were placed at the top of each section for feeding and sampling purposes. To minimize the boundary layers' effect on the vicinity of membrane during experiments both sections were stirred vigorously by magnetic stirrers.

### 2.4. Membrane characterization

#### 2.4.1. FTIR spectra

FTIR test were carried out to provide information about the chemical structure of membranes using a single beam Fourier transform-infrared spectrometer (Galaxy series 5000). Scans of the samples were taken in the spectral range of 4000–500 cm$^{-1}$.

#### 2.4.2. Morphological studies

Due to the structure of prepared membrane especially the spatial distribution of ionic site can affect the membrane behavior

**Table 1**
Composition of casting solution used for membranes' preparation.

| Membrane | Zinc oxide nanoparticle (additive:total solid) (w/w) |
|---|---|
| Sample 1 | 0:100 |
| Sample 2 | 5:100 |
| Sample 3 | 10:100 |
| Sample 4 | 15:100 |
| Sample 5 | 20:100 |

(Solvent (THF):Polymer (PVC) (v/w): (20:1)); (Resin particles:Polymer (w/w): (1:1)).

**Table 2**
Flowsheet of membrane preparation procedure.

| | The procedure for IEMs preparation |
|---|---|
| Step 1 | Resin particles draying (at 30 °C for 48 h( |
| Step 2 | Resin particles pulverizing (−300 + 400 mesh) |
| Step 3 | Polymer dissolving into solvent (for 5 h) |
| Step 4 | Resin particles and additive dispersing in polymeric solution |
| Step 5 | Sonication of polymeric solution (for 1 h) |
| Step 6 | Mixing of polymeric solution (for another 30 min) |
| Step 7 | Casting (at 25 °C) |
| Step 8 | Film drying (at 25 °C for 30 min) and immersing in water |
| Step 9 | Membranes pretreatment by HCl and NaCl solutions |