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Fabrication of Mixed Matrix ion Exchange Membrane by Using Activated Carbon Nanoparticles Modified by Chitosan: Investigation of Electrolyte Concentration and pH Effects on Transfer Properties

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INTRODUCTION

Nowadays, ion exchange membranes (IEMs) are widely studied and utilized as active separators in various electrically driven processes. In this kind of membrane charged groups attached to polymer backbone are freely permeable to opposite sign ions under the influence of electrical field [1]. Moreover, the ion exchange membranes are efficient tools in desalting brackish waters, reconcentrating brine from seawater, production of table salt, recovery of valuable metals from industrial effluents and also food and pharmacy processing like desalination of cheese whey and demineralization of sugarcane juice as well as manufacturing of basic chemical products. Moreover, they play some important parts in environmental protection, treating industrial and biological effluents and many more processes [2, 3]. A lot of researches have already been performed to improve the IEMs' physico-chemical properties, which they are resulted in various modification techniques. Furthermore, variation of functional groups type, selection of different polymeric matrices, polymers blending, additives loading, alteration of cross-link density and surface modification are the important techniques to obtain superior IEMs [2-5]. Preparing the novel heterogeneous cation exchange membranes with appropriate physico-chemical properties for the application in electro-dialysis processes related to water recovery and treatment was the primary target of current research. For the purpose, Polyvinylchloride based heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. Modified activated carbon nanoparticles by chitosan were also employed as filler additive in membrane fabrication in order to improve the IEMs physico-chemical properties.

EXPERIMENTAL PROCEDURE

Activated carbon-co-chitosan NPs was prepared by surface modification method using chitosan polymer solution according to the reported literature [6]. Moreover, lab-made cation exchange membranes were provided by casting solution/phase inversion method. For the purpose, different concentrations of composite nanoparticles were combined with PVC-THF solutions. Gained homogeneous solutions were then sonicated. Fabrication was followed by casting of solutions onto clean and smooth glass plates with the constant film thickness of 400 µm by a homemade applicator. The membrane was dried at ambient temperature and was dipped in distillated water. Finally, membrane was

immersed in a 0.5 M sodium chloride solution for 48 h. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Scanning optical microscopy (SOM), water content, ion exchange capacity, selectivity, transport number, ion permeability and ionic electrical resistance were applied to study the composite nanoparticles and fabricated membranes.

RESULTS AND DISCUSSION

The SEM images of the composite NPs are shown in Fig. 1. As it can be seen, nanoparticles have got desirable uniformity. Fig. 2 represents the AC-co-CS NPs FTIR spectroscopy. The wide peak at around 3426.27 cm⁻¹ indicates the –OH and – NH stretching vibrations. Moreover, the peaks at 3001.75 cm⁻¹ and 2935.70 cm-1 are attributed to -CH stretching vibrations. The strong peaks at 1577.14 cm-1 and 1424.42 cm⁻¹ were also assigned to carbonyl group (C=O) and amide group (–NH2) respectively. The adsorption peaks at 1151.87 cm⁻ ¹, 1043.66 cm⁻¹, 1012.61 cm⁻¹, and 923.59 cm-1 ascribed to asymmetric stretching of the C–O–C. In addition, two peaks at 649.14 cm⁻¹ and 620.09 cm⁻¹ are related to C-H bond, which these peaks suggest the possibility of functional groups such as hydroxyl, amine and carboxyl in the composite nanoparticles [6,7].



Figure 1: SEM images of composite nanoparticles.



Figure2: FTIR spectra of composite NPs.

Also, SOM image (Fig. 3) displays a fairly uniform distribution for the prepared membranes.

Utilizing of AC-co-CS in the membrane matrix led to an increase in water content and ion exchange capacity for the homemade membranes (Fig. 4), which this occurrence is due to an increase in membrane heterogeneity and functional groups of CS.

Results revealed that membrane transport number and selectivity were increased initially

by enhancing NPs concentration up to 0.5 wt.% due to an enhancement in IEC. Subsequently, by increasing NPs content ratios, from 0.5 to 8 wt. %, permselectivity and transport number showed a downward trend due to increase of membrane water content and structural heterogeneity. The effect of electrolyte environment pH on selectivity and electrical resistance of membranes are given in Tables 1 and 2.



Figure 3: SOM image of fabricated membrane.



Figure 4: The water content and ion exchange capacity for the homemade membranes.

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| рН | Sample 6 (0.5 wt.%) | Sample 6 (8 wt.%) |
|----|---------------------|-------------------|
| | selectivity | selectivity |
| 4 | 79 | 77 |
| 7 | 90 | 85 |
| 10 | 83 | 82 |

| Table 2: The effect of p | I on areal e-resistance. |
|--------------------------|--------------------------|
|--------------------------|--------------------------|

| рН | Sample 6 (0.5 wt.%) | Sample 6 (8 wt.%) |
|----|---------------------|-------------------|
| | AER | AER |
| 4 | 19.1 | 10.3 |
| 7 | 20 | 11 |
| 10 | 19.8 | 10.9 |

CONCLUSIONS

The effect of electrolyte concentration and pH effects on transfer properties of mixed matrix cation exchange membranes was studied. The images showed uniform particles dispersion and uniform surface for the membranes. The membrane water content and ion exchange capacity were improved. The selectivity and areal electrical resistance were enhanced initially and then decreased. Also, the selectivity of mixed matrix membrane was increased initially by increasing electrolyte concentration and then showed decreasing behaviour by more increase in electrolyte concentration. The areal electrical resistance of membranes was also decreased by increasing electrolyte concentration. Finally, an increase in electrolyte pH initially caused to enhancement of membrane areal electrical resistance; however, areal electrical resistance declined again at higher pH values.

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