Novel PES Membrane Reinforced by Nano-WS$_2$ for Enhanced Fouling Resistance

Jiuyang Lin, Wenyuan Ye, Arcadio Sotto, and Bart Van der Bruggen

Abstract—Application of nanoparticles as additives in membrane synthesis for improving the resistance of membranes against fouling has triggered recent interest in new membrane types. However, most nanoparticle-enhanced membranes suffer from the tradeoff between permeability and selectivity. In this study, nano-WS$_2$ was explored as the additive in membrane synthesis by non-solvent induced phase separation. Blended PES-WS$_2$ flat-sheet membranes with the incorporation of ultra-low concentrations of nanoparticles (from 0.025 to 0.25%, WS$_2$/PES ratio) were manufactured and investigated in terms of permeability, fouling resistance and solute rejection. Remarkably, a significant enhancement in the permeability was observed as a result of the incorporation of ultra-low fractions of nano-WS$_2$ to the membrane structure. Optimal permeability values were obtained for modified membranes with 0.10% nanoparticle/polymer concentration ratios. Furthermore, fouling resistance and solute rejection were significantly improved by the incorporation of nanoparticles into the membrane matrix. Specifically, fouling resistance of modified membrane can increase by around 50%.

Keywords—Nano-WS$_2$, Nanoparticle enhanced hybrid membrane, Ultralow concentration, Antifouling.

I. INTRODUCTION

MEMBRANE separation processes are prevalent methods in industrial separation and purification [1]. However, membrane fouling resulting from the accumulation of organic pollutants on or inside membrane matrices is a critical limitation. Many efforts have been made to modify the surface of membranes chemically for improving the fouling resistance, but the efficiency is not satisfied to avoid fouling of organic pollutants [2].

Over the past decade, nanotechnology has developed rapidly for a wide range of purposes [1]. Nanoscale structures are used in membrane synthesis to combine these functionalities with membrane separation, or to alter the morphology and properties of (polymeric) membranes. This not only could overcome the tradeoff between permeability and selectivity, but also improve the fouling resistance [3], [4]. Examples are mainly focused on polymeric membranes enhanced by zero-valent metals [5], oxide nanoparticles [6], [7], and carbon nanotubes [8].

In order to extend the application of nanoparticle in membrane synthesis, more and more new materials should be explored as additives. Nano-WS$_2$ with an excellent chemical

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and physical property shows the wide promising applications in different fields [9]-[11]. As reported, the incorporation of nano-WS$_2$ well dispersed in the polymers, e.g., poly(ether ether ketone), offers the ability to improve the thermal stability, mechanical strength and other properties of hybrid nanocomposites [12]. Thereby, nano-WS$_2$ offers a promosing option as an additive in organic-inorganic membrane synthesis for the water treatment in the harsh environments.

In this paper, a new-type hybrid PES membrane, which was modified by nano-WS$_2$, was successfully synthesized by a non-solvent induced phase separation method. Ultralow content of nano-WS$_2$ ranging from 0.025% to 0.25% (WS$_2$/PES ratio) was adopted for membrane synthesis, aiming at improving the permselectivity and fouling resistance properties.

II. APPROACH

A. Preparation of Membranes

The membranes in the study were prepared by using non-solvent induced phase separation process. A high concentration of 23.0 wt.% PES polymer powder which was dissolved in 1-methyl-pyrrolidone (NMP) was used as the membrane polymer matrix. The polymer solution embedded by nano-WS$_2$ was prepared by dispersing different quantities of nano-WS$_2$ in the fixed volume of NMP by mechanical stirring at 500rpm and room temperature for 3h. Before dissolving the PES polymer in NMP solvent, the different WS$_2$ concentrations, including 0.025, 0.075, 0.10, 0.15 and 0.25 wt.% (WS$_2$/PES ratio), were fully dispersed for 1 h to form the homogeneous suspended in NMP solvent with UP200S ultrasonic processor (Hielscher, Belgium). Afterwards, the PES polymer powder was poured to the suspended solution gradually, stirred for 24h at 600rpm and room temperature. And then the air bubbles trapped in the polymer solution was removed by vacuum pump. Subsequently, the polymer films were casted on a glass plate with non-woven support with initial thickness of 250µm by a filmograph (K4340 Automatic Film Applicator, Elcometer) to obtain a defect-free membrane. The polymer solution was casted at a constant relative humidity of 30%. The casted films were evaporated in the atmosphere for 15s, and then immersed in distilled water bath (23±1°C) for precipitation. And then, the resulting membranes were washed with distilled water to remove the residual NMP solvent, and stored in the pure water for further testing.

B. Characterizations of Membranes

Hydrophilicity were measured in term of contact angle by using a DSA 10 Mk2 (Krüss, Germany) measurement system to determine the affinity of water molecule to the membrane surface.

The permeability (*Perm*) of pure water is determined at the dead-end filtration cell at the different operation pressures (ranging from 2 to 6 bar). The *Perm* was defined according to the following equation:

$$Perm = \frac{J_w}{\Delta P} \quad (1)$$

where pure water flux (J_w) at different transmembrane pressures; ΔP denotes the TMP of membrane for filtration.

Furthermore, the antifouling property of membrane in the testing condition was evaluated in term of fouling resistance by using humic acid (HAC) as a foulant.in the same condition. The intrinsic (R_m) and fouling resistance (R_f) for membrane which denote the antifouling property were determined by the following expression:

$$R_t = R_m + R_f \quad (2)$$

$$R_m = \frac{\Delta P}{\eta \cdot J_w} \quad (3)$$

$$R_f = \frac{\Delta P}{\eta \cdot J_s} - R_m \quad (4)$$

where J_s denotes the flux of feed solution at a steady state, and η presents the viscosity of feed solution at room temperature.

III. Results and Discussion

A. Hydrophilicity Assessment of Membranes

Fig. 1 shows the measured hydrophilicity (contact angle) for control PES membranes and modified membranes with different nanofiller contents.
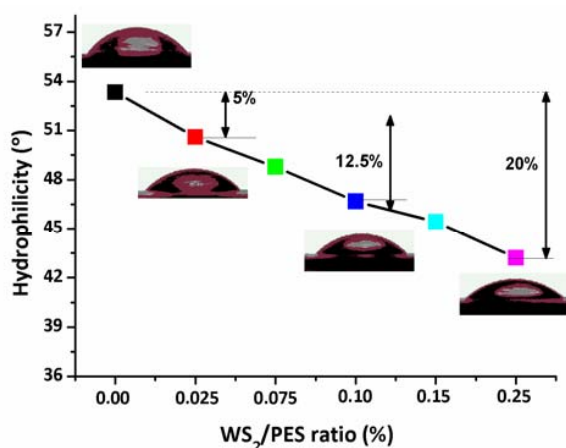

Fig. 1 Hydrophilicity of control and modified membranes with different nano-WS$_2$ contents

As indicated in Fig. 1, it can be clearly observed that membrane hydrophilicity was enhanced as the concentration of the added nanoparticle increased.

Considering that all the membranes was manufactured in the same condition, e.g., type and polymer concentration, the observed increase of hydrophilicity should be only influenced by the addition of nanofillers. In general, two facts can be involved for the further explanation on this phenomenon: (1) the structure change on the surface of membrane, such as pore size and roughness; (2) the intrinsic hydrophilic character of nanofiller, resulting in that the number of hydrophilic centers on the membrane surface increases. Therefore, water molecules are more strongly attracted by the polymeric matrix due to the property of membrane changes. Generally both effects positively alter the membrane hydrophilicity. For this experiment, PES membrane was synthesized as the dense membrane (23.0% content of PES). Thereby, it can be considered that the addition of ultralow concentration of nanofillers has no direct impact on the pore size of membrane surface. The increase in the hydrophilicity of modified membranes mainly results from the hydrophilicity of nanofiller. However, the hydrophilic character of WS$_2$ nanoparticles is under discussion in the literature. Some authors proposed its hydrophobic nature that the hydrophilic amorphous oxide material can't wet the WS$_2$ layers during the production of WS$_2$ nanotubes in a fluidized bed reactor [13]. However, Shahar et al. pointed out that the coordination between the sulfur and tungsten atoms in WS$_2$ crystal is in general not fully satisfied and water molecules adsorbed to these sites make these zones of the nano-WS$_2$ surface hydrophilic for adsorbing water molecule [14]. On the other hand, the small amount of WO$_3$ determined by EDS and XRD in nanoparticles can make some contribution for enhancing the hydrophilicity of modified membranes, due to its high affinity to water [12]. From Fig. 1, it is also concluded that the nanoparticle offers the critical role for enhancing the hydrophilicity of membranes. Only 0.10% (WS$_2$/PES ratio) nano-WS$_2$ was required to achieve an improvement of ca. 12.5% in hydrophilicity of modified membrane. Furthermore, the membrane hydrophilicity increased by ca. 20% with the addition of 0.25% nanofillers in the polymer matrix.

C. Permeability Test of Membranes

The permeability of the control membrane and modified membranes with different contents of nanofiller is shown in Fig. 2.
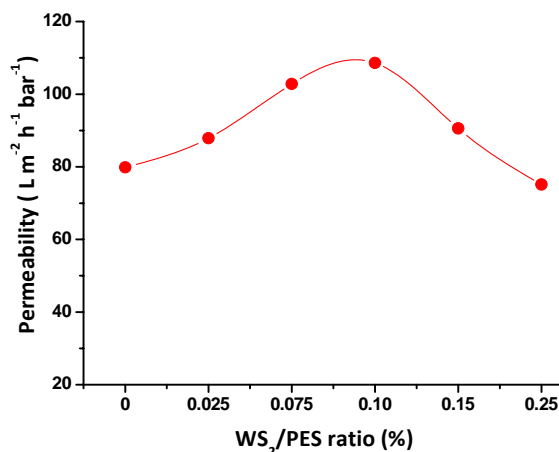
Fig. 2 Pure water permeability of control and modified membranes

As indicated in Fig. 2, it can be clearly observed that a maximum membrane permeability is achieved at 0.10% of nanofillers. The increase of membrane permeability at the low concentration of WS_2, ranging from 0 to 0.1%, is resulted from the enhancement of the membrane hydrophilicity and the change of the membrane structure. The addition of lower nanoparticle contents yields a more hydrophilic membrane surface, improving the affinity to water molecule to some extent, and reducing the resistance of water to permeate through the membranes. However, while the nanofiller contents were above 0.10%, the permeability of modified membranes was reduced although the hydrophilicity still displayed the increasing trend. Therefore, the permeability of nanoparticle embedded membranes, in this high concentration interval (above 0.10%), is mainly due to the alteration in the membrane morphology instead of hydrophilicity improvements. In generally, as commonly assumed in the literature, at the high concentration of nanofiller interval, the pore plugging due to the accumulation of nanoparticles on the membrane surface can play a critical role for reducing the permeability of membrane.

D. Anti-Fouling Evaluation of Membranes

In this study, humic acid is a common foulant during membrane filtration for drinking water treatment, which also can be deemed as the main component for natural organic matter (NOM) in the water environment [15], [16]. The membrane flux for the humic acids solution as a function of time was shown in Fig. 3.

As shown in Fig. 3, at the beginning period of the filtration duration, the relative flux declined fast, and was remained in a steady state after 60 min's filtration. Comparing with the control membrane, the membrane entrapped with nanoparticle shows the high antifouling property. With the addition of 0.25% nanoparticle (WS_2/PES ratio), the modified membrane had a steady relative flux for the humic acid solution 10.5% higher than the control membrane, which is comparable with the literature, using higher contents of other types of nanoparticles [17].
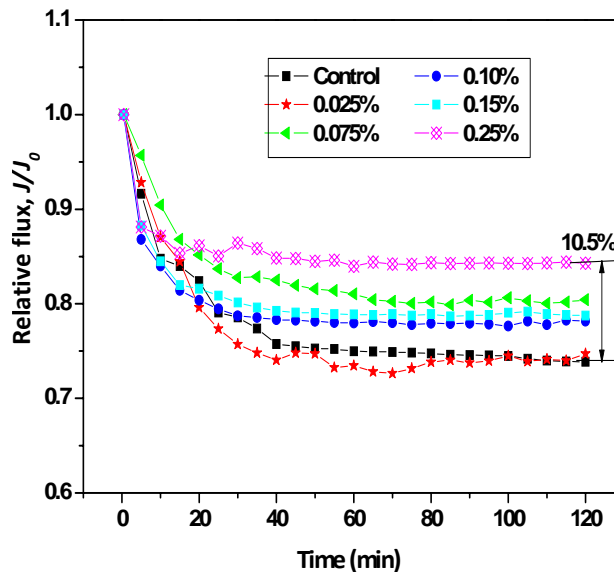

Fig. 3 Time dependency of membrane relative flux for humic acids solution

IV. Conclusions

Nano-WS_2 was used as an additive to the polymer casting solution to modify the membranes aiming at improving the performance of hybrid membranes. The experimental results indicate that the incorporation of nano-WS_2 can improve the permeability and fouling resistance of modified membranes. The ultralow concentration of nanofiller can significantly enhance the hydrophilicity of membranes, obtaining an improvement of 20% at the nanofiller content of 0.25%. The The maximum permeability of membranes was obtained with the addition of 0.10% nanofillers. However, the higher concentration of nanofillers can make the negative impact on the permeability, and this maybe resulted from the pore plugging. Furthermore, the incorporation of nanofillers in the PES membranes enhanced the antifouling performance against humic acid. The relative flux for humic acid solution for the membrane modified by 0.25% nanofiller was improved by 10.5%, compared to the control membrane.

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