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High performance functionalized MWCNT/PES membrane for oil-in-water treatment

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Abstract: Membrane filtration is a promising technology for oily wastewater treatments considering its high separation efficiency along with simplicity and fairly short process time. However, the application of this technology has been limited by severe fouling caused by oil droplets in the oil-in-water separation resulted in less performance. In this study, pure polyethersulfone membrane was modified by two different functionalized multi-walled carbon nanotube, Carboxylated MWCN and Hydroxylated MWCNT, to increase its hydrophilicity and oil resistant. Carboxylated and Hydroxylated MWCNT/PES mixed matrix membranes were manufactured via NIPS method. Nanocomposite / polymer solutions for membrane formation were prepared in DMF with 16 wt% PES and 1 wt% PVP. The functionalized MWCNTs were added to the casting solution in different concentrations (based on the polymer constituents) and dispersed by sonication stirrer. The effect of these functionalized MWCNTs on the performance of PES membranes permeability was investigated in terms of oil water flux via cross-flow flat sheet module. The results indicated that the performance of the membrane was enhanced by blending functionalized MWCNT to the casting solution. Carboxylated MWCNT increased the oil/water flux by 80 percent, however, the hydroxylated MWCNT increased the flux by only 50 percent. Comparison of the flux in different concentrations of MWCNT also showed that membrane has the best permeability at 0.1% of Carboxylated MWCNT and 0.15% of Hydroxylated MWCNT. Higher concentration of MWCNT showed a reverse effect on the permeability and decreased the flux due to the aggregation of the nanoparticles in the membrane matrix.

Key words: PES membrane, Carboxylated MWCNT, Hydroxylated MWCNT, Membrane performance, Permeate flux

1. INTRODUCTION

Membrane technologies have gained an important place in separation techniques, specially their remarkable performance in removing oil from wastewater produced from industries (Pagidi et al., 2014). Although membranes have superior advantages because of their low energy consumption, high quality water produced, simpler process design and low amount of chemicals used compared to other treatment techniques, they are not without difficulties. Fouling is a serious problem in membrane filtration caused either by oil droplets, blocking membrane pores or accumulation of an oil layer on the membrane surface, decreasing the performance of the membrane and a significant flux decline (Celik et al., 2011).

Non-solvent induced phase separation (NIPS) is a technique mostly used for preparation of polymeric membranes in which, the solution is cast onto a glass support using a casting knife, and then is immersed into a coagulation bath. At the interface, the solvent diffuses out to coagulation bath, while the non-solvent transfers into the casting solution. Subsequently, phase inversion occurs between casting solution and coagulation bath resulting in formation of membrane film (Yin et al., 2013).

Polyethersulfone (PES) is a well-known polymer with characteristics such as excellent toughness, good thermal stability and approved for being used in food, water and medical applications. High hydrophobicity is the main disadvantage of PES membrane resulting in fouling and extremely lower flux decreasing the membrane lifetime and increasing the operation cost (Daraei et al., 2014).

Many studies have been done to increase the antifouling capacity of prepared membranes by improving the membrane hydrophilicity, however, it has been still remained challenging. Substantial effects of nanoparticles, added in the casting solution, have been reported by many researchers. It is well accepted that interactions between the polymeric chains and nanoparticle surface during the membrane fabrication process result in more hydrophilic membrane and increase of the membrane performance. According to the superior properties such as high hydrophilicity nature, high flexibility and low mass density, multi-wall carbon nanotube is an excellent modifying additive for PES membranes (Vatanpour et al., 2014).

Fabrication of hydrophilic modified membrane using these additives for membrane preparation faces two problems. Firstly, MWCNTs have unsuitable dispersion and dissolution in various organic solvents. Secondly, there is a weak interaction of the interface between the MWCNTs and the polymer matrix. Hence, to obtain uniform dispersion of nanoparticles in the polymeric solution and amplify stability of nanoparticles in polymer matrix, hydrophilic functional groups are introduced into the surface of the MWCNTs via functionalization by chemical agents and attaching polar groups to MWCNT sidewalls. Hydroxyl and carboxyl groups are two approved functional agents widely used to overcome the undesirable dispersion of MWCNTs into the polymer matrix (Vatanpour et al., 2011).

This work is a comparative study on the effects of embedding two different functionalized MWCNTs on PES membrane performance in order to find the optimum amount of nanoparticles that profoundly enhance the performance of fabricated membranes. Carboxylated-MWCNTs and hydroxylated-MWCNTs were added into the casting solution in a selected number of concentrations to obtain optimum level and avoid aggregation of nanoparticles. The trends of changes in performance of modified membranes are obtained via oil-water flux runs through cross flow flat sheet module.

2. EXPERIMENTAL

2.1 Materials

Functionalized multi-wall carbon nanotube (95% of purity) with 10–30 nm in outer diameter and 3 wt% of OH and COOH content was obtained from Neutrino Corporation (Iran). Polyethersulfone (PES, E6020p) was purchased from BASF. Dimethylformamide (DMF) were provided from MERCK. Polyvinylpyrrolidone (PVP) of k25 grade (MW ~ 25,000 g/gmol) was kindly obtained from Rahavard Tamin Pharmaceutical Company (Iran). Distillated water was used as the non-solvent in the coagulation bath and also in all flux runs.

2.2 Preparation of functionalized MWCNT/PES mixed matrix membranes

Nonsolvent-induced phase separation (NIPS) was used to fabricate functionalized MWCNT/PES mixed matrix membranes using casting solutions containing PES (16 wt%) as the base polymer, polyvinyl pyrrolidone (PVP, 1 wt%) and measured amount of functionalized MWCNT in DMF as solvent in order to increase the hydrophilicity of PES membranes. Exact amount of functionalized MWCNT (0, 0.05, 0.1, 0.15 and 0. 2 wt% with respect to PES concentration) were ultrasonicated in DMF for 20 min until uniform MWCNT solution was obtained. After preparation of well dispersed MWCNTs in the solvent, PES and PVP, were dissolved in the dope solution by continuous stirring and heating at 45 °C to obtain homogenous casting solution. 5 min of ultrasonication was again used to remove the air bubbles produced during stirring. The solution then was casted on a glass plate using a casting knife with 180 μm thickness, and the glass plate was immediately immersed in the non-solvent bath (distilled water at 25 ±1 °C). A thin polymeric film was separated from the glass within a few minutes. Eventually, the formed membranes were washed with and stored in distillated water for 24 h to attain full leach out of residual solvent and additives.

2.3 Membrane performance

A flat sheet module in a lab scale experimental setup with 50 cm^2 of effective area at ambient temperature was used to examine the performance of prepared membranes. This setup was employed in previous works of this research team (Fouladitajar et al., 2013: De Lannoy et al., 2013). The flow pattern on this module is cross flow with feed flow rate, trans membrane pressure (TMP) and the oil concentration of 2 L/min, 2 bar, and 2000 mg/L, respectively. All fabricated membranes were applied under the cross flow pattern process at the same operating conditions.

2.4 Feed preparation

The oil-in-water emulsion was prepared by mixing gasoil (Tehran Refinery) and surfactant for 20 min at a mixing rate of 10,000 rpm. Polyoxyethylene (80) sorbitanmonooleate (Tween 80, Merck) was used as the surfactant at concentration of 100 mg/L (Ghandashtani et al., 2015). COD test was used to measure the amount of oil rejection in each experiment which is an important parameter for analysis of membrane separation performance. For all modified cases, oil rejection was higher than 95%.

3. RESULT AND DISCUSSION

Permeate flux was used to investigate effects of hydroxyl and carboxyl groups on modification properties of MWCNTs along with percentage of functionalized MWCNTs in the dope solution on the performance of fabricated membranes.

3.1 Permeate flux reduction

Fig. 1 shows the permeate flux of feed, after 20 minutes of distilled water circulation in flat sheet module. A sharp initial decline of permeation flux at the beginning of separation process was observed which is due to deposition of organic particles and formation of fouling layer on the membrane surface as well as internal fouling caused by deformation of oil droplets during migration to the bulk of membranes (Sun et al., 2010). After this rapid reduction, decline of flux was gradually slowed down until a relatively constant value was achieved. Note that obtained permeate flux of pristine PES membrane was 63 $L/m^2.h$.

3.2 MWCNTs concentration

The trends of permeate fluxes shown in Fig. 1 indicates that addition of nanoparticles has increased the permeate flux of membranes up to the optimum concentration of functionalized MWCNTs which was observed at 0.1% and 0.15% for COOH-MWCNTs and OH-MWCNTs, respectively. Permeate flux of membranes is reduced with further increase of nanoparticles in the solution due to the pore blockage caused by aggregation of nanoparticles in the membrane structure, despite the increased hydrophilicity.

The cross-sectional FESEM images of the membranes in different concentration of nanoparticles exhibited in Fig. 2 are used to explain this phenomenon. A typical characteristic of a dense skin top-layer along with asymmetric porous structure with finger-like macro-pores was observed for all membranes. Smallest pores in the top-layer appeared in the pristine PES membrane (Fig. 2a). Macro finger-like structure started to appear by addition of low amounts of nanoparticles due to hydrophilic nature of functionalized MWCNTs increasing the mass transfer rate between solvent and non-solvent during phase inversion. The finger-like pores were promoted in membrane structure till addition of 0.1 wt% nanoparticles (Fig. 2b-c). Irregular positioning of MWCNTs in the membrane structure appeared by exceeding this optimum concentration due to aggregation of nanoparticles. The tendency of MWCNTs to migrate to lean-polymer phase of solution and their aggregation in the membrane structure demolishes the uniform dispersion of nanoparticles in the polymeric solution and consequently blocks the pores in bulk of membrane matrix which results in smaller pores and thus a flux decline. A better look of aggregation in the bulk of membrane matrix is shown in Fig. 3. As shown, pores blockage is occurred by aggregated nanoparticles which obstruct the feed from passing easily through the film.

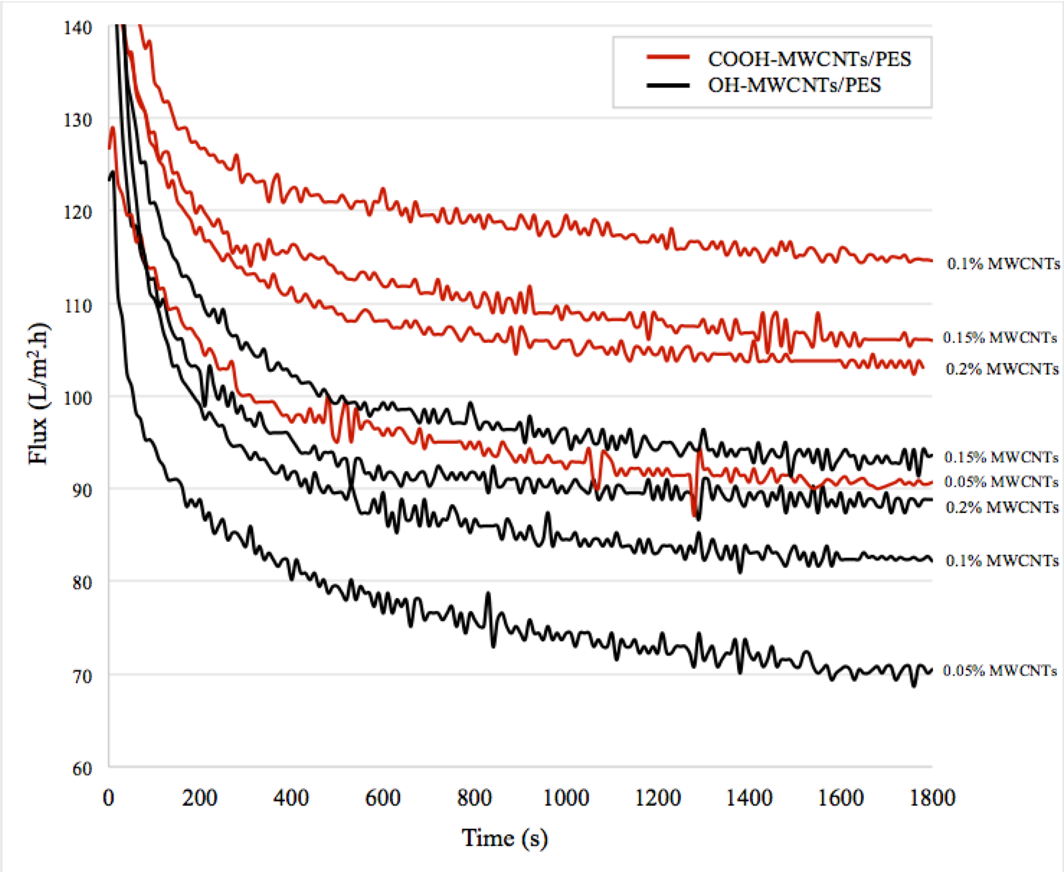

Figure 1. Permeate flux of functionalized-MWCNT/PES membranes.

3.3 Comparison of different functionalized MWCNTs

As illustrated in Fig. 1, at equal amount of nanoparticle, all COOH-MWCNTs/PES membranes exhibited better permeate flux, therefore better performance compared to OH-MWCNTs/PES membranes. Two reason could describe the preferable effects of the former than latter. On one hand, carboxylated functional group have better ability to form hydrogen bond with water molecules during the phase inversion process which reduces the interface energy between solvent and non-solvent. As a result, an increase in membrane porosity thus a higher flux is obtained. On the other hand, compared to linear spatial geometry of hydroxylated functional group, more empty spaces are formed between polymeric chains of PES due to V-shape spatial geometry of carboxylated functional group in which solvent gets trapped. Solvent leaves these spaces during phase inversion causing more porous structure in the bulk of the membrane. The authors believe that this reason, neglected in other studies, is of a great importance to appearance of the porosity in fabricated membranes. As a result, mentioned increase in the porosity of membrane matrix leads to a higher permeate flux. This argument goes in good agreement with the trend of porosity variation of the prepared membranes.

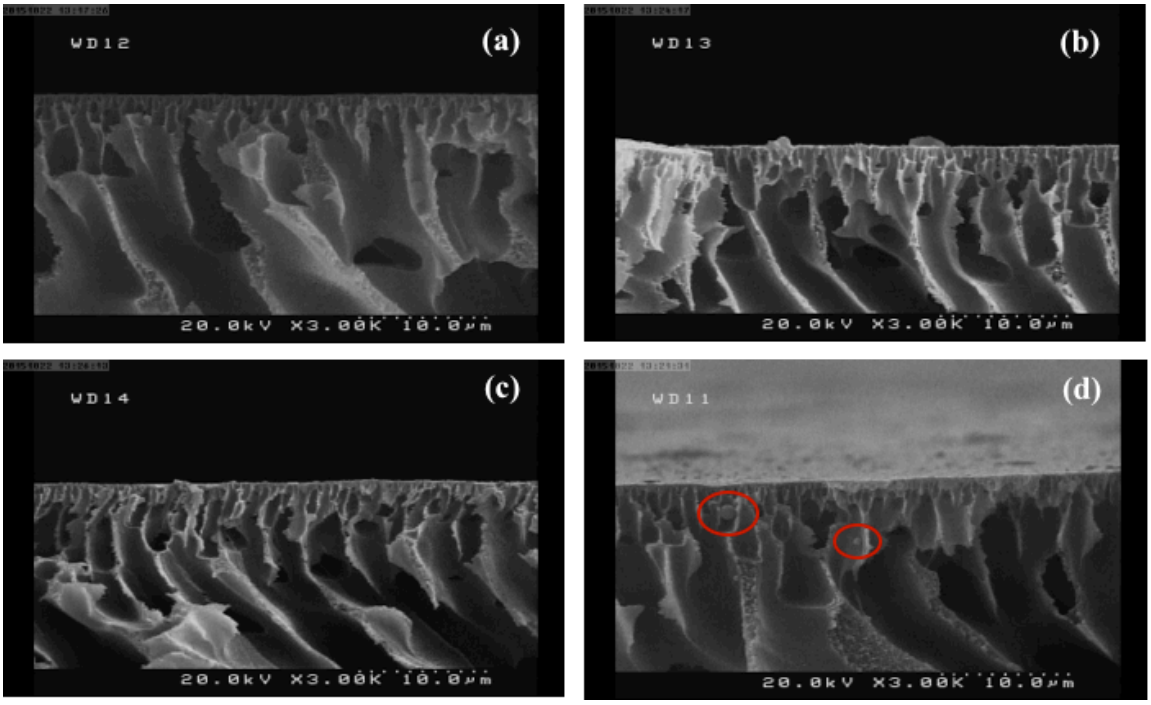

Figure 2. Cross-sectional FESEM images of membranes with different blend compositions of MWCNTs. (a) Pristine PES, (b) 0.05 wt% COOH-MWCNTs/PES (c) 0.1 wt% COOH-MWCNTs/PES (d) 0.15 wt% COOH-MWCNTs/PES

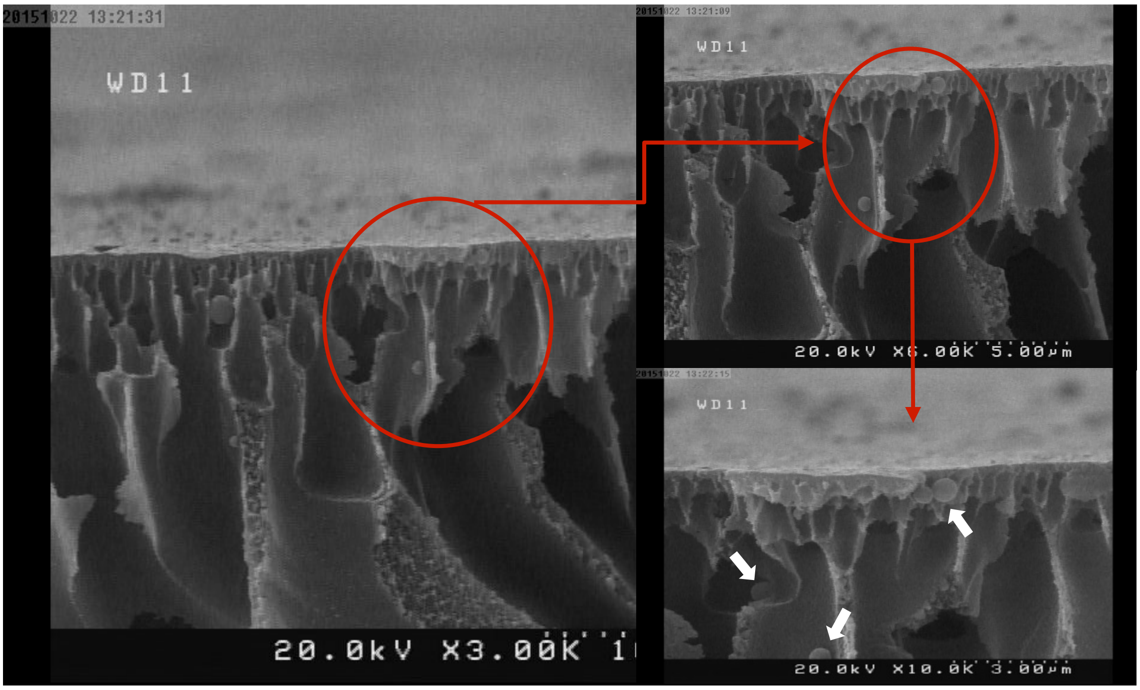

Figure 3. Cross-sectional FESEM images of membrane with aggregation in the bulk.

Table 1 compares the flux of COOH and OH functionalized MWCNTs/PES membranes with their porosity at different content of nanoparticles. As shown in Table 1, all carboxylated-MWCNTs/PES membranes showed more porosity than membranes modified with hydroxylated-MWCNTs which resulted in higher flux of the former which confirms the favourable effects of COOH functional group compared to less desirable effect of OH functional group on the performance of the prepared membranes. Although, as explained before, lower porosity of the fabricated membranes is observed at nanoparticle content higher than optimum concentration due to the aggregation of functionalized nanoparticles which adversely influenced the uniform dispersion of MWCNTs.

Table 1. Comparison of porosity of different functionalized MWCNTs/PES membranes

Carboxylated-MWCNTs/PES			Hydroxylated-MWCNTs/PES		
Nanoparticle (%)	Flux (L/m2.h)	Porosity (%)	Nanoparticle (%)	Flux (L/m2.h)	Porosity (%)
0.5%	90.6	70.16	0.5%	70	66.57
0.1%	115	73.84	0.1%	82.3	67.8
0.15%	105.9	72.05	0.15%	93.8	70.04
0.2%	102.5	69.51	0.2%	88	68.21

4. CONCLUSIONS

In this paper, the effect of hydroxylated and carboxylated multi-walled carbon nanotubes on the performance of PES membrane permeability in oily water separation was investigated in term of permeate flux via cross-flow flat sheet module. The results indicated that the performance of the membrane was increased by embedding functionalized MWCNTs to the casting solution, however, carboxylated MWCNT showed a better modifying effect on the membrane permeability and increased the oil/water flux by 80 percent, where hydroxylated MWCN increased the flux by only 50 percent. Comparison of the flux in different concentration of MWCN also showed that the optimum concentration for hydroxylated and carboxylated MWCN in polymeric solution were 0.15% and 0.1%, respectively. Flux reduction was observed at higher concentration of MWCNT due to the aggregation of the nanoparticles in the membrane matrix.

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