Synthesis, characterization, thermal behaviour and transport properties of polyvinyl chloride based zirconium phosphate composite membrane

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ABSTRACT

The polyvinyl chloride (PVC) based zirconium phosphate composite membrane was synthesized by co-precipitation method. The composite membrane was characterized by using Fourier transform infrared (FTIR) spectroscopy, thermogravimetry analysis (TGA) and scanning electron microscopy (SEM). The order of charge effectiveness was found to be $HgCl_2 < PbCl_2 < CdCl_2$. This composite membrane showed potential applications in the area of separation of heavy metal ions from wastewater because of good stabilities, long lifetimes and cost effectiveness.

Introduction

Heavy metal pollution by the natural and anthropogenic sources is causing persistent toxicity to the wastewater. Consequently, tremendous health hazards are occurring not only for human beings but also for animals and plants. Hence, waste water should be free from toxic pollutants to avoid the threats for the survival of living organisms. In a general practice, these heavy toxic metals are being discharged into water bodies without prior treatment in spite of various recommendations of different environmental protection agencies [1–7].

For the separation and removal of these toxic metal ions various methods like ion exchange, adsorption, ultrafiltration, microfiltration, osmosis, reverse osmosis and electrodialysis can be applied. However, during last few decades, ion-exchange membrane electrodialysis has been considered most prospective method for the separation and preconcentration of heavy toxic metal ions [8–14].

To ascertain the viability of a membrane for electrodialysis the determination of ion-transport at the membrane electrolyte interface is pre-requisite. A number of studies have been carried out to study the ion-transport at the membrane interface using only NaCl as electrolyte by potentiometry [15–17]. However,

concerning to the heavy metal toxicity in water bodies, no studies are carried out by using heavy toxic metals as electrolytes. Therefore, in this study, heavy metal electrolytes are selected to study the charge transport properties by using PVC based Zr(IV) phosphate composite membrane.

Experimental

Materials

Trisodium phosphate, zirconium chloride, cadmium(II) chloride, lead(II) chloride, mercury(II) chloride, HCl, NaCl, HNO_3, H_2SO_4, NaOH, $KMnO_4$ and PVC were obtained from E. Merck, Mumbai, India. All other reagents were used of analytical reagent grade.

Instruments

Scanning electron microscopy (SEM), ZEISS EVO Series Scanning Electron Microscope EVO 50, Fourier transformed infrared (FTIR) Interspec 2020 spectrometer; spectrolab (UK), thermogravimetric analyzer (TGA) (Shimdzu DTG-60H) and Digital potentiometer (Electronics India model 118) were used.

Preparation of composite membrane

Zirconium phosphate precipitate was prepared by mixing of 100 ml solutions of each 0.2 M zirconium chloride and 0.2 M trisodium phosphate. The precipitate was washed well with

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deionized water to remove free reactant and then dried and powdered. Membrane was prepared by using (1:3) wt/wt ratio of binder and Zr(IV) phosphate. The precipitate was ground into fine powder and was sieved through 200 mesh (granule size < 0.07 mm). The PVC was also ground and sieved through 200 mesh. The mixture was then kept in a pellet casting die having a diameter of 2.45 cm and placed in an oven maintained at 200 °C for about an hour to equilibrate the reaction mixture [15,16]. The die containing the mixture was then transferred to a pressure device, and 100 MPa of pressure was applied during the fabrication of the membrane. The membrane was subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface and only those which had smooth surface and generate reproducible potentials were considered.

Method for measurement of chemical stability, thickness and ion-exchange capacity of composite membrane

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze. To estimate its chemical stability the membrane was exposed to acidic, basic and strongly oxidant media solutions. The ion exchange capacity was determined by standard column method. One gram of the dry cation-exchanger in the H⁺ form was taken into a glass column having an internal diameter (1 cm) and fixed with glass wool support at the bottom. The bed length was

approximately 1.5 cm long. 1 M NaNO₃ as eluent was used to elute the H⁺ ions completely from the cation-exchange column, maintaining a very slow flow rate (∼0.5 ml min⁻¹). The effluent was titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the ion exchange capacity was determined [18,19].

Scanning electron microscopy (SEM) investigation of composite membrane

Scanning electron microscopic image was taken to confirm the microstructure of composite membrane. Sample was mounted on a copper stub and sputter coated with gold to minimize the charging.

Fourier transformed infrared (FTIR) studies

The FTIR spectrum of PVC based Zr(IV) phosphate composite membrane dried at 80 °C and was taken by KBr disc method.

Thermogravimetric analysis (TGA) of the composite membrane

Thermogravimetric study of composite membrane was also carried out on heating the composite material up to 600 °C at a constant rat 20 °C min⁻¹ in the nitrogen atmosphere.

Measurement of membrane potential

Membrane potential was measured by using digital potentiometer. The freshly prepared charged membrane was placed at the centre of the measuring cell, which had two glass containers, on either side of the membrane. The various salt solutions (chlorides of Hg^{2+}, Pb^{2+}, and Cd^{2+}) were prepared using deionized water. Both collared glass containers had cavity for introducing the electrolyte solution and saturated calomel electrodes. The half-cell contained 25 ml of the electrolyte solution while the capacity of each of the half cells holding the membrane was about 35 ml.

Results and discussion

The FTIR spectrum of PVC based Zr(IV) phosphate composite material (Fig. 1) showed the presence of the external water molecules in addition to the metal–oxygen and metal–OH stretching band. In the spectrum a broad band in the region at 3417 cm⁻¹ may be due to the presence of external water molecules. The broad absorption peak at 2366 cm⁻¹ and 1621 cm⁻¹ indicated the C–H and C=C stretching, respectively. The peak of P–O of phosphate group is present at the appropriate position (1462 cm⁻¹). The two sharp peaks 555 and 467 cm⁻¹ may be due to presence of C–Cl bond and Zr metal. The FTIR spectrum confirmed the formation of PVC based zirconium phosphate composite membrane [20].

The ion exchange capacity and thickness of PVC based Zr(IV) phosphate composite were found to be 0.73 meq g⁻¹ and 0.085 cm, respectively. It is clear from Table 1, the low order of ion-exchange capacity with less thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites.

The composite membrane was kept in acidic, basic and strongly oxidant media to study the chemical stability. Significant modified observations were obtained after 25, 45 and 165 hr in acidic (1 M HNO₃), basic media (1 M NaOH) and strong oxidant (KMnO₄) demonstrating that the membrane was quite effective in such cases. The synthesized membrane became fragile in 45 h and broken after 165 h and lost mechanical strength [21].

The scanning electron microscopy (SEM) has been used for the characterization of membrane surface morphology. It is clear from