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Modifying the Separation and Structural Properties of PES Based Nanofiltration Membrane Using Sulfonated Silicon Dioxide Nanoparticles

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Abstract

In this study, nanocomposite PES based membranes were prepared by using sulfonated silicon dioxide (SiO_2-SO_3H) nanoparticles through phase inversion method. PVP and N-N-dimethylacetamide were used as pore former and solvent respectively. The effect of nanoparticles' concentration on the separation performance of prepared membranes was studied. The structures of membranes were investigated by scanning electron microscopy (SEM) and scanning optical microscopy (SOM). Obtained results showed modified membranes had significant improvements in flux and rejection with increasing sulfonated silicon dioxide nanoparticles. Also, the tensile strength increased in the range of 15 to 25% for prepared membranes containing nanoparticles. Results showed that nanocomposite membrane containing 0.1 wt.% SiO_2-SO_3H nanoparticles has an increase in the flux of 200% compared to the unmodified membrane and salt rejection of 75%. Also, the flux decreased the ratio of the optimum sample was 7.14 that showed better antifouling properties with a decrease to of 75% relative to the PES one.

Keywords: Membrane, Nanofiltration, Polyether Sulfone, Sulfonated Silicon Dioxide Nanoparticles, Desalination.

Introduction

Scarcity of the drinking water soon is a global concern. So, there is a need to find new methods with lower cost, less energy and minimizing the use of chemicals to purify water and to improve the efficiency of existing water purification technologies [1-3]. In this field, the membrane process is an attractive industrial technology that operates under physico-chemical specifications of the membranes. Compared with the other membranes, NF membrane with low operating pressure, high permeate flux, high rejection of multivalent salts and organic solutes gained much attentions. Recently some efforts aiming membranes modification/improvement of structure and performance was performed. In most cases the organic/inorganic composite membranes showed better performance. In the present work, SiO_2-SO_3H nanoparticles with various amounts were incorporated into the PES NF matrix. One of the most hydrophilic, non-toxicity, wide resource and low-price nanoparticles used for membrane modification is silicon dioxide (SiO_2). It was tried to modify firstly SiO_2 surface with sulfonating process to upgrade its properties with negative charge.

Experimental

The SiO_2–SO_3H nanoparticles were prepared according to the reported literature [4]. Moreover, the composite membranes were fabricated by phase inversion method through immersion precipitation technique. For the purpose, different concentrations of SiO_2–SO_3H nanoparticles were combined with PES-DMAC solutions. Gained homogeneous solutions were then sonicated to ensure removing air bubbles. Fabrication was followed by casting of solutions onto clean and smooth glass plates with the constant film thickness of 150 µm by a homemade applicator. Dipping of polymeric films immediately after casing into the deionized water as coagulation bath was as the next step. Scanning electron microscopy (SEM), pure water flux, permeability flux, salt rejection, water content, porosity, pore size, water contact angle and tensile strength were applied to study the prepared membranes performance and properties. Also Fourier transform infrared spectroscopy (FTIR) was used to characterize the sulfonated SiO_2 nanoparticles for ensuring the successful sulfonating process.

Results and Discussion

The FTIR spectra of composite membranes filled with SiO_2-SO_3H nanoparticles (Figure 1) showed a new absorption peak at 1171 cm^{-1} which is attributed to the stretching vibration of Si-O-SO_3H.

SEM images of membranes are shown in Figure 2. All membranes have asymmetric shape, dens-top layer and porous-sub layer. A thinner top-layer observed by using SiO_2–SO_3H nanoparticles. There are some big pores in to sublayer in mixed matrix membranes which can not be seen in bare PES. Higher affinity between hydrophilic SiO_2–SO_3H nanoparticles and water make faster phase inversion relative to bare PES [2].

Table 1 exhibited that contact angle of membrane was decreased from 54° to 46° by addition of SiO_2–SO_3H nanoparticles into the membrane matrix leading to the higher surface hydrophilicity. Improvement of hydrophilicity can be attributed to the hydrophilic nature of SiO_2–SO_3H nanoparticles.

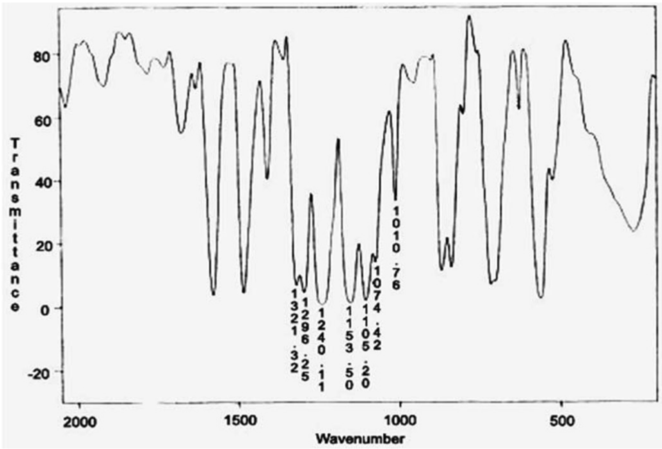

Figure 1: FTIR spectra of composite membranes filled with SiO_2-SO_3H nanoparticles

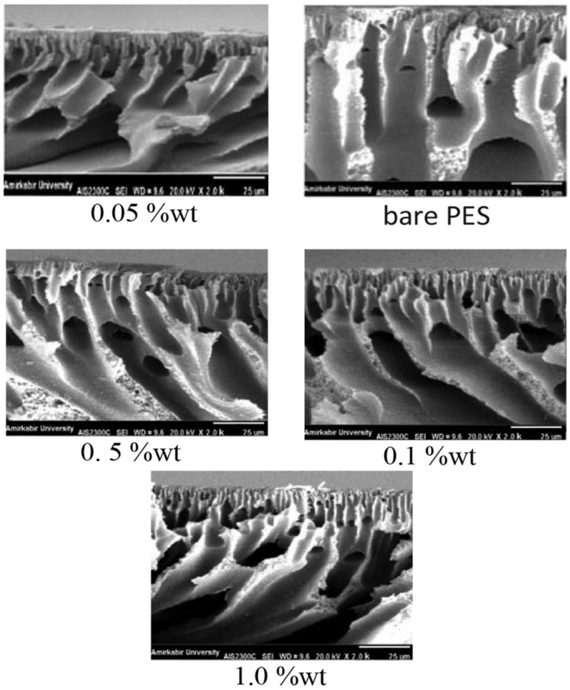

Figure 2: Cross-section SEM images of membranes with different concentrations of SiO_2-SO_3H nanoparticles

Table 1: Effect of SiO_2-SO_3H nanoparticle dosages on contact angle

SiO_2-SO_3H (wt %)	contact angle (°)
0	54
0.05	45
0.1	44
0.5	46
1	46

The results of membranes performance were shown in Figure 3. The results revealed that permeability flux was improved by using $SiO_2–SO_3H$ nanoparticles. The flux of bare PES membrane is the lowest compared with the composite ones. Enhancement of flux can be attributed hydrophilicity improvement. The membrane rejection was also improved from ~60 % to ~75% by addition of $SiO_2–SO_3H$ in the membrane structure. The migration of used nanoparticles to the skin surface during phase inversion process reduces the surface pore size. In this condition, the number of ions and salt molecules traffic through the membrane will reduce which lead to the enhancement of rejection. Furthermore, it is widely accepted that aggregation of foulants molecules on to the hydrophilic surface is lower than hydrophobic ones and improves rejection.

The determined values for decreased flux ratio were shown in Figure 4. As can be seen, decreased flux ratio of membranes filled with $SiO_2–SO_3H$ nanoparticles greatly are smaller than that of unfilled PES membrane. This phenomenon indicates that a higher antifouling property can be expected for the prepared mixed matrix membranes. Thus, $SiO_2–SO_3H$ nanoparticles incorporated into the PES nanofiltration membrane enhanced antifouling performance with improvement of membrane hydrophilicity. The results (Figure 5) also revealed that tensile strength was enhancement by addition of nanoparticles in to the matrix due to strong interfacial bonding formed between the polymers and nanoparticles [5].

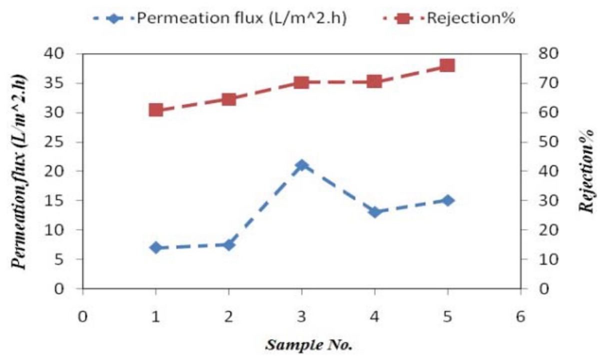

Figure 3: The effect of SiO_2-SO_3H nanoparticles concentrations on water flux and rejection

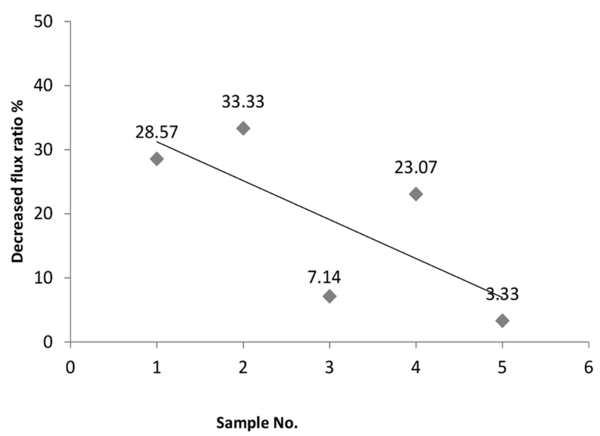

Figure 4: Decreased flux ratio after filtrating for the prepared membranes

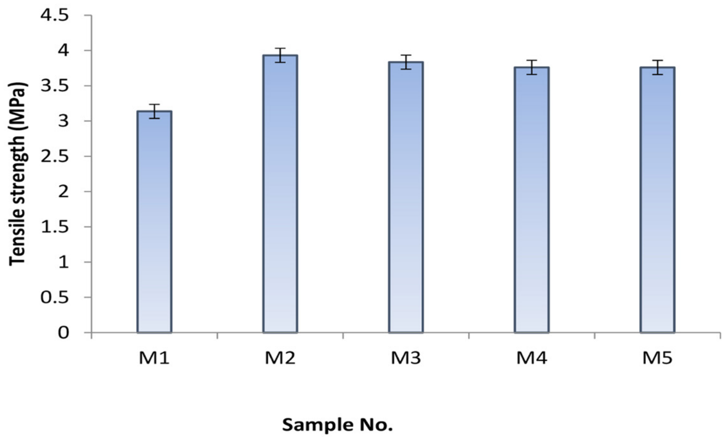

Figure 5: The effect of SiO_2-SO_3H nanoparticles on tensile strength

Conclusions

PES membranes with various concentrations of sulfonated SiO_2 nanoparticles were prepared through phase inversion method. The effects of sulfonated on the membrane performance and morphology such as water flux, salt rejection, contact angle, FTIR, and SEM images and mechanical properties were investigated. Utilizing of nanoparticles in the membrane matrix improved salt rejection and permeability flux. Addition of sulfonated SiO_2 led to the higher porosity and bigger macrovoides in the sub layer. The flux which decreased the ratio of the prepared membranes was also estimated and showed that mixed matrix PES/ SiO_2-SO_3H membranes had better antifouling properties relative to the bare PES one. The contact angle experiment showed that the membrane hydrophilicity generally was improved by the addition of sulfonated SiO_2. With the increase of sulfonated SiO_2 nanoparticle dosage in casting solution, the tensile strength of prepared membranes improved in comparison with bare PES membrane.

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