

Polyaniline modified organic–inorganic hybrid cation-exchange membranes for the separation of monovalent and multivalent ions



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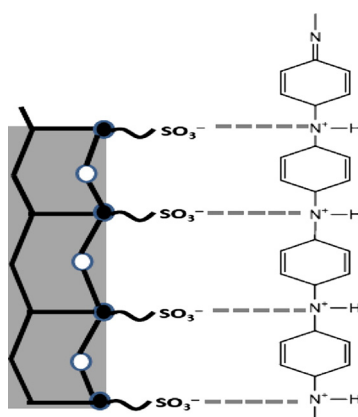
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HIGHLIGHTS

- PANI modified organic–inorganic hybrid cation-exchange membranes were fabricated.
- The developed CEM/PANI hybrid membranes were dense and thermally stable.
- The selectivity of PANI modified CEM/PANI membranes was enhanced.
- The electro-dialytic separation of Na⁺ from Na⁺/Zn²⁺ and Na⁺/Al³⁺ mixture solutions was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic–inorganic hybrid cation-exchange membranes (CEMs) were chemically modified by in situ polymerization of aniline in acidic medium using FeCl₃ as an oxidizing agent. The presence of polyaniline (PANI) on the surface and inside membrane matrix was confirmed from PANI coating density and scanning electron microscopy. Membranes were characterized in details by estimating water uptake, ion-exchange capacity, fixed ion concentration, counter-ion transport number and membrane conductivity. The values of Na⁺ transport number across the membranes were unchanged, whereas the values of Zn²⁺ and Al³⁺ transport number were decreased after modification with PANI. The dense nature of PANI modified membranes was evaluated through an electro-osmotic study. The selectivity of PANI modified membranes towards Na⁺, Zn²⁺ and Al³⁺ ions was investigated by electro-dialysis using single or binary mixture of electrolyte solutions (Na⁺/Zn²⁺ and Na⁺/Al³⁺). The current and separation efficiencies of CEM and PANI modified membrane (CEM/PANI-120) for Na⁺, Zn²⁺ and Al³⁺ were determined at varied applied current densities and electrolyte solution feed concentrations. The obtained values of current and separation efficiencies for CEM/PANI-120 membrane suggested the suitability of PANI modified membrane in electro-dialysis selective separation of Na⁺ from the binary mixture (Na⁺/Zn²⁺ and Na⁺/Al³⁺) in aqueous solutions.

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1. Introduction

Separation of monovalent and multivalent ions from their mixture in aqueous/wastewater solution is a challenging task for researchers

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working in academics and industries. The demand of membrane based separation processes is increasing day via day for their use in treatment of aqueous and wastewater solutions containing monovalent and multivalent ions [1–3]. Electro-membrane based separation processes have been applied for brackish water desalination, removal of toxic metal ions from industrial effluents, separation of inorganic ions from organic mixtures, and recovery of transition metal ions from industrial effluents [4–6]. Ion-exchange membranes (cation-exchange membranes; CEMs and anion-exchange membranes; AEMs) are used as separators in chlor-alkali process, electrodialysis (ED), electro-membrane reactors, electro-deionization, and diffusion dialysis [7–12]. However, the efficiency and durability of ion-exchange membranes are the two key factors for their applications in electro-membrane processes as these factors are dependent on the physicochemical and electrochemical properties [3]. Hence, highly stable and selective ion-exchange membranes are urgently required for electro-membrane processes to achieve the separation and removal of mono- and multi-valent ions from their mixture in aqueous solution/wastewater.

The monovalent cation selective membranes have been developed for the separation of mono- and bi-valent cations by adjusting the degree of crosslinking. Meanwhile, the degree of crosslinking reduces the process efficiency. Due to this reason, crosslinking is not a suitable approach for the preparation of monovalent cation selective membranes [13]. The surface modification procedures have been explored to enhance the selectivity of CEMs towards the monovalent cations and the surface modified membranes are selective for monovalent cations [14]. Moreover, PANI modified CEMs are more selective for monovalent cations in comparison to the multivalent ions in aqueous solutions [15,16]. PANI, a well-known conductive polymer, used in the preparation of free-standing membranes for gas separation, pervaporation and ED applications [17–19]. Nagarale et al. had modified CEM and AEM by an in situ polymerization of aniline using ammonium peroxisulfate. The separation of binary electrolyte ($\text{Na}_2\text{SO}_4/\text{CaCl}_2$ and $\text{Na}_2\text{SO}_4/\text{CuCl}_2$) solution was achieved using the PANI modified membranes in ED [19]. Tan and Belenger have performed an extensive characterization of Nafion/PANI composite membranes for the conduction of protons. The highest conduction of protons was achieved for a membrane containing highest fraction of PANI [20].

The hybrid CEMs have also been prepared from high-impact polystyrene and PANI using a screw extruder method. Optimum Zn^{2+} ion extraction was achieved in ED, when acids were used as doping agents in the hybrid CEMs [21]. Thus, the modification of CEMs with PANI is an efficient approach for improving the stability and selectivity of ion-exchange membranes towards monovalent ions. On the other hand, efforts have not been rendered to modify organic–inorganic hybrid CEMs with PANI by an in situ polymerization and their application in ED separation and removal of monovalent and multivalent ions in aqueous solution/wastewater. In this study, efforts have been rendered to develop PANI modified organic–inorganic hybrid CEMs by an in situ polymerization of aniline in acidic medium using ferric chloride (FeCl_3) as an oxidizing agent. The detailed investigations were performed to assess the suitability of PANI modified organic–inorganic hybrid CEMs in ED separation of Na^+ from binary mixture of ($\text{Na}^+/\text{Zn}^{2+}$ and $\text{Na}^+/\text{Al}^{3+}$) in aqueous solutions.

2. Material and methods

2.1. Materials

Analytical reagent (AR) grade poly(vinyl alcohol) (PVA, MW: 125,000; degree of polymerization: 1700 and degree of hydrolysis: 88%), formaldehyde, hydrogen peroxide solution (37–40% w/v), Na_2SO_4 , NaCl , ZnCl_2 , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, HCl , NaOH and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were received from Sigma-Aldrich and Merck Chemicals. The chemicals and reagents were used without further purification. Tetraethyl orthosilane (TEOS), mercaptopropylmethyl dimethoxysilane (MPDMS) and aniline

(99%) of reagent plus grade were purchased from Sigma-Aldrich. Aniline was distilled before use and double distilled water (DDW) was used in this study.

2.2. Membrane preparation

The detailed procedure for the preparation of organic–inorganic hybrid CEM is described elsewhere [22]. In brief; 10 g PVA was dissolved in 100 ml DDW at 90 °C under continuous stirring and then, desired amount of MPDMS precursor was added to PVA solution. The resulting mixture was further stirred for 2 h and thereafter, predefined amount of TEOS was added to the mixture. The pH of resulting mixture was adjusted to 2 by adding few drops of 4 M HCl solution and subsequently the reaction mixture was stirred for 12 h at 30 °C. Thus, a white color viscous gel was obtained, which was then casted onto a clean and dry glass plate by solution casting method [22]. The obtained membrane was dried at 30 °C for 12 h and was kept in an oven at 60 °C for 24 h to remove the traces of moisture. The resulting membrane was cross-linked in acidic solution containing HCHO at 60 °C for 2 h and the sulfonic groups ($-\text{SO}_3\text{H}$) were anchored into the membrane matrix by the oxidation of $-\text{SH}$ groups using H_2O_2 solution. The AEM was prepared by adopting previously reported method [10]. The CEM and AEM were equilibrated in 1 M HCl and NaOH solutions consecutively for 24 h to convert them in H^+ and OH^- form. The acid and base treated membranes were thoroughly rinsed with DDW to remove acid and base contaminants. Finally, cleaned membranes were kept in 1 M NaCl solution for further characterization and use. The physicochemical and electrochemical properties of AEM are given in Table S1 (Supporting Information).

2.3. Membrane modification with polyaniline

Organic–inorganic hybrid CEM was equilibrated in 1 M HCl solution for 24 h before being modified with PANI. The modification was performed in a PVC cell, which was divided into two compartments (compartment 1 and 2) by placing CEM between cathode and anode. Compartment 1 was filled with 0.1 M FeCl_3 solution in 1 M HCl, while compartment 2 was filled with DDW. The membrane was then left for 24 h to convert into Fe^{3+} form. Thereafter, the FeCl_3 solution was removed from compartment 1 and the activated surface of membrane was properly cleaned with DDW. Subsequently, compartment 1 was filled with 10% (v/v) aniline in 1 M HCl solution. Polymerization of aniline was carried out under constant stirring at varied time intervals (min). The membrane turned to green after polymerization at specific time interval. The PANI modified membrane was taken out from the cell and was then kept in 1 M HCl solution for 24 h to remove the unreacted PANI. Similar procedure was adopted to modify other membranes with PANI. The PANI modified membranes were designated as CEM/PANI-X, where X represents the polymerization time for aniline (min).

2.4. Instrumental characterization

Fourier transform infrared spectra (FTIR) of unmodified and PANI modified membranes were recorded using Fourier transform infrared spectrometer in the attenuated total reflectance (ATR) mode (Spectrum GX series 49387) at an average of 32 scans with a resolution of $\pm 4.0 \text{ cm}^{-1}$. The thermal stability of membranes was investigated in temperature range 50–650 °C by using a thermo-gravimetric analyzer (Mettler Toledo TGA/SDTA851 with Star^c software) with N_2 flow at $10 \text{ }^\circ\text{C min}^{-1}$ heating rate. Differential scanning calorimetry (DSC) measurements were performed in temperature range 30–250 °C using a differential scanning calorimetric analyzer (Mettler Toledo TGA/SDTA851 with Star^c software) with N_2 flow at $5 \text{ }^\circ\text{C min}^{-1}$ heating rate. The SEM images were recorded using LEO microscope (Kowloon, Hong Kong) after gold sputtering on the membrane samples. The effect of PANI coating on membrane crystallinity was observed by recording their WXR

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