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Research paper

Enhancement of nonwoven cellulose triacetate forward-osmosis membranes by surface coating modification

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Abstract

Forward osmosis (FO) is considered as one of the emerging techniques in membrane technology. The enhancement of FO performance is governed by two major factors: the first one is development of high-performance draw solutions and the second is utilizing of high efficient FO membranes. The aim of this work is to investigate chemical surface coating modification of commercial nonwoven forward osmosis membrane with new hydrophilic coating materials namely, o-phenylene di-amine and benzoyl chloride. The effect of coating addition at different concentrations was studied. The membrane morphology and chemical structure characterization of modified membranes proved the formation of dense layer and higher membrane porosity. Finally, it was demonstrated that increasing of coating material concentration gradually increases porosity and membrane performance till 0.75 g/l. By further increasing of coating materials, the porosity and membrane performance tend to decrease.

Keywords: *Desalination; Forward osmosis; hydrophilic coating materials; nonwoven membranes; Surface coating modification.*

1. Introduction

FO is an emerging membrane technology where many contributions were made to enhance its overall process efficiency from both academic researchers and industries [1], [2], [3]. The theory of FO process depends on using natural osmotic process to draw water molecules through a semipermeable membrane from a diluted feed solution (FS) to a higher concentrated solution that named the draw solution (DS). Hence, the driving force is generated naturally by the difference in osmotic pressure between DS and FS. This gives several advantages over hydraulic pressure-driven membrane processes (e.g.RO); like lower energy requirements and reduced membrane fouling possibility [4]. The absence of applied hydraulic pressure in the FO process has not only the potential to lower both capital and operating cost but can also be useful for fouling control compared to pressure driven membrane processes. Where, fouling in the FO process was found to be physically reversible which reduces the use of chemical cleaning [5], [6]. FO technology is faced by several challenges that limit its application in large scale processes. The enhancement of FO can be governed by two major factors; development of high-performing draw solutions and highly efficient FO membranes. It is the fact to say that, the core of the advancement in the FO process is dedicated to membrane materials development to fabricate high-performance FO membranes. The optimum FO membrane must has high permeability of water and solute rejection, low concentration polarization (CP) and low fouling tendency in addition to high mechanical and chemical stability [7].

Recently, numbers of developed FO membranes based on cellulose ester were fabricated in both hollow fiber and flat sheet modules [8], [9-11]. These membranes have two skin layers, which decreases the tendency to internal concentration polarization (ICP) [12]. Su et al. [13] investigated employing of different rates of phase inversion and extent of thermal annealing during fabrication of FO membrane with “double-skinned cellulose acetate (CA) hollow fibers comprising of an inner or outer selective layer. The dense outer layer significantly increased FO efficiency with comparing to those thermally treated at the lumen side. Similarly, Sairam et al. [14] fabricated CA flat sheet FO membranes by using different pore forming agent include zinc chloride, maleic acid, and lactic acid at different annealing temperatures. They illustrated that membranes with zinc chloride pore forming agent gave relatively high water flux and salt rejection. The fabrication of thin film composite (TFC) membranes conducted by supporting of an ultra-thin selective layer on a chemically different porous support layer, this can combine the advantages of two separate layers and can lead to good FO membranes performance [15]. Typical TFC membrane involves a top skin layer with thickness ranged from ~100 to 300 nm and fabricated in most cases from polyamide (PA), this layer formed at the surface of a micro porous substrate by an interfacial polymerization reaction [16]. While, support substrate usually consists of polysulfone (PSf) or polyethersulfone (PES) cast over a polyester fabric by a phase inversion technique [4]. The key factors of optimal TFC FO membrane include employing of extremely thin selective layer with high water permeability and solute selectivity. In addition, support layers must be thin, highly porous, and minimally tortuous [16 -18] to diminish ICP [19], [4]. Surface modification proved to greatly increase membrane surface hydrophilicity and reduce fouling propensity in FO membrane process. There are several methods for membrane surface modification depends on introduction of hydrophilic substances onto the surface of hydrophobic membranes such as: adsorption, surface coating [20–22]; chemical reactions induced by high energy substances (UV, plasma) or strong acids [23], [24] and surface grafting [25–27]. Recently, the most common commercially FO membrane is the asymmetric cellulose triacetate (CTA) membrane from Hydration Technology Innovations (HTI, Albany, OR). The relatively hydrophilic nature of CTA favors osmotic transport. But its applications are limited because of its susceptibility to relatively low water permeability and flux [21].

The aim of this work is the investigation of chemical surface modification of commercial non-woven CTA-FO membrane using surface coating with o-phenylenediamine and benzoyl chloride which forming benzimdiazol compound on the membrane surface. The effect of hydrophilic substance concentrations on membrane characterization and performance was studied.

2. Materials and methods

2.1. Materials

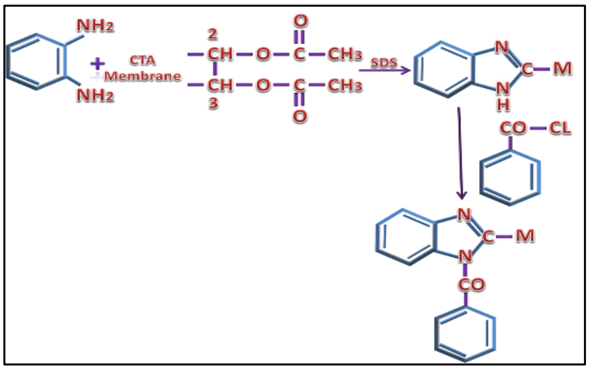
The membrane selected for this investigation is commercial non-woven FO membrane from HTI, where CTA casted onto a non-woven backing consists of polyester fibers. O-phenylenediamine, benzoyl chloride and isopropyl alcohol (IPA) were manufactured by Sigma Aldrich. The sodium chloride, and sodium dodecyl sulfate (SDS) were purchased from Fisher Scientific (Pittsburgh, PA).

2.2. Experimental methods

2.2.1. Membrane coating

Prior to coating of membrane, it soaked in IPA at room temperature to wet out the pore structure. The IPA was then rinsed out by washing the membrane three times with distilled water, and the membranes preserved by storing in distilled water at 5 ºC.
The coating step proceeded at room temperature and performed in only one side of the membrane. The membrane soaked in phenylendiamine solution at concentrations ranging from 0 to 1 g/l for 30 minutes in the presence of 0.1% SDS as a catalyst [28], then the membrane removed from this solution and air dried. After that, the membrane soaked in a solution of benzoyl chloride in hexane with a concentration ranging from 0 to 1g/l for 30 minutes. Finally, the modified membranes washed with water for 24 h, and air dried.

2-aryl benzimidazole was synthesized in aqueous media through reaction of o-phenylenediamine with ortho ester in presence of sodium dodecyl sulphate as a catalyst [28], the mechanism of reaction on membrane surface is shown in the following scheme:



Scheme of reaction

2.2.2. FO Experimental set-up

The bench scale system, as described in our previous work [29], consists of a membrane cell having two parallel channels 55 mm long, 29 mm wide, and 1.4 mm deep and the effective membrane surface area is 56 cm^2. A schematic drawing of the designed system is illustrated in Figure (1). Feed and DS re-circulated from their respective tanks and back to the tanks using a piston dosing pump. The DS and FS flow counter- currently in each channel on both sides of the membrane. Osmotic flux tests carried out with the membrane oriented as the active layer faces the draw solution. The DS tank placed on an analytical balance (Vibra, Pine Brook, NJ), and the rate of DS weight change recorded for water flux calculation through the membrane. The conductivity meter Myronn L Ultrameter used for TDS measurements. In this system, distilled water was used as FS for evaluation of modified membrane performance, while, NaCl at different concentrations (0.5- 2M) was used as DS.

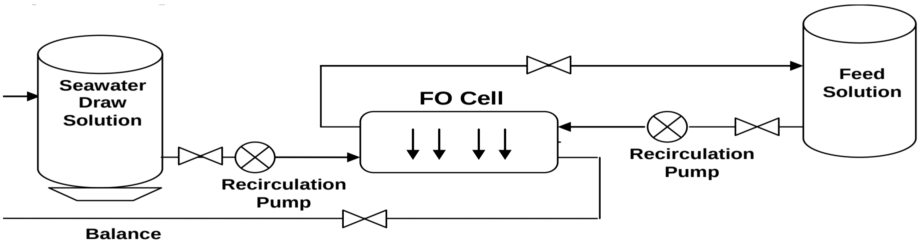


Fig. 1: Closed –Loop Bench- Scale Forward Osmosis Experimental.

2.3. Characterization of modified FO membranes

2.3.1. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the morphology of the FO membranes with and without chemical modification; however samples of membranes were coated with gold to provide electrical conductivity. The cross sections of membranes were taken on a JEOL 5410 scanning electron microscope (SEM) which was operating at 10 kV. Where, significant views of surfaces were recorded.

2.3.2. FO membrane chemical structure

FTIR (Fourier transform infrared spectroscopy) spectroscope (JASCO FTIR-6100) spectrophotometer over the range of 700–4000 cm^{-1} in the attenuated total reflectance (ATR) mode source was applied to study the chemical changes on the membrane surface before and after chemical modification. Prior to the measurements, the samples were dried under vacuum at 75ºC for 24 hours.

2.3.3. FO membrane water uptake and porosity

Water uptake rate and porosity of modified FO membranes were determined by measuring the change in weight after hydration. The membrane was first soaked in deionized water at ambient temperature for 24 h. Then the membrane was weighed quickly after wiping the surface using filter paper to determine the weight of wetted membrane (W_w). After that, the wet membranes were placed in an air-circulating oven at 80˚C for 24 h to be completely dried and finally, the dried membranes were weighed (W_d).
The percentage of water uptake was calculated by using the following equation (Lai and Chen, [30]).

$$\text{Water uptake } \% = (W_W - W_d)/W_d \times 100 \qquad (1)$$

The porosity of membranes was calculated using the following equation (Zheng et al. [31]):
$$P\ \% = (W_W - W_d)/V \times 100$$

Where P is the membrane porosity; W_w and W_d are the weights of wet and dry membranes (g), respectively; V= A*t where A is the membrane surface area (cm^2) and t is the membrane thickness (cm).

2.4. Performance of modified FO membranes

The effect of various coating concentration on the membrane performance compared with virgin membrane was investigated, these include measuring of water and reverse solute flux across the membrane. In addition, the effect of different draw solute concentrations of (0.5 to 2 M) using modified FO membrane prepared at optimum conditions on membrane performance was studied.

3. Results and discussions

3.1. Membrane characterization

3.1.1. Membrane surface morphology

Morphological observations of uncoated and coated membranes at different coating material concentrations (0-1g/l) are displayed in Figure (2). With increasing of coating materials concentrations the thin layer thickness slightly increased while the membrane porosity gradually increased till 0.75 g/l. With further increase in coating materials concentrations (1g/l), the thin layer become thicker due to the accumulation of coating materials at the membrane surface.

3.1.2. FTIR spectra

Figure (3) and Table (1) illustrate the changes in chemical structure of surface modified NW membranes as compared with virgin one by ATR-FTIR. For the original CTA membrane, the characteristic absorption broad band observed between 3,344 and 3,600 cm^{-1} range which is OH stretching vibrations. This is due to the overlapping of the band associated with the hydroxyl groups in cellulose esters with the bands associated with OH stretching vibrations of the sorbet water molecules. The CH_2 bending, CH_3, and CH_2 stretching vibration of aliphatic group appeared at 3340 cm^{-1} and at 2903 and 2884 cm^{-1} respectively. Also, the represented characteristics peaks of cellulose acetate acetyl groups showed spectra at 1774 cm^{-1} (–C=O), 1405 cm^{-1} (CH_3) and 1273 cm^{-1} (C-O) [32] & [33].
While, with increasing of coating concentration the broad band of OH converted to sharp band, where there are a disappearance of CH_2 bending at 3340 cm^{-1} and appearance of CH aromatic group at wave length 3026 cm^{-1} for all coating concentrations. The peak of CH_3 group at 2960 cm^{-1} disappeared at coating concentration ranged from 0.25 to 0.75 g/l then it appeared again at coating concentration of 1g/l. At concentration of 0.75 g/l there are new peaks at 3000 to 2375 cm^{-1} and 1697 to 1546 cm^{-1} which characterized by the presence of hydrophilic function groups NH_2, NH and NH_4 respectively. This may be referred to the formation of imidiazol compound [34], [35] & [36].
At higher concentration of 1 g/l, the benzoyl chloride (hydrophobic compound) peaks for C-Cl at 811,776,665 appeared [37].

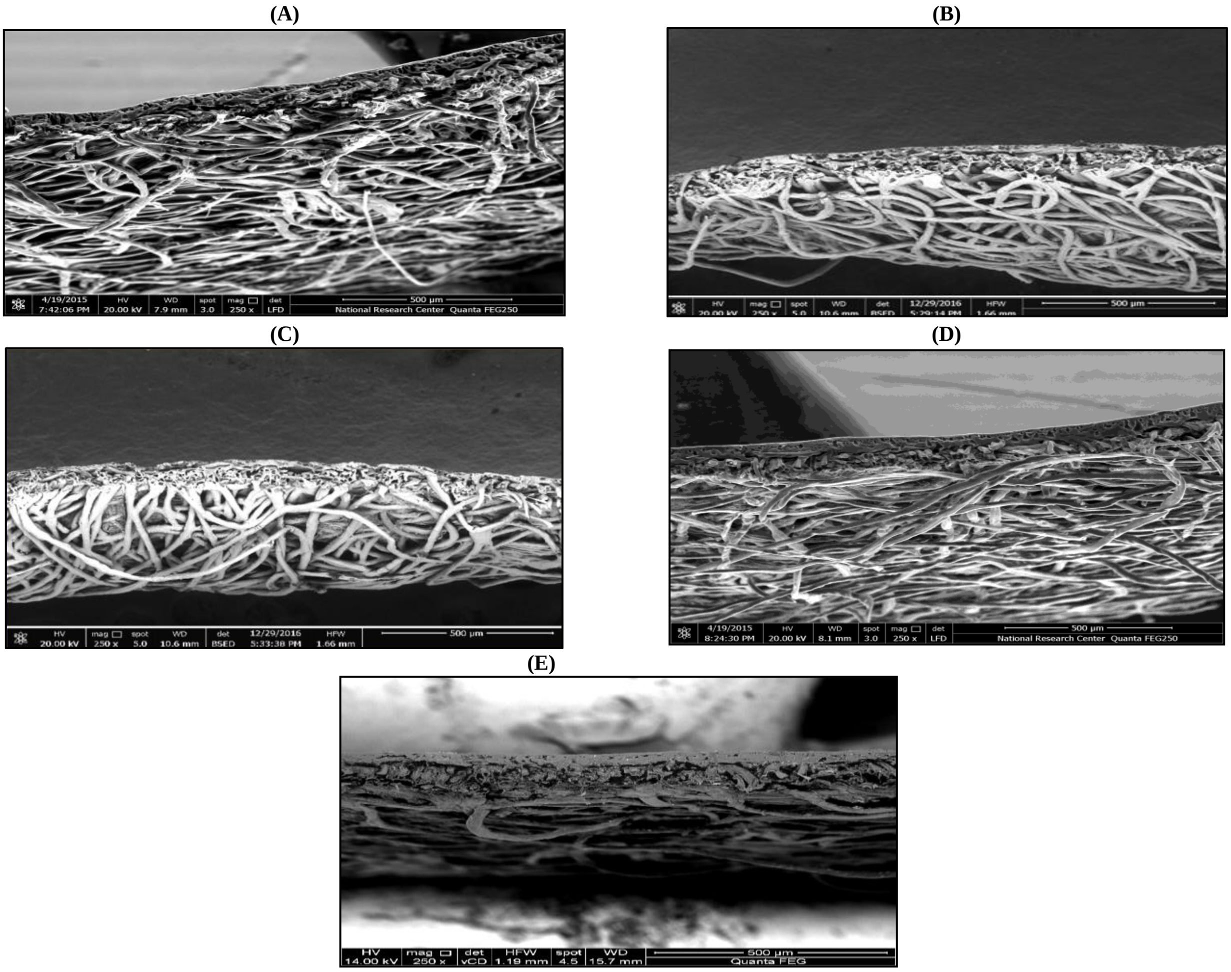


Fig. 2: Cross section morphology of uncoated and coated membranes at different coating material concentrations; (a): 0 g/l, (b): 0.25 g/l, (c): 0.5 g/l, (d): 0.75 g/l & (e): 1 g/l.

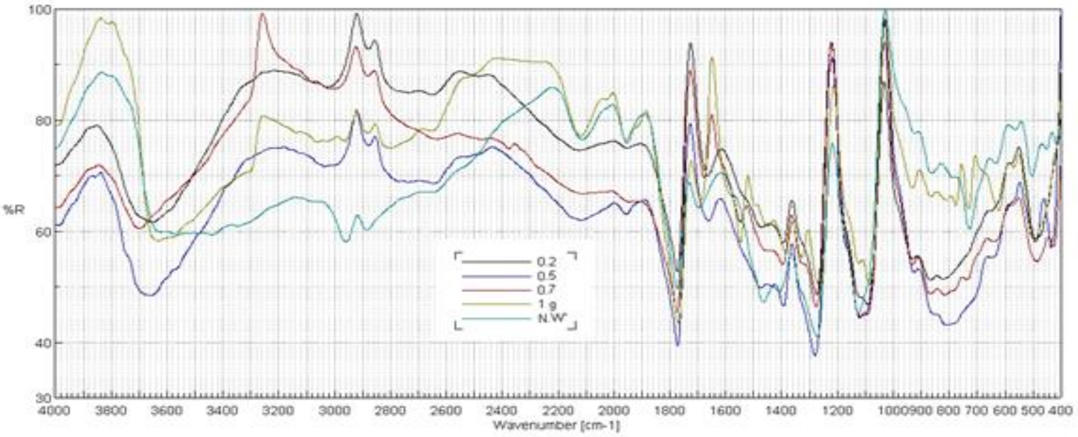


Fig. 3: FTIR of Commercial NW CTA and Surface Modified NW Membrane with Different Coated Material Concentrations.

Table 1: Function Groups for Different Coated Material Concentrations

Function group	Coating concentration (g/l)				
Wave length (cm^{-1})	0	0.25	0.5	0.75	1
3600-3344	OH	----	-----	-----	----
3600	----	OH	OH	OH	OH
3439	CH_2 bending	---	----	----	-----
3026	---	CH aromatic	CH aromatic	CH aromatic	CH aromatic
2960	CH_3,	----	----	------	CH_3
2884	CH_2	CH_2	CH_2	CH_2	CH_2
2732-2500	----	OH	OH	-----	OH
2651	------	C-N	----	-----	C—N
2632-2644	-----	-----	C=N	C=N	-----
3000-2375	----	----	-----	NH,NH_2,& NH^+_4	-------
2117-2278	-------	------	------	------	C ≡ C
2265	-------	------	-----	------	C ≡ N
1774	C=O	C=O	C=O	C=O	C=O
1697	C=C	C=C	C=C	C=C	C=C
1546	------	-----	-----	Benzimidiazol (CN)	Benzimidiazol
1470	------	C=C-CH_3	C=C-CH_3	------	------
1396-1385	---------	COOH	COOH	COOH	COOH
1327	------	C-CN	C-CN	C-CN	C-CN
1273	C-O	C-O	C- O	C-O	C- O
924	C-C	C-C	C-C	C-C	C-C
811,776,665	-------	------	-----	------	Benzoylchloride(Hydrophobic)

It is clear that at 0.75 g/l concentration, the coated membrane became more hydrophilic due to the formation of more than functional groups which confirm the formation of hydrophilic membrane [38, 39, 40 & 41].

3.1.3. Water uptake and porosity of surface FO modified membrane

Figure (4) shows water uptake of virgin and surface coated membranes at different coating material concentrations. It is demonstrated that membrane surface modification gradually increase water uptake from 6 % for virgin one to reach maximum of 62.3 % at 0.75 g/l concentration. This is due to the increasing of membrane hydrophilicty by formation of aminated cellulose triacetate on the membrane surface. While by further increase of coating concentration up to 1 g/l, the water uptake suddenly decrease to 22%, this can attributed to the accumulation of benzoyl chloride on the membrane surface which considered as hydrophobic compound as confirmed by FTIR analysis.

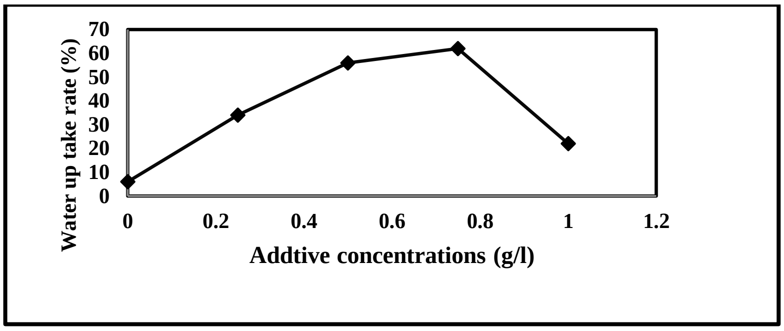


Fig. 4: Effect of Additive Concentration on Water up Take Rate.

The above result is in agreement with Jason et al. [42] and Han et al., [43], they reported that the surface coating with phenylendiamin plays a positive role in the preparation of the selective layer on the membrane surface, which is realized by formation of hydrophilic smooth layer with smaller and narrower pore size distribution, as well as enhancing the hydrophilicity of the pore-wall inside the substrate layer. Moreover, Albrecht et al., [34] and Trimpert et al., [36] reported that high contents of amine groups make the membranes more hydrophilic.

The effect of coating material concentration on the porosity of surface modified membranes are illustrated in Table (2).

Table 2: Coated Membranes Porosity

Coating Concentration (g/l)	Porosity (%)
0	55
0.25	77
0.5	80
0.75	85
1	60

It is obvious that the increasing of coating material concentration gradually increase porosity till 0.75 g/l, where it reaches to 85%. By increasing the concentration to 1 g/l, the porosity tend to decrease to 60%. This may be attributed to the blocking of surface pores by the accumulation of coating material on membrane surface as confirmed by membranes surface morphologies. This result agree with literature [21], [38], [42] & [44].

3.2. Membrane performance:

3.2.1. Water and reverse salt flux at different additive concentrations

The impact of different coating concentrations on the performance of modified commercial membranes was illustrated in figures (5 & 6). It was observed that the flux increased with increasing coating concentrations from 0 to 0.75 g/l then decreases with further increasing of coating material. Also, reverse salt flux gradually decreased with increasing of coating concentration till 0.5 g/l then it slightly decreased with further increasing in coating concentration.

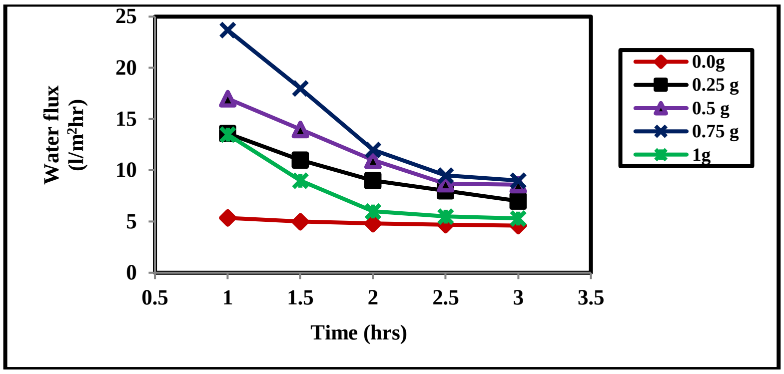


Fig. 5: Effect of Time on Water Flux for Modified Nonwoven Membrane at Different Additive Concentrations Using Distilled Water FS and 1 M Nacl DS.

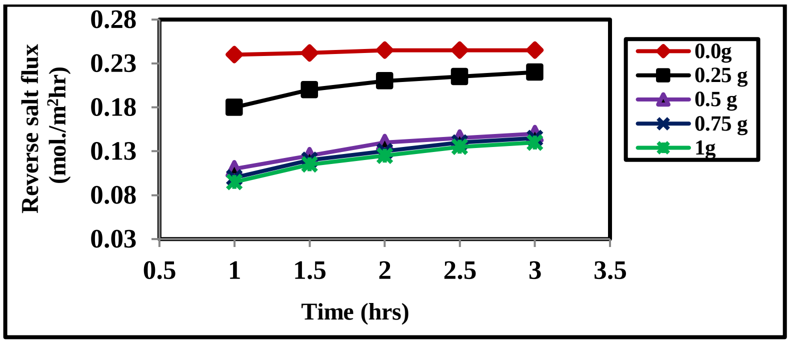


Fig. 6: Effect of Time on Reverse Salt Flux for Modified Nonwoven Membrane at Different Additive Concentrations Using Distilled Water FS and 1 M Nacl DS.

This may be attributed to the increasing of membrane porosity and hydrohflicity by increasing of coating materials as confirmed by SEM, FTIR and water uptake rate investigation. The improvement of water flux by increasing of membrane hydrohflicity can be explained by Jason et al., [42] who revere that increasing of wetted porosity promotes water transport through the support layer and to the interior interface, also promotes salt diffusion through the support layer after it diffuses across the selective polyamide layer. Also, as illustrated previously, the decline of membrane performance by increasing coating concentration above 0.75 g/l can be attributed to the accumulation of coating material on membrane surface that leading to surface pores blocking as confirmed by membranes surface morphologies. This is in good agreement with literature [21], [38], [42] & [44].

In addition, it was observed that high flux value was obtained in the beginning of operation, then it decreased gradually by increasing of permeation time till 3 hours, this can be attributed to dilution of DS with time that reducing osmotic pressure difference. In addition, the flux decline with time behavior was explained by Zhao and Mulcahy [45], they illustrated that the two effects of internal concentration polarization (ICP) and membrane fouling decrease osmotic water flux and increase mass transfer resistance by the concentrating of feed solution due to water permeation from feed to draw side and reverse salt diffusion from draw to feed side [46].

3.2.2. Water and reverse salt flux at different draw solute concentrations:

The effect of draw solution concentration on the performance of optimum modified membrane at 0.75 g/l coated concentration was studied. Figure (7) illustrates water flux and reverse solute flux at various NaCl DS concentration ranging from 0.25 to 2 M using distilled water as FS. It is clear that both water flux and reverse solute flux were increased as DS concentration increased up to 1.5 M. By increasing DS concentration to 2 M, a slight increase in membrane performance was observed, where water flux increased to 45 l/m^{2}hr and reverse solute flux reached to 0.32 mol/m^{2}hr.

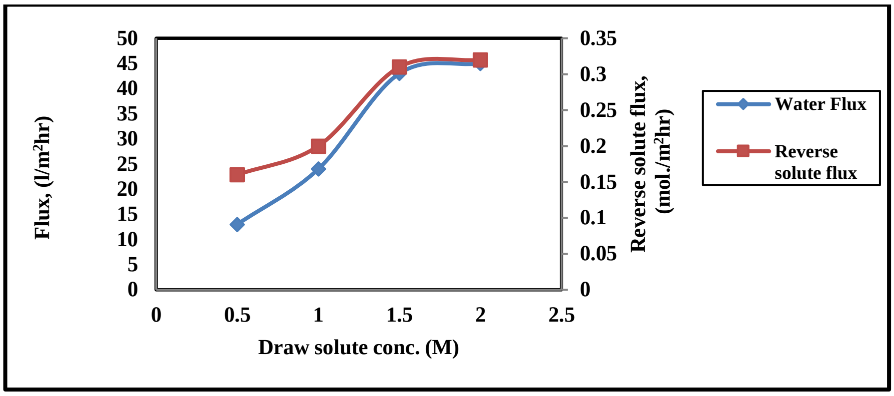


Fig. 7: Effect of Draw Solute Concentration on Water Flux and Reverse Solutes Using 0.75 G/L Coated Membrane and Distilled Water as FS.

Arkhangelsky et al. [46] indicated that water flux did not increased linear by increasing of DS concentration. At higher DS concentrations, accumulation of salt ions within the membrane support layer that facing the DS increased ICP and reduced water flux [47], [48], [50]. In addition, the two effects of ICP and membrane fouling decreased osmotic water flux and increased mass transfer resistance as the feed water becomes more concentrated during FO permeation time [51].

4. Conclusions

In this work chemical surface coating modification of commercial nonwoven forward-osmosis membrane using PBI was investigated. The effect of coating material concentration on the membrane characterization and performance was studied in the range from 0 to 1 g/l. It was found that increasing of coating concentration gradually increased both hydrophilicity and porosity till 0.75 g/l, where they reach to 85%. By increasing the concentration to 1 g/l, the porosity tend to decrease to 60%. Moreover, water uptake increased from 6 % for virgin one to reach maximum of 62.3 % at 0.75 g/l concentration then suddenly decreased to 22% at 1 g/l. In addition, the flux increased with increasing coating concentrations from 5.4 l/m^{2}hr for virgin membrane to optimum value of about 24 l/m^{2}hr at 0.75 g/l then decreased with further addition. Also, reverse salt flux gradually decreased with increasing of coating concentration till 0.5 g/l then it slightly decreased with further increasing in coating concentration. Finally, the performance of optimum modified membrane (0.75 g/l) was tested at different NaCl draw solute concentrations; it was found that water flux and reverse solute flux were increased as DS concentration increased up to 1.5 M. By increasing DS concentration to 2 M, a slight increase in membrane performance was observed, where water flux increased to 45 l/m^{2}hr and reverse solute flux reached to 0.32 mol. /m^{2}hr.

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