Novel Polyethersulfone (PES) Alpha-Zirconium Phosphate (α-ZrP) Ion Exchange Mixed Matrix Membranes for Effective Removal of Heavy Metals from Wastewater

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Abstract
In this study, novel polyethersulfone (PES) alpha-zirconium (α-ZrP) ion exchange mixed matrix membranes were fabricated via phase inversion method using nano-sized alpha-zirconium phosphate (α-ZrP-n) and polyvinylpyrrolidone (PVP) as dispersant nano-additives in the dope solution preparation. The impact of α-ZrP-n loading on the removal of Cu(II), Zn(II), and Ni(II) from wastewater effluent was studied by varying the α-ZrP-n concentrations from 0.1 up to 1 wt.% while fixing the PES concentration at 10 wt.%. The composite membranes surface morphology was characterized using scanning electron microscopy (SEM) and contact angle. The pure water flux was also determined under vacuum filtration while the removal of all heavy metals was carried out via the inductively coupled plasma - optical emission spectrometry (ICP-OES). The optimal results incorportaing 0.3 wt.% α-ZrP (i.e. Z-2 membrane) showed 98, 86, and 99% removal efficiency of Cu(II), Zn(II), and Ni(II); respectively, and a water flux of 3013.5 L/m^{2}h (MH) that was higher than that reported using the pristine PES membrane (i.e. 985 LMH). These findings suggested that the use of α-ZrP nanoparticles in membranes offers significant potential in heavy metal removal with a considerable high water flux.

Keywords: Wastewater; membrane; zirconium phosphate; heavy metals; removal.

1. Introduction

The increased development of industries, including mining, manufacturing, chemicals, and metal plating facilities, wastewaters nowadays almost constantly contain heavy metal contaminants (Fu and Wang, 2011). Dissimilar to organic pollutants, heavy metal elements are non-biodegradable, toxic, carcinogenic, and tend to amass in living organisms, causing disastrous health effects. Currently, stringent environmental regulations and increased public awareness are making heavy metal contaminants a leading ecological concern. Thus, industries are always encouraged to remove heavy metals from their wastewater effluents before discharging into the environment. Numerous methods of removing heavy metals from wastewaters exist, including adsorption, electrochemical process, ion exchange technologies, and membrane filtration. Membrane filtration technologies have attracted huge attention in the management of wastewater and acquired numerous industrial applications because of their high extraction efficiency, lower footprint compared to most conventional treatment approaches (Bolisetty et al., 2019). Nonetheless, the performance of these technologies in terms of water flux and removal efficiency can be further improved by incorporating different nanoparticles to the membrane matrix. Zirconium hydrogen phosphate, monohydrate nanoparticles (α-ZrP) is an example of a nanoparticle that has a promising potential in the removal of heavy metals from wastewater because of their exceptional chemical and physical properties they exhibit (Andersen et al., 1982; Pan et al., 2007). Among the many properties, these nanoparticles have, their very high ion-exchange ability is the predominant one. No attempts were reported in literature to combine such a high ion-exchange nanoparticle with membrane technologies. Therefore, the aim of this study was to fabricate an ion-exchange polyethersulfone (PES) alpha-zirconium (α-ZrP) (i.e. PES/α-ZrP) mixed matrix membranes and investigate their performance in terms of heavy metal removal, flux, thermal stability, and others.

2. Material and Methods

PES/α-ZrP membranes were fabricated via phase inversion method (KESTING, 2009). Five different concentrations of α-ZrP nanoparticles were dispersed in a mixture of N-Dimethylformamide (DMF) and N-methyl-2-pyrrolidinone (NMP) solvents and ultrasonicated using Branson 1510 Ultrasonic tool at 40 KHz frequency for 60 min for exfoliation. Following that, PVP and PES were dissolved/added to the above solutions and each mixture was stirred continuously with a magnetic stirrer for 48 h at 70^{o}C and 120 rpm. Table 1 shows the concentrations of all dope solutions prepared. The dope solutions were left aside to remove all entrapped air bubbles. Then, they were cast on a polyester membrane support using a casting knife with a thickness of 200 µm and with the aid of MTI Corporation's MSK-AFA-III Compact Tape Casting Coater at a traverse speed of 10 mm/s. The membranes were subsequently immersed into deionized water (DI) (with a resistivity of 13 MΩ.cm) for 24 h. Lastly, the membranes were removed from the water bath and left to dry at room temperature of 23^{o}C for 24 h.

Table 1. Different concentrations used in the preparation of the composite membranes.

Name	PES%	PVP%	α-ZrP%	Solvent%
PES	10	1.0	0.0	89.0
Z-1	10	1.0	0.1	88.9
Z-2	10	1.0	0.3	88.7
Z-3	10	1.0	0.5	88.5
Z-4	10	1.0	0.7	88.3
Z-5	10	1.0	1.0	88.0

3. Results and Discussion

The surface morphology of the pristine PES and ZrP-incorporated membranes was examined via the SEM images (Fig. 1 (a)). Both types of membranes showed a porous surface structure. Furthermore, the ZrP-incorporated membranes reported higher water flux when compared to the pristine PES membrane. For example, the highest water flux of 3587.6 L/m^{2}h (LMH) was observed at the Z-5 membrane compared to only 985 LMH in the PES membrane (Fig. 1 (b)). The increase in water flux can be attributed to the interfacial gaps formed between the PES matrix and the α-ZrP nanoparticles creating more water channels that enhance the passage of water through the membrane active layer (Zhu et al., 2014). In addition, the improvement in hydrophilicity after the addition of α-ZrP was evident from the contact angle measurements shown in Fig. 1 (c). For instance, the contact angle of the pristine PES membrane was 91^{o} while it decreased to 32^{o} in the Z-5 membrane (i.e. higher hydrophilicity). Lastly, the heavy metal removal efficiency was summarized in Fig. 1 (d). The highest removal was observed at Z-2 membrane with of 98, 86, and 99% removal efficiency for Cu(II), Zn(II), and Ni(II), respectively (Fig. 1 (d)).

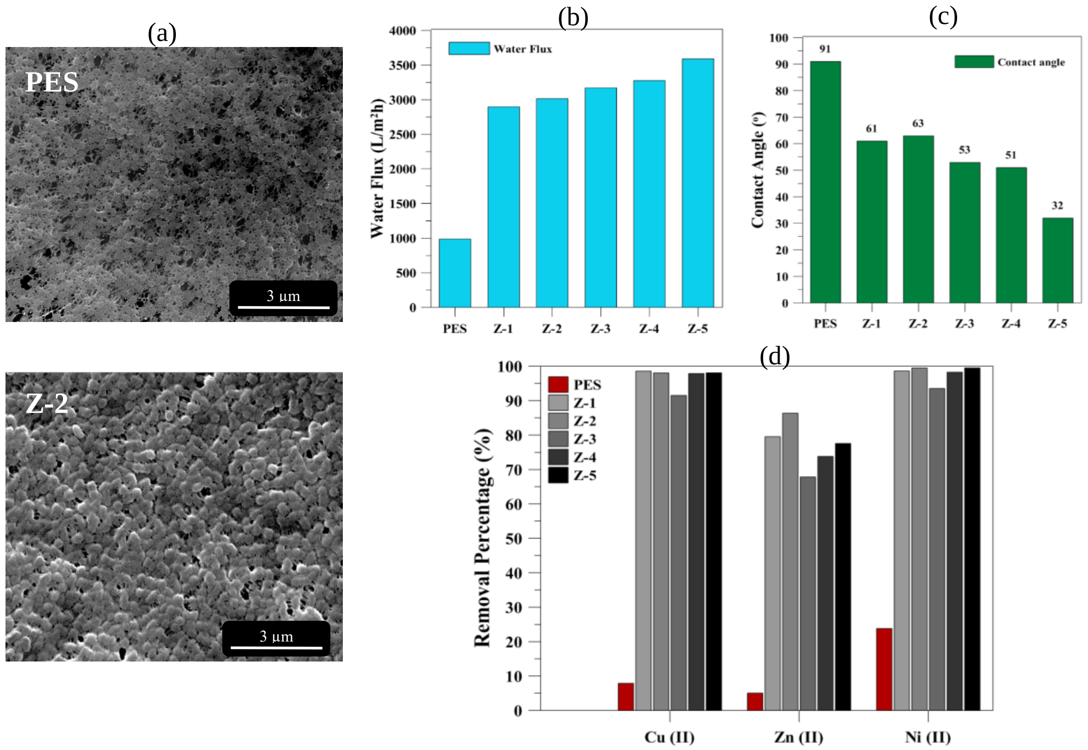

Figure 1. (a) SEM images, (b) water flux analysis, (c) contact angle, and (d) heavy metal removal results

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