Development of highly flux antifouling RO Polyethersulfone membrane using woven support

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Abstract

Over the next decades, many regions worldwide will likely face dramatic changes in the availability of water. Desalination of sea water appears as the perfect mean to ensure water supply. To this end, membrane technologies represent a promising technology since they can achieve high levels of purification and are simple technically, energy efficient and typically scalable. However, membrane fouling, characterized by the deposition of solid material onto and into the membrane surface, is still the main problem of this treatment.

In the present work, a novel highly flux antifouling membranes were prepared via phase inversion technique using Polyethersulfone (PES) blending with a nano-materials solution of sodium dodecyl sulfate (SDS), Titanium dioxide (TiO_2) and Triethanol amine (TEA), in*N*-Methyl-2-pyrrolidone (NMP) as a solvent. The prepared polymeric solution was cast on woven fabric as supporting material. The SEM results prove that prepared membranes have dense top layer and small finger like structure in the middle, while the bottom layer is porous due to woven support. The prepared membranes exhibit excellent mechanical behavior. Desalination test was carried out using real samples from Mediterranean sea. The membranes performance results indicate that salt rejection reached 96% with high flux 134.9 Kg/m^2h under operating pressure up to 40 bar.

Keywords: antifouling, polyethersulfone membranes, desalination, woven support

1. Introduction

Nowadays, development in membrane technology has attracted great attention in improvement in membrane preparation process, environmental protection, health sector, desalination and water treatment processes (Goncharuk *et al*.2011; Sohrabi *et al*. 2010; Abu Seman *et al*. 2011). Most membrane fabrication processes depend on casting of polymeric solution on glass plate or non woven support using film applicator, then the membrane formation step is carried out using coagulation bath which contains mostly water. Polyethersulfone membranes mostly are prepared without support or with non-woven polyester support. The use of the support enhances the strength of the membranes (Aerts *et al*.2006) and they are dominantly used to fabricate membranes in an industrial scale (Hou *et al*.2014). The support can also limit shrinkage which provides stretching action on the nascent membrane during the coagulation stage (Bottino *et al*. 2004;Kang *et al*.2014). Most special type of polyethersulfone membrane support is non-woven polyester. The merits of the prepared PES membrane supporting by non-woven polyester is the improvement in mechanical properties, where the membranes can carry high pressure during operation (Feng *et al*. 2004;Fan *et al*.2013). The novelty of this work is using compacted woven support as supporting material for blend nano-material polyethersulfone membrane in order to gain highly permeate flux along with high salt rejection and an improvement of antifouling surface property.

2. Experimental

2.1. Materials

Polyethersulfone and N-methyl pyrrolidone as a solvent were purchased from BASF Company (Germany). Sodium dodecyl sulphate (SDS), triethanol amine and Commercial TiO_2 anatase powder were obtained from Merck, Germany. Woven support was purchased from Egypt local market and non-woven support was purchased from Holykem company, China. Commercial NaCl was used in desalination experiments. Also, real sea water samples from Mediterranean Sea were obtained from Alexandria port Egypt.

2.2. Fabrication of asymmetric RO polyethersulfone membranes

The RO asymmetric PES membranes were fabricated by phase inversion induced by immersion precipitation method using casting solutions containing PES (20-25wt.%), 6% nano-materials solution containing 0.5% sodium dodecyl sulphate(SDS) , 1% triethanol amine and 1% TiO_2 in water. These chemicals were dissolved in N,methyl pyrrolidone (NMP) as solvent and stirred for 8 h and the polymer mixture solution was stand in refrigerator for 24 h to remove air bubbles.

Three kinds of membranes were fabricated; first the polymeric solution was casted onto a clean glass plate with

100 µm thickness. For the second one, the polymeric solution was casted on a woven support with 150 µm thickness. For the third one, the polymeric solution was casted on non-woven support with 150 µm thickness. The casted membranes were immersed horizontally into distilled water at room temperature. Then, the membranes were stored in fresh distilled water for 24 h to complete phase separation.

2.3. Membrane characterization

2.3.1. Membrane morphology

Scanning electron microscopy (SEM) was used to study the morphology of prepared membranes, The cross-sectional snapshots of membrane were taken on a JEOL 5410 scanning electron microscope (SEM) and conducted at 10 kV.

2.3.2. Mechanical properties

Mechanical properties of three prepared membranes were investigated. The tensile strength and membranes elongation were measured using mechanical testing system (INSTRON-5500R).

2.3.3. Membrane porosity and BET area

The inner surface of the prepared membranes were determined using the Brunauer-Emmett-Teller (BET) method. The analysis was conducted at the National Research Centre, Giza, Egypt. Porosity of prepared membranes also, determined from this test.

2.4. Membrane performance measurements

The experiments were carried out on the lab desalination unit as shown in Figure1. This system contains flat sheet membrane module of three openings for feeding, concentrate and permeate.

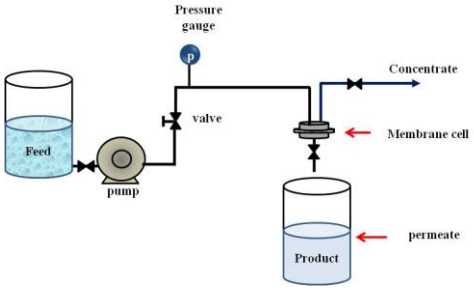

Figure 1. Schematic drawing of lab desalination testing unit

The feed was continuously fed to the membrane module from a closed feeding tank (50 L) using a high pressure pump. The product was collected from downstream of the membrane module. Different prepared membranes wer elocated in stainless steel plate module of 10 cm in diameter. In all the experiments, Mediterranean sea samples was continuously fed to the membrane module at pressure 50 bar and temperature of 25°C. Table 1 illustrates the analysis of seawater sample. Flux and salt rejection were determined and measured.

Table. 1. Sea water sample analysis

Parameters	Unit	Result
Total Dissolved Solids (TDS)	mg/l(ppm)	35,800
pH		7.5
Total Hardness	mg/l	5760
Calcium Hardness	mg/l	1760
Magnesium Hardness	mg/l	4000
Sodium	mg/l	16,040
Alkalinity as bicarbonates	mg/l	14,000
Hydroxides	mg/l	0
Carbonates	mg/l	0.004

2.5. Membrane fouling testing

Experiments were carried out using the same desalination lab unit on whey solution and on sea water. Firstly, the distilled water was permeated through membranes for 3 h and the permeate flux J_{w1} was measured. Secondly, the whey solution in pH = 7.0 ± 0.1 was permeated through membranes for 3 h. The permeate flux J_p (Kg/m^2 h) was measured based on the amount of produced water permeated from the membranes at 30 bar for 3 h. The fouled membranes were washed with distilled water for 30 min after removing whey solution. Finally, distilled water was passed though membranes again for 3 h and the permeate flux was measured J_{w2} (Kg/m^2 h). The same sequence was repeated using sea water. The flux recovery ratio (FRR) was calculated as follow:

$$FRR\% = \frac{J_{w2}}{J_{w1}} x100$$

The total fouling ratio (Rt) was calculated as following:

$$R_t\% = \left(1 - \frac{J_p}{J_{w1}}\right) X100$$

Where Rt was the degree of total flux loss caused by total fouling. Reversible fouling ratio (Rr) and irreversible fouling ratio (Rir) can be calculated by following equations, respectively (Kang *et al* 2007;Madaeni *et al*.2007;Peng *et al*. 2011):

$$R_r\% = \left(\frac{J_{w2} - J_p}{J_{w1}}\right) x100$$

$$R_{ir}\% = \left(\frac{J_{w1} - J_{w2}}{J_{w1}}\right) x100$$

Generally, Rt was the sum of Rr and Rir.

3. Results and discussion

3.1. Characterization asymmetric RO polyethersulfone

3.1.1. Membrane morphology

Figure 2 shows cross –sectional SEM image of prepared membrane without support (M_1). The membrane has asymmetric structure with top dense layer, a porous sublayer, and large macro pores at the bottom.

Figure 3 illustrates cross section of the fabricated membrane using non-woven support (M_2). The image indicates highly dense top layer, with narrow wall of finger-like structure in the middle due to addition of nano-particles of sodium dodecyl sulphate and titanium dioxide in the polymeric solution.

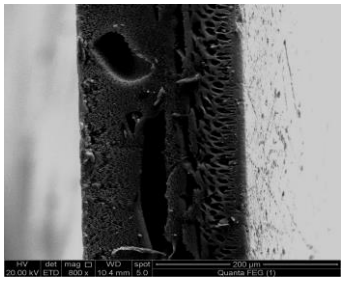

Figure2. The cross-section SEM images of prepared membrane (M1)without support

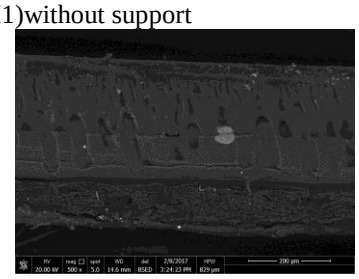

Figure .3. The cross-section SEM images of prepared membrane (M2) with non-woven support

Figure 4 illustrates cross section of the fabricated membrane using woven support (M3). The snapshot indicates highly dense top layer, with small length of finger-like structure in the middle due to impregnation of the woven support fabric part of the polymeric solution. The bottom layer has porous structure according to the woven support pores.

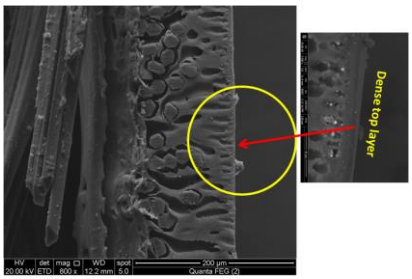

Figure .4. The cross-section SEM images of prepared membrane (M3) with woven support

3.1.2. Mechanical properties

The tensile strength and elongation of the blend membrane was obtained using mechanical testing system. Figure 5 shows the relation between tensile strength, elongation and the support type. This Figure presents that the maximum tensile strength (152 kg/m^2) and the maximum elongation % (36.6%) reachedfor M3, as woven support provides highest tensile strength and highest elongation along the grain and the closer the weave the stronger and firmer the fabric.

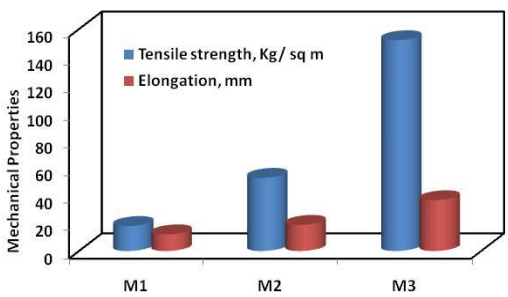

Figure 5. Mechanical properties of prepared membranes, M1: membrane without support, M2: membrane with non-woven support and M3: membrane with woven support

3.1.3. Membrane porosity and BET area

For all the prepared PES membranes with different supports, the pore size distribution became narrower around the mean pore diameters. The total pore volume and the mean pore diameter are listed in Table 2. It can be found that the pore size of the PES membranes were in nano-size due to using Titanium dioxide and SDS, which was in agreement with the analysis of membrane morphology. M3 provides highest porosity of 40.9%, and highest BET area that could be attributed to to using woven support which gives best pore distribution on all membrane surface.

Table.2. Measurement of BET area and pores characterization

Membrane Type	BET area m^2/g	Total pore volume (cm3/g)	Mean pore diameter (nm)	Porosity
M1	6.7	1.092E-2	6.5	35.7
M2	6.75	1.0925E-2	6.47	35.6
M3	7.8E-2	1.72E-2	8.8	40.9

3.2. Membrane performance measurements

Average water permeate flux and average salt rejection % of prepared membranes with different supports were studied using lab desalination system unit. The effects of support on water flux and salt rejection% of prepared membranes using different salt water concentration are shown in Figures 6 and 7, respectively.

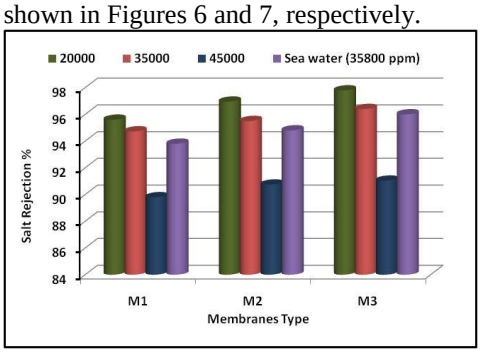

Figure 6. Effect of support on salt rejection of prepared membranes, M1: membrane without support, M2: membrane with non-woven support and M3: membrane with woven support

The average flux reached to maximum using M3 with woven support. While, the salt rejection in all feed concentration are close to each other. The salt rejection reached to 96% with high flux 134.9 Kg/m^{2}h under operating pressure up to 40 bar using M3 with applying on the sea water.

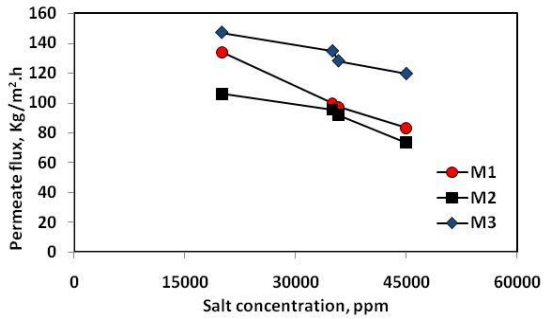

Figure7. Effect of support on salt permeate flux of prepared membranes, M1: membrane without support, M2: membrane with non-woven support and M3: membrane with woven support

3.3. *Membrane fouling testing*

The anti-biofouling and fouling performance of the prepared membrane M3 (using woven support) was tested by measuring of water flux recovery after fouling by whey solution and sea water respectively. The fouling can occur due to different parameters such as interactions between molecules and membrane surface, polymer chemistry, pH of solution and membrane structure (Peng *et al.* 2011). Figure 8 illustrates the biofouling test, where the pure water fluxes before and after whey separation were measured and permeate flux solution from whey separation was also measured. After that, the flux recovery ratio (FRR) and resistance parameters were calculated to assess the anti-biofouling properties.

Figure 8 indicates that the permeate flux of membrane (M3) decreases after using whey solution due to several factors; high fouling of membrane and concentration polarization. The fouling of membrane may be attributed to adsorption or deposition of protein molecules on the membrane surface. Small pores on the top membrane surface being clogged, play an important role for flux decline. Flux recovery ratio was calculated for M3 and found to be 70.53%. The higher FRR shows good antifouling property for the membrane. The total fouling ratio (Rt), reversible fouling ratio (Rr), and irreversible fouling ratio (Rir) values for the prepared membrane M3 were calculated. The adsorption of protein on the membrane surface causes reversible fouling, that was easily removed by backwash and so R_r was 28.4%. On the other hand, irreversible fouling produced due to adsorption of protein molecules on the membrane surface or clogging of protein molecules the pores on the surface, where R_{ir} was 29.5%and R_t was 57.9%. The results indicates that the reversible and irreversible resistance were close, this clearly finalize the arguments that the main effective fouling reason was clogging of pores by protein molecules (Kang *et al* 2007).

On the other hand, antifouling test using sea water was studied as the same sequence of whey solution. Firstly, the pure water flux was recorded, then the sea water was applied on membrane and the permeate treated water flux was recorded, the membrane washed and finally the water flux was measured again. Figure 9 illustrates that the permeate flux of M3 decreases after using sea water due to concentration polarization and diffusion of salts through the membrane pores, which causes fouling.

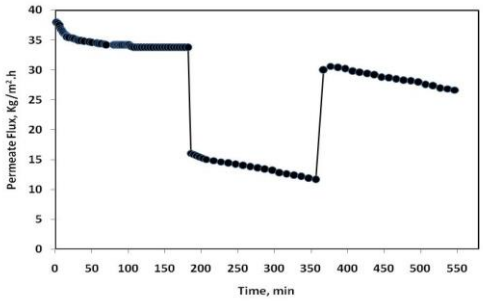

Figure 8. Permeate flux verses time for prepared membrane supported by woven support (M3) during Biofouling test

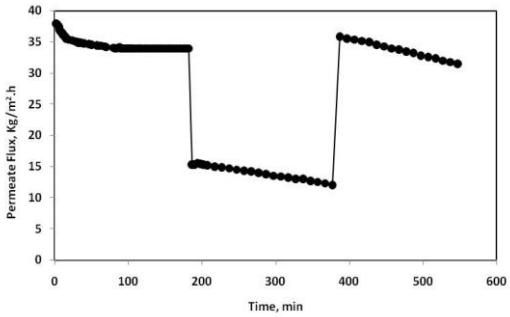

Figure 9. Permeate flux verses time for prepared membrane supported by woven (M3) during fouling test-usingseawater.

Meanwhile, Flux recovery ratio was calculated for M3 which was 94.5%. The FRR is very high which means the membrane is super antifouling. The total fouling ratio (Rt) was calculated to be 59.74%, reversible fouling ratio (Rr) was 54.2%, and irreversible fouling ratio (Rir) was 5.53% that means the main fouling was reversible fouling, which can be easily removed by membrane cleaning and it was only on the membrane surface, while low value of irreversible fouling ratio indicates that using nano-titanium dioxide with sodium dodecyl sulphate blending with polyethersulfone membrane increases the hydrophilicity and decreases the pores size of membrane. The membrane also acquires property of photocatalytic, where a group of oxygen vacancies are produced on the surface, where the water molecules can occupy the empty sites and adsorbed OH groups that are formed on the membrane surface and lead to an increase in the hydrophilicity of the membrane surface (Madaeni *et al*.2007). Also, on the surface can prevent the deposition of proteins and salts which is the reason of the fouling.

4. Conclusion

The asymmetric antifouling membranes of PES blending with a nano-materials solution of sodium dodecyl sulfate (SDS), Titanium dioxide (TiO_2) and Triethanol amine (TEA), in *N*-Methyl-2-pyrrolidone (NMP) were successfully fabricated by phase inversion method without and with using woven and non woven supporting fabric. M3 using woven support exhibits highest mechanical properties, and provides excellent results for all salt concentrations. The salt rejection reached to 96% with high flux134.9 Kg/m^{2}h under operating pressure up to 40 bar using samples from Mediterranean sea. Antifouling testing on M3 was studied using whey separation and sea water. M3 provides superior fouling resistance where Flux

recovery ratio was 70.53% at using whey and 94.5% using sea water.

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