Fabrication and Modification of PVDF/PES-Based Nanofiltration Membranes by Zinc Oxide Nanoparticles

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Introduction

Recently, nanofiltration membranes were known as an important practical technology for application in desalination and wastewater treatment [1,2]. The major methods for reduction of these challenges are incorporation of hydrophilic nanomaterial [3-5]. In this study, the nanofiltration membranes were prepared by incorporation of ZnO nanoparticles into the polyvinylidene fluoride (PVDF) and polyether sulfone (PES). The morphology of prepared membranes characterized by scanning electron microscopic (SEM). Moreover, the filtration performance of prepared membranes was examined by pure water flux (PWF), Na₂SO₄ rejection.

Experimental Procedure

Materials
Poly ether sulfone (PES) with molecular weight of 5800 g/mol and PVDF as polymer matrix were purchased from Merck. Zinc oxide nanoparticles (ZnO) as additives was used, dimethyl acetamide (DMAc) as solvent was supplied from Merck.

Membrane Preparation
The nanofiltration membranes were prepared from the phase inversion method and immersion precipitation. The membranes were named M1, M2, M3, M4 and M5 at 0, 0.05, 0.1, 0.5 and 1 wt.% ZnO nanoparticles respectively.

Results and Discussion

Membrane Analysis
In Figure 1, the ATIR analyses of M1 and M3 membranes are shown. The peak in the range of 561 cm⁻¹ related to ZnO stretching. The peaks in 1485-1404 cm⁻¹ are assigned with CH₂. The symmetric and asymmetric CF₂ groups determined in the peak of 1178 and 1275 cm⁻¹. Moreover, the carbonyl groups (C=O) are clear in 1675 cm⁻¹[6].

Fig. 1 The ATIR spectra of M3.
In Figure 2, SEM images of prepared membranes are shown. The images show the asymmetric structure of membranes with selective layer on the top of membrane and a porous layer. The porous structure of prepared membranes increased by increasing nanoparticles into the membrane [7, 8].

![Fig. 2 The SEM images of a) M1, b) M3.](image)

**Filtration Performance of Membranes**

The performance of membrane filtration was examined by pure water flux and Na\(_2\)SO\(_4\) rejection. As shown in Figure 3, the membrane hydrophilicity increased with an increase in ZnO nanoparticle loading due to present hydroxyl groups on the nanoparticle surface [9] that leads to an increase in pure water flux as shown in Figure 4. Moreover, the membrane porosity and pore sizes increase by incorporation of ZnO nanoparticles that its result is improvement of pure water flux. However, the flux decreases in high concentration of ZnO nanoparticles due to nanoparticle agglomeration and filling pores with nanoparticles. The highest pure water flux was obtained 19.97L/m\(^2\)h in 0.1 wt.% nanoparticles.

![Fig. 4 Pure water flux of prepared membranes.](image)

Since hydroxyl groups in ZnO nanoparticle increase negative charges on the membrane surface [10, 11] that lead to repulse SO\(_4^{2-}\) ions on the membrane surface, the Na\(_2\)SO\(_4\) rejection enhanced with incorporation ZnO nanoparticles into the membrane as shown in Figure 5. Moreover, improvement membrane hydrophilicity decreased membrane roughness and accumulation salt ions on the membrane surface and thus increased salt rejection. Furthermore, the active sites increased for adsorption of Na\(_2\)SO\(_4\) ions. The highest Na\(_2\)SO\(_4\) rejection (82%) was revealed for M3 in 0.1 wt.%. However, the salt rejection decreased in high concentration of nanoparticles due to nanoparticle agglomeration and reduction of active sites for salt adsorption.

![Fig. 5 The Na\(_2\)SO\(_4\) rejection of prepared membranes.](image)

**Conclusions**

This study investigated the incorporation of ZnO nanoparticles as additives into the PVDF/PES as polymer matrix. The prepared membranes analyzed by ATIR and SEM. The membrane evaluation showed the highest pure water flux and Na\(_2\)SO\(_4\) rejection for 0.1 wt.% ZnO nanoparticles. Finally, this study shows the potential of ZnO nanoparticles in fabrication of nanofiltration membranes with excellent separation performance.

**Nomenclatures**

PES: Poly ether sulfone  
PWF: Pure water flux  
SEM: Scanning electron microscopic
References


