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Investigation of preparation conditions of Nano-SiO_2 embedded PES membranes for producing clean water from wastewater

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Abstract: The goal of this study was to determine the desired preparation conditions of Polyethersulfone (PES) membrane for producing clean water. Membranes were fabricated via a combination of vapor induced phase separation (VIPS) and non-solvent induced phase separation (NIPS) methods. SiO_2 nanoparticle were used as the hydrophilicity modification agent in the casting solutions which led to a negative impacts on the permeate flux in high concentrations due to aggregation. Nowadays one of the biggest problems of most of industries, especially petroleum and petrochemical industries is water pollution with oil materials, hence study of such systems is highly applicable. VIPS and NIPS are two methods for porous membrane fabrication each of which needs some modifications for formation of the membrane with regular pore size distribution and regular structure, so the combination of these two methods is such beneficial that VIPS can help to produce a neat surface pores and NIPS can generalize this surface structure to the whole membrane and then form a membrane with suitable morphology for highly water production. In this study, oil-water separation process has been accomplished for fabricated membranes under the same operating conditions and effects of each preparation factor on permeate flux investigated and amount of rejection has been calculated by COD test and finally the best membrane for this separation was selected.

Key words: membrane formation; water purification; vapor induced phase separation; non-solvent induced phase separation; PES membrane

1. INTRODUCTION

Nowadays one of the biggest problems in most industries is water pollution with oil, so finding an economical way with high efficiency is necessary. In recent years, the use of the membrane technology has been beneficial while the type of membrane and its properties determine the performance of oil-water separation process. Experience has shown that PES is an appropriate material for wastewater treatment but the type of materials which are used in polymeric casting solution (such as solvent, non-solvent and additives) and preparation method are very important in membrane structure (Takht Ravanchi et al., 2009; Cheryan et al., 1998; Karakulski et al., 1995). Polyethersulfone (PES) was selected as a membrane material because of its commercial availability, processing ease, favorable selectivity, permeability characteristics, and good mechanical and thermal properties. PES is an amorphous glassy and hydrophilic polymer containing sulfone groups (Wu et al., 2008).

There are two very common methods for preparation of porous membranes. in Nonsolvent induce phase separation (NIPS) method, there are three important and separable species (polymer, solvent and non-solvent) which have different interactions on each other based on thermodynamic concepts, so selection of solvent and non-solvent in this system have vital effect on membrane morphology and consequently on membrane performance (Susanto et al., 2009). The other method is vapor induced phase separation (VIPS) which is the most common method for the formation of ordered micro-porous thin films and has received much attention (Huang et al., 2012). Combination of these two mentioned methods is feasible and effective in fabrication of suitable membrane for waste water treatment as observed in previous research (Vatanpour et al., 2012). In fact control of this suggested method is difficult because there are several effective parameters such as, selected solvent, selected non-solvent, amount of relative humidity, exposure time in humid condition, coagulation bath temperature and etc. which directly influence on the structure of the produced membrane (Fouladitajar et al., 2013, 2014).

PES which is used in this study has desired properties for oily wastewater treatment membranes as previously mentioned, but its hydrophobic properties causes deposition of organic particles in membrane surface and pores which consequently limits the permeate flux and sometimes results in irreversible fouling that leads to shorten the membrane life and increase in the costs. So using nanoparticles in polymeric casting solution has attracted much interest because it causes significant change in composition and solution properties by interaction between the nanoparticle surface and polymeric chains or solvent during the membrane fabrication process. Also the wetting properties of nanoparticles can prevent and control the fouling phenomenon.

The objective of this study was preparation a proper membrane for oily waste water treatment. In order to reach this aim we investigated the effect of preparation condition parameters including exposure time in humid condition and SiO_2 nanoparticle concentration on membrane performance, which occurs in high flux as well as high rejection.

2. EXPERIMENTAL

2.1 Materials

Polyethersulfone (PES) with molecular weight of 400,000 g/mol was purchased from BASF, the solvent DMF (Dimethylformamide) was supplied from MERCK Company as polymer solvent, SiO_2 nanoparticles (average particle size of 10 nm, specific surface area of 380 m^2/g, containing hydrophilic groups) were obtained from MERCK Company and Deionized water was used as a non-solvent in coagulation bath.

2.2 Membrane preparation

For preparation method (combination of VIPS and NIPS) at first the different amounts (0%, 0.2%, 0.7%, 1.2% and 1.4% based on the polymer weight) of dry SiO_2 particles were added into DMF, the solution was ultrasonicated for 20 min to ensure good dispersion of the particles. PES was dried at 110 ºC under vacuum for 12 hours, after that polymer (14 wt%) was dissolved in the solution and subjected to magnetic stirrer for 5 hours to obtain a homogenous solution.

While the solutions were forming due to vigorous stirring, many air bubbles were generated so to remove these bubbles they were kept in room condition without stirring overnight for complete degassing. In NIPS method The casting solution was cast with 180 µm casting knife onto a glass plate at room temperature and immediately was immersed in coagulation water bath but in combined technique the nascent membrane was put in humid chamber with 70% relative humidity at 25 ºC temperature for specific time, then was immersed in coagulation water bath (25 ºC), where an exchange of solvent and non-solvent occurred and membrane sheets were formed. After a few minutes, PES membrane film was detached from the glass plate. After primary phase separation, the membrane was transferred to fresh distilled water for 24 h to leach out the remaining solvent from the membrane structure. The list of fabrication parameters which considered in this study are as below, Table 1.

Table 1. Values of variables

Variables	Values				
Nano particle concentration (wt. %); C_{SiO2}	0	0.2	0.7	1.2	1.4
Exposure time (s); t	6	10	20	30	34

2.3 Membrane performance

The membrane performance was investigated with respect to microfiltration. The performance of the prepared membranes was examined by a flat sheet module, which was used in previous studies of this research team (10, 11), with an effective membrane area of 50 cm^2 at ambient temperature. All prepared membranes were processed at same operating conditions, TMP (trans-membrane pressure) and feed flow rate are 3 bar and 3 L/min, respectively. The oil-in-water stable emulsion was made using gasoil (Tehran Refinery) with the dispersed oil prepared by mixing gasoil and surfactant at a mixing rate of 12,000 rpm for 30 min. The surfactant used was polyoxyethylene (80) sorbitanmonooleate (Tween 80, Merck) at concentration of 100 ppm. For analysis of membrane performance, the amount of oil rejection which is an important parameter was measured by COD test that presented the permeate oil content.

3. RESULTS AND DISCUSSION

The main purpose of this study is investigation of performance of different fabricated membrane which can be affected by the preparation method along with nanoparticle concentration and exposure time in humid box. The effect of these probed as below.

3.1 Effect of Nano concentration

For investigation the effect of Nano concentration, different membrane were fabricated in five different level of Nano concentration as mentioned in Table 1 with considering only 20 s as exposure time in 70% humidity of humid box. Fabricated membrane evaluated in main process for oil-water separation and the result of them for permeate flux in same operation condition show as Figure 1.

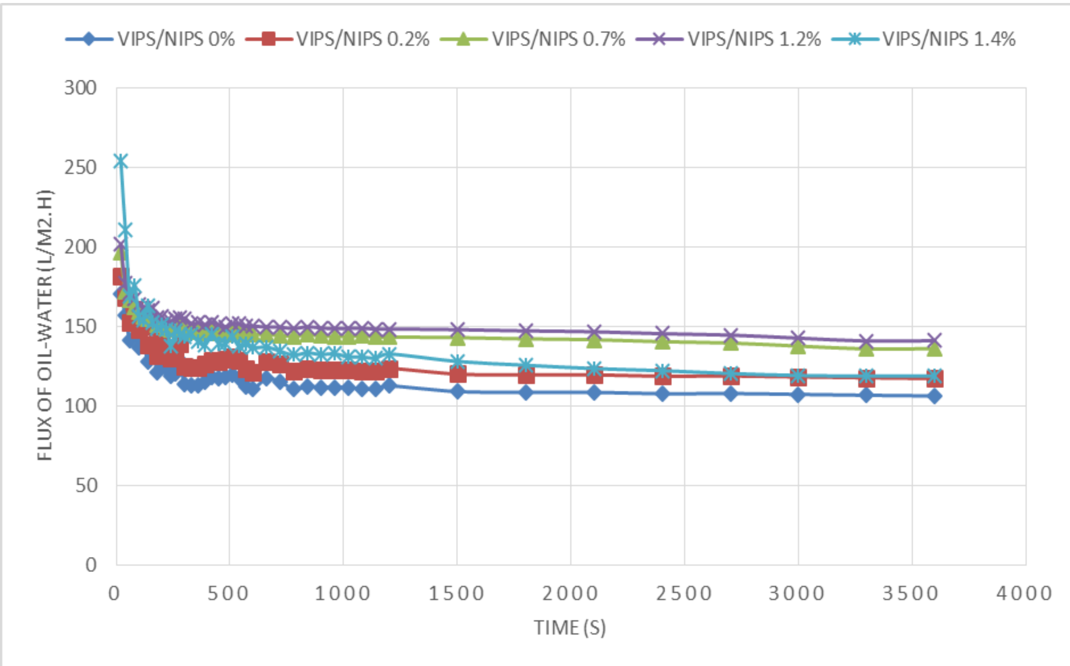

Figure 1. Flux of oil-water for membrane with different nanoparticle concentration

The results show that the permeate flux of different cases increased by increasing nanoparticle concentration until a specific value (1.2 Wt. %) and after this value presence of a higher SiO_2 concentration caused a negative effect on the permeate flux. The incorporation of SiO_2 nanoparticle enhanced the hydrophilicity of membrane which improved the permeation. But further increasing in concentration results in permeate flux reduction which might be attributed to the agglomeration of particles in the membrane.

3.2 Effect of exposure time

Water vapor can be easily absorbed into a polymer solution which cause a primary phase inversion and form the surface pores. The exposure time in this process is an essential factor which can improve the membrane structure while in some cases lead to an adverse effect on the membrane performance (Huang et al., 2012). As indicated in Figure 2, at the condition in which humidity is 70% with Nano concentration of 0.7%, increasing the time exposure has positive effect on permeate flux.

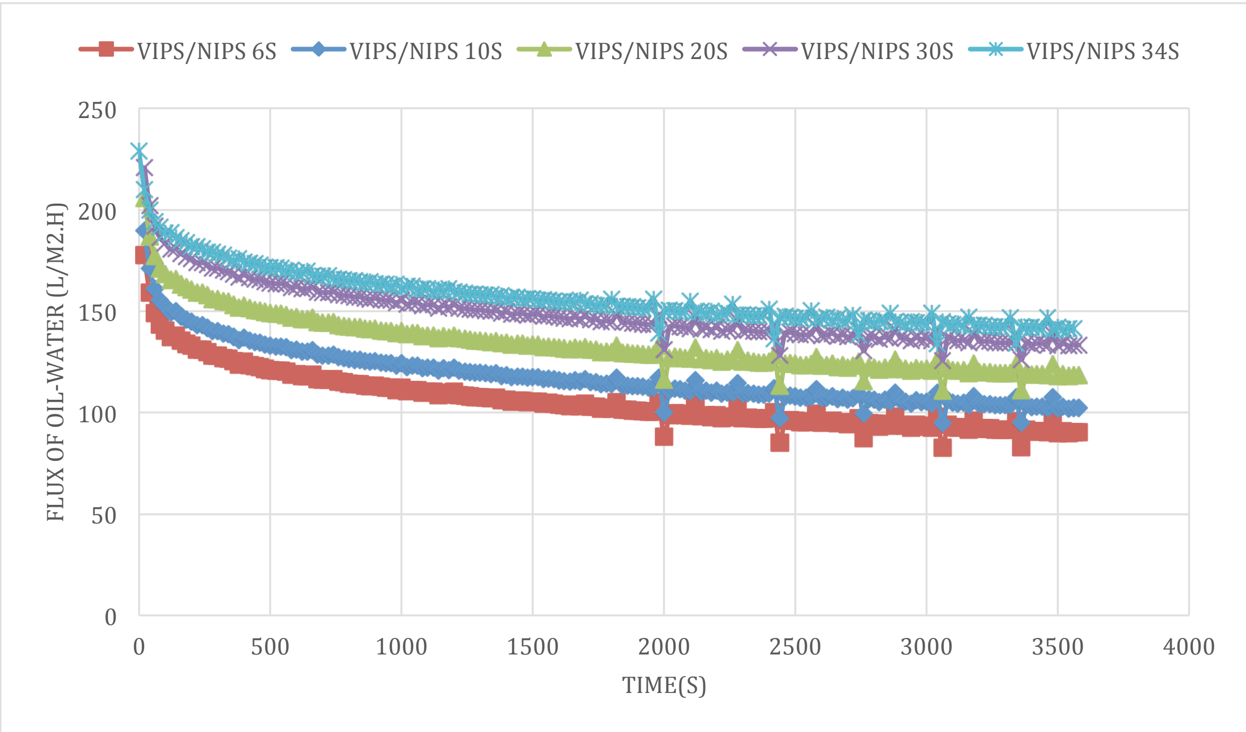

Figure 2. Flux of oil-water for membrane with exposure time

In this preparation method when humidity is applied, although the top surface of polymeric film adsorbs water droplets, the bulk remains unchanged. But after precipitation in coagulation non-solvent bath, those changes on the surface generalized to the whole of the final obtained membrane. Thus, one of the most important factors in the first step of phase separation in the humid chamber is to adjust the effective conditions that not only influence on the surface structure but also can change the bulk morphology.

The plasticity nature of the cast film let vapor drops leave their footprint on the surface in contrast to solid surface and intensity of these traces can produce different morphologies based on considered conditions. Immediately after inserting the cast film to the humid chamber the water vapor droplets intended to cover the film surface due to the high affinity between DMF and water. In fact the physical properties of solvent which are evaporation rate and solvent-non-solvent interaction caused a competition between water vapor condensation on the surface and evaporation of solvent from the polymeric film which inhere based on Figure 2 the higher time exposure the water vapor condensation, in the other word in 70% humidity and 0.7% Nano concentration increasing the time will help vapor droplet to make more pores on the surface of casing film which finally effect on membrane performance.

3.3 Rejection measurement

After examinations of each fabricated membrane the obtained permeate water was provided for COD test which reveals the oil content. The performance of each membrane in separation process was determined by using this parameter. For all fabricated membranes, the rejection was more than 98%. This amount of separation for oil-water feed showed the pore size is not very large to let the oil through but changing of preparation conditions could improve the permeate flux significantly with the same amount of rejection.

4. CONCLUSION

A novel approach was applied to fabricate high performance Nano-SiO_2 embedded PES membranes by combination of VIPS and NIPS methods for microfiltration of oil-in-water emulsion. SiO_2 nanoparticles were used as the hydrophilicity modification agents which resulted in more adsorption of water vapor droplets onto the film surface in VIPS step, while made larger pores on the membrane surface during rapid phase separation in NIPS step. All membranes were examined in constant operating conditions and the results showed a regular trend for permeate flux in case of 70% humidity and 0.7% Nano concentration with increasing the exposure time in which the best performance of membrane obtained in the higher exposure time. But the behavior of fabricated membrane with high SiO_2 content in fabrication process implies vice versa effect on performance, high addition of nanoparticles caused a reduction in permeate flux which is due to the aggregation of particles in the membrane surface and the bulk of membrane resulting to the pore blockage. The COD test have been done for all experiments. Results showed about more than 98% rejection for each fabricated membrane which indicates that with maintaining the high rejection, permeate flux has increased by increasing the SiO_2 concentration until 1.2% in 70% and 34s exposure time.

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