

## ORIGINAL ARTICLES

### Polysulfone/Polyvinyl alcohol thin film nano-composite membranes: synthesis, characterization and application for desalination of saline groundwater

Abdel-hameed M. El-Aassar

*Desalination unit, Hydro geochemistry Dept., Desert Research Center, El-Mataryia, Cairo, Egypt.*

---

#### ABSTRACT

The aim of the present work is synthesis, characterization and performance evaluation of modified Polysulfone/ polyvinyl alcohol (PS/PVA) thin film composite (TFC) membranes. The modification was carried out for PS support layer and/or crosslinked PVA barrier layer using titanium dioxide (TiO<sub>2</sub>) nanoparticles. Gultaraldehyde (GA) was used as a cross-linker of PVA. The synthesized thin film composite (TFC) or thin film nanocomposite (TFNC) membranes were characterized by measuring the contact angle, ATR-FTIR spectroscopy and scanning electron microscopy (SEM). The membranes performance included permeate flux (L.m<sup>-2</sup>.hr<sup>-1</sup>) and salt rejection (%) was evaluated as a function of synthesis and operation conditions. The obtained results showed that the membranes prepared from PS coated with TiO<sub>2</sub> (0.25 wt. %) for 30 min immersing time, 0.1wt. % PVA crosslinked with GA solution concentration of (3% wt. %) and cured at a temperature of 75±2°C for 60 min gave the optimum performance. Also, the modification of PS-PVA/TFC membranes using TiO<sub>2</sub> nanoparticles improved permeate flux from 9.32 to 11.56 (L.m<sup>-2</sup>.hr<sup>-1</sup>) with a slight increase in salt rejection from 76.79 to 78%. The salt rejection percent increased with increasing the cross-linker concentration, curing time and temperature as well as applied pressure and decreased with the feed concentration and vice versa in case of permeate flux for such factors except applied pressure. The desalination of two groundwater samples (brackish and saline) were performed using the best synthesized TFNC membrane to study the behavior of hypothetical salts during the desalination process.

**Key words:** *Polysulfone-polyvinyl alcohol; thin-film composite; titanium dioxide, characterization; reverse osmosis performance.*

---

#### Introduction

In the past decades a wide variety of new achievements in thin-film composite (TFC) membrane development has been reported around the world, although only some of TFC membranes have reached commercial status. In the preparation of TFC membranes, attention has always been focused on the formation of dense but ultra-thin skin layer on top of a micro-porous support membrane. Among many processes, dip-coating and interfacial polymerization methods have been widely used (Cadotte, 1981; Cadotte *et al.*, 1981; Kurihara *et al.*, 1982; Rozelle *et al.*, 1977).

Polyvinyl alcohol (PVA), a water-soluble biodegradable polymer, with its highly hydrophilic character, good film-forming properties and outstanding physical and chemical stability, is a kind of excellent membrane material for preparation of a hydrophilic membrane. In particular, PVA polymer seems attractive for the preparation of membranes because of its low cost, commercial availability, high water permeability and good film-forming properties. It is also known that PVA is little affected by grease, hydrocarbons, and animal or vegetable oils; it has outstanding physical and chemical stability against organic solvents. PVA is readily soluble in water and no other solvent is necessary. Thus, PVA is being used as a selective skin layer in the formation of thin-film composite membranes (Koops and Smolders 1991). To make stable PVA films or films with a desired salt selectivity, PVA can be cross-linked through a variety of methods (Bolto, 2009). There are many past studies of PVA membranes developed for reverse osmosis (Bezuidenhout *et al.*, 1998; Lang *et al.*, 1994; Lang *et al.*, 1995; Lang *et al.*, 1996; Yang 1995; Immelman *et al.*, 1993; Sanderson 1993; Sanderson *et al.*, 1993; Chu and Yang 1992) and nanofiltration (Jegal and Lee 1999; Jegal *et al.*, 2000; Jegal *et al.*, 2001). Most of these membranes give relatively low flux and rejection, which might be caused by unsuitable coating methods, improper cross-linking reaction, or excessive coating layer thickness. These past attempts use the dip-coating method followed by surface cross-linking to prepare PVA membranes, which leads to relatively thick and minimally cross-linked PVA layers (Gohil and Ray 2009).

Polysulfone (PS) is one of the most extensively applied ultrafiltration (UF) membrane materials in industry area for mechanical strength, compaction-resistance, chemical stability, thermal resistance and in wide pH value

range application (Yang and Wang 2006). But its hydrophobic nature is also well known, which results in the adsorption and deposition of hydrophobic solute on the membrane surface (Ramesh and Gaikar 2001). The adsorption and deposition can cause severe membrane fouling due to the formation of thick gel-layer and the block of the pores, which will result in the flux decline and short-life of membrane. Although the modification of PS have been widely explored such as the modification of membrane surface (Gancarz *et al.*, 2002) and membrane material (Yoo *et al.*, 2003), the problems such as tradeoff between permeability and selectivity, the process complexity, the manufacturing costs and stability still remain to be unsolved.

It is well known that nanoparticles improve the capabilities of polymers in a certain extent because of their small sizes, large ratio surface areas and strong activities (Cao *et al.*, 2006; Bottino *et al.*, 2000; Bottino *et al.*, 2001; Hester *et al.*, 2002; Li and Lu 2001; Wang *et al.*, 2002). Among the introduced nanoparticles to polymer membranes, there is titanium dioxide (TiO<sub>2</sub>). TiO<sub>2</sub> has been the focus of numerous investigations for innocuity, resisting and decomposing bacteria and UV-proof and super hydrophilicity (Cao *et al.*, 2006) in recent years. Therefore, it has been applied to a variety of problems of environmental interest in addition to water and air purification (Bottino *et al.*, 2000). Its nanoparticles can not only improve the hydrophilicity of membranes to enhance the flux but also kill bacteria and mitigate the fouling of RO membranes (Cao *et al.*, 2006, Bae and Tak 2005; Kim *et al.*, 2003; Li *et al.*, 2004).

In this study, PS/PVA-TiO<sub>2</sub> TFNC membranes were synthesized via dip coating technique. The improving of PS support layer and/or PVA barrier layer was carried out using TiO<sub>2</sub> nanoparticles as a trail to enhance the RO performance. Synthesized membranes were characterized to elucidate and optimize the preparation conditions of synthesized membranes. The synthesized membranes were characterized using contact angle measurements, ATR-FTIR spectroscopy and SEM. Also, the RO performance of synthesized membranes for water desalination was evaluated through studying the effect of different parameters of preparation conditions, feed water salinity and applied pressure. Also, attempts for desalination of natural brackish and saline water were performed using the best membrane to study the behavior of hypothetical salts during the desalination process.

## 2. Experimental:

### 2.1 Materials and reagents:

Asymmetric polysulfone (PS) support membrane on non-woven polyester fabric was supplied from Dow Water & Process Solutions (Edina, MN). Polyvinyl alcohol (99+ % hydrolyzed, with MW 146,000-186,000) was used as received from Sigma-Aldrich (St. Louis, MO). Gultaraldehyde (GA), cross-linking agent, was obtained as a 50% (w/w) aqueous solution, Aldrich Chemical Co., USA. Hydrochloric acid 1N standard solution was used as received from Acros, New Jersey, USA. Other chemicals were reagent grades and were used without any further purification. Deionized (DI) water was generated by a Milli-Q Advantage A10 vacuum purification system (Millipore, Billerica, MA).

Acrylic plastic plates (8 in x 11 in x 0.24 in) were used to support the PS membranes during TFC membranes preparation. Additionally, plastic frames (inner size: 6 in x 9 in) were cut from these plates. Rubber gaskets having the same size of the plastic frames were purchased from Advanced Gasket & Supply (Fort Worth, TX, USA).

### 2.2 Preparation of thin-film composite membranes:

PS/PVA thin film composite or PA/PVA-TiO<sub>2</sub> thin film nano-composite membranes were synthesized via dip-coating technique as follows: PS support membranes with dimension of 20x20 cm were immersed in DI water for at least one hour. For modified PS membrane, PS membrane was immersed in 3L of pre-dispersed aqueous solutions with different concentrations of TiO<sub>2</sub> nanoparticles with vigorous stirring and sonication. After certain time, PS membranes were removed from the solution and washed by DI water several times.

Neat PS or modified PS-TiO<sub>2</sub> membranes were positioned on a plastic plate. A rubber gasket and a plastic frame were placed on top of the support membrane, and binder clips were used to hold the plate-membrane-gasket-frame stack together. Aqueous PVA solution of 0.1 wt. % concentration was prepared by dissolving a definite weight of the polymer in DI water with heating at 90°C until obtaining homogenous solution. PVA solutions were cooled to ambient temperature (25°C). GA solution as a cross-linking agent was added to PVA solution in presence of HCl as a catalyst to produce crosslinked PVA casting solution, with stirring for 1hr. PVA casting solution with or without TiO<sub>2</sub> nanoparticles was poured into the frame and allowed to contact the PS membrane with continuous shaking using rocker (speed 4) for 15 min before draining the excess PVA solution. This residence time allowed PVA to penetrate into the pores of the porous PS support layer. The frame and gasket were disassembled and the PS wet membranes with PVA were dried in vertical position for 15 min at ambient temperature. This process was repeated two times to avoid any defects in the PVA barrier layer. Finally

the prepared membranes were heated at certain temperature for adequate time to complete curing and immersed in DI water until characterized or used in cross flow experiments.

### 2.3 Characterization of polyamide-thin film composite (PA-TFC) membranes:

Oil-in-water contact angle analysis was performed using a Ramé-Hart Model 200-F1 Standard Goniometer with DROP image Standard Edition 2.4 software (Ramé-Hart Instrument Co., Netcong, NJ). A strip of membrane was mounted in a sample holder with active barrier layer side facing down and was placed in DI water environment. An n-decane oil droplet was dispensed onto the bottom side of the membrane strip from a Gilmont Instruments 0.2 ml micrometer syringe (Cole-Parmer Instrument Co., Vernon Hills, IL) with a hooked Hamilton N732 needle (OD: 0.009 in, Hamilton Co., Reno, NV). Contact angles were measured through the water phase, and the reported contact angle is the average value of the left and right side contact angles, at least three oil droplets placed at different spots in each sample (any membrane was measured using 3 samples). A smaller angle indicates a more hydrophilic surface.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the chemical structure of the synthesized TFC membranes. A Thermo Nicolet Nexus 470 FTIR with an Avatar Smart Miracle ATR accessory and a ZnSe crystal (Thermo Fisher Scientific Inc., Waltham, MA) was used. Spectra were collected in air, in the mid-infrared region ( $600\text{-}4000\text{ cm}^{-1}$ ), using 128 scans at resolution 4. After each measurement, a background spectrum was obtained using polysulfone membrane and subtracted from that of the membrane to remove any atmospheric absorbance peaks.

Also, PS/PVA-TFC and PS/PVA-TiO<sub>2</sub> TFNC synthesized membrane surface and cross-section morphology was characterized by scanning electron microscopy (SEM, Zeiss Supra 40 VP, Carl Zeiss NTS, Peabody, MA). High voltage ETH mode was used and the voltage was set to 5 kV. An In Lens detector was selected, and the working distance was between 5 and 7 mm. Samples were prepared by peeling away the no-woven polyester backing fabric and fracturing the remaining polysulfone and PVA layers after immersion in liquid nitrogen. A Cressington 208 Bench-top Sputter Coater (Cressington Scientific Instruments LTD., Watford, England) having a Pt/Pd metal target was used to coat the samples. The coating thickness was set 10 nm to ensure adequate sample surface conductivity.

### 2.4 Reverse Osmosis performance of synthesized membranes:

The reverse osmosis performance of the synthesized PVA-TFC membranes was evaluated through measuring both permeate flux ( $\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ ) and salt rejection (%). Permeate flux and salt rejection were measured using crossflow filtration using aqueous feed solution contained 2000 ppm NaCl with pH range  $7\pm 0.2$  at  $25^\circ\text{C}$ . The flow rate was 1 gallon per minute and the applied pressure was 225 psi (15.5 bar). All flux and salt rejection (%) measurements were evaluated after 30 min from the starting the crossflow experiment to ensure that the filtration process had reached steady state.

The permeate flux ( $J_w$ ) through a membrane area ( $A$ ) was calculated as the volume ( $\Delta V$ ) collected during a time period  $\Delta t$  (Lonsdal *et al.*, 1965):  $J_w = \Delta V / A \cdot \Delta t$

Also, the salt rejection ( $R_s$  %) was calculated by measuring the electric conductivity of both feed and permeate solutions using an Oakton CON 11 conductivity meter (Cole-Parmer Instrument Co., Vernon Hills, IL). The salt rejection percent ( $R_s$  %) was calculated as follows:

$$R_s\% = (C_f - C_p / C_f) \times 100$$

Where,  $C_f$  and  $C_p$  are the concentrations of the feed and permeate water (product), respectively.

### 2.5 Water samples and analysis:

Two groundwater were collected and subjected to chemical analyses according to the methods adopted by U.S. Geological Survey, Rainwater and Thatcher 1960, Fishman and Friedman 1985, including the determination of total dissolved solids (TDS), EC, soluble cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) and anions ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ ). The samples were kept at ambient temperature until the time of use.

## Results and Discussion

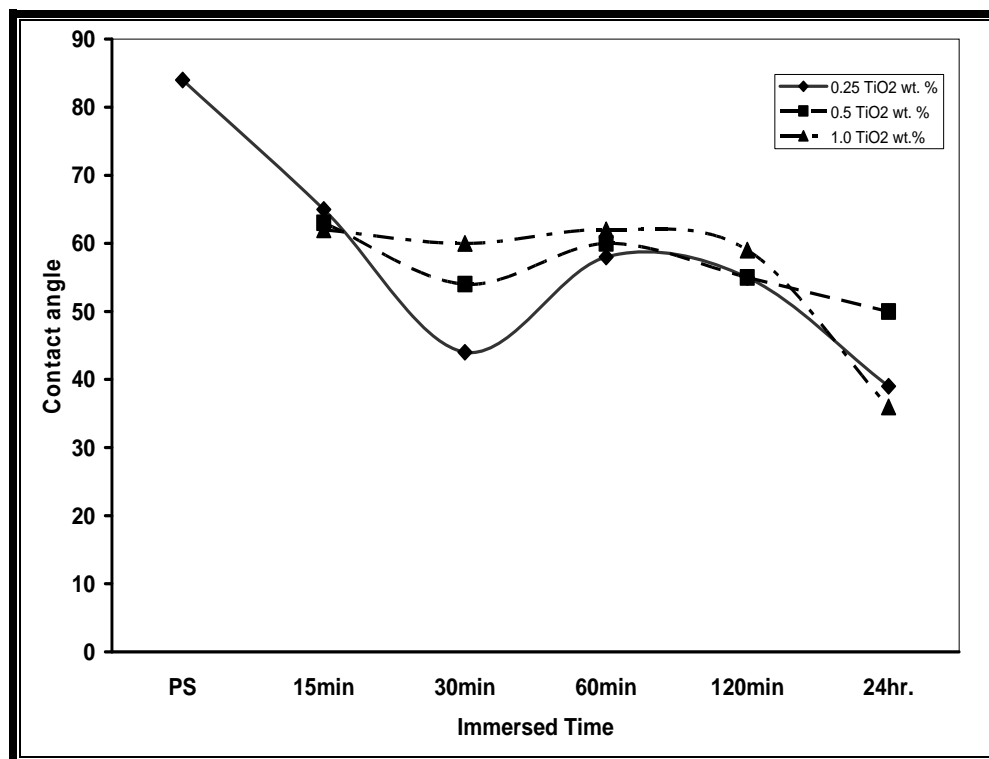
### 3.1 Synthesis and characterization of the synthesized membrane:

To optimize the synthesis conditions of PS/PVA-TFC and PS/PVA-TiO<sub>2</sub>-TFNC membranes, the effect of different parameters on the synthesized membranes characteristics was studied.

Figure (1) shows the contact angle of PS support layer immersed in different concentrations of TiO<sub>2</sub> solution for different times. Neat PS membrane showed the highest contact angle of  $85^\circ$ . In general, the contact

angle decreased with ex-situ coating with TiO<sub>2</sub> nanoparticles indicating the enhancement in hydrophilicity of the membranes. The best condition to improve PS layer was that used lowest concentration of TiO<sub>2</sub> nanoparticles (0.25 wt. %) for shortest time (30 min.) that gave low contact angle (44°). In case of using high concentration of TiO<sub>2</sub> nanoparticles, higher contact angles were obtained; this can be explained by that increasing nanoparticles concentration increase the possibility of aggregation of TiO<sub>2</sub> nanoparticles.

Also, the contact angles of synthesized PS/PVA-TFC using different concentrations of both cross-linker and TiO<sub>2</sub> nanoparticles are shown in table (1). As the concentration of GA solution increases from 1 to 3wt. %, the contact angle increases from 36.3 to 68°. The selected GA concentration was 3 wt. %. By modification PVA barrier layer using in-situ TiO<sub>2</sub> nanoparticles, the hydrophilicity of synthesized membranes increases and the contact angle decreases from 68 to 56.4° using 1 wt. % of TiO<sub>2</sub> nanoparticles. By further increase in the concentration of TiO<sub>2</sub>, the possibility of aggregation of TiO<sub>2</sub> nanoparticles increases, so the hydrophilicity slightly decreases, i.e., the contact angle slightly increases.



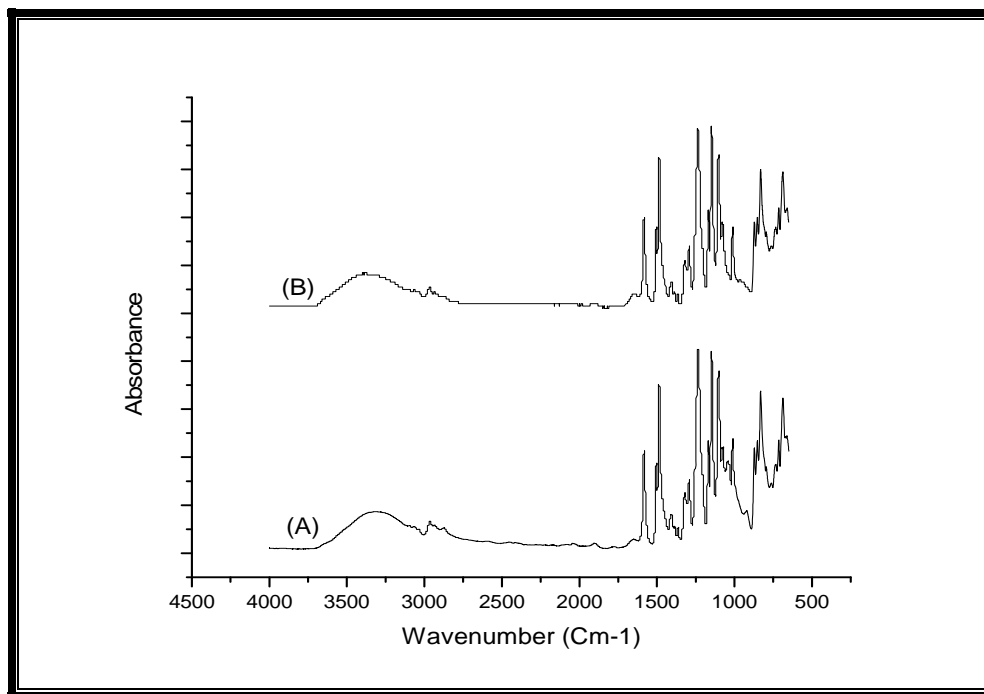
**Fig. 1:** Effect of TiO<sub>2</sub> concentration and its immersed time on contact angle of PS support layer.

**Table 1:** Effect of cross-linker concentration and TiO<sub>2</sub> concentration on contact angle of the barrier layer of synthesized TFC and TFNC membranes.

Membrane type	Cross-linker concentration (wt. %)	TiO <sub>2</sub> Concentration (wt. %)	Contact angle (°)
PS/PVA	1	-	36.3± 0.4
	2	-	61.6 ± 1
	3	-	68± 0.9
PS/PVA-TiO <sub>2</sub>	3	0.5	62± 1
		1	56.4 ± 0.4
		2	58± 1

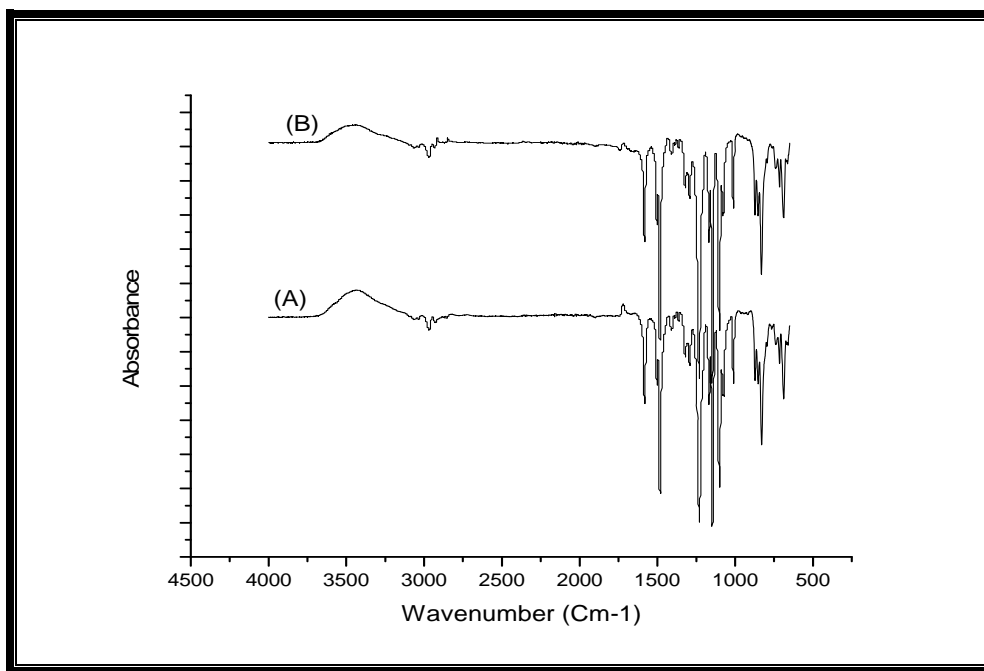
Also, four membranes included PS, PS-TiO<sub>2</sub>, PS/PVA-TFC and PS/PVA-TiO<sub>2</sub> TFNC membranes were chosen for studying characterization using ATR-FTIR, as shown in Figs. (2, 3). The purpose of FTIR spectroscopy is to examine the presence of functional groups present in the skin surface layer of membrane samples.

The spectrum of the PS membrane, Figure (2-a), shows peaks at 1587- 1487, 1324, 1294, 1235, 1150-1106 cm<sup>-1</sup> assigned to C-C, C-H, O=S=O (symmetric), C-O-C and O=S=O (asymmetric), respectively. Also, by doping TiO<sub>2</sub> nanoparticles with PS/PVA, no significant change was observed except a very small peak at 750 cm<sup>-1</sup>, as shown in Fig. (2-b).



**Fig. 2:** ATR-FTIR of (A) PS support layer, (B) PS-TiO<sub>2</sub> membrane.

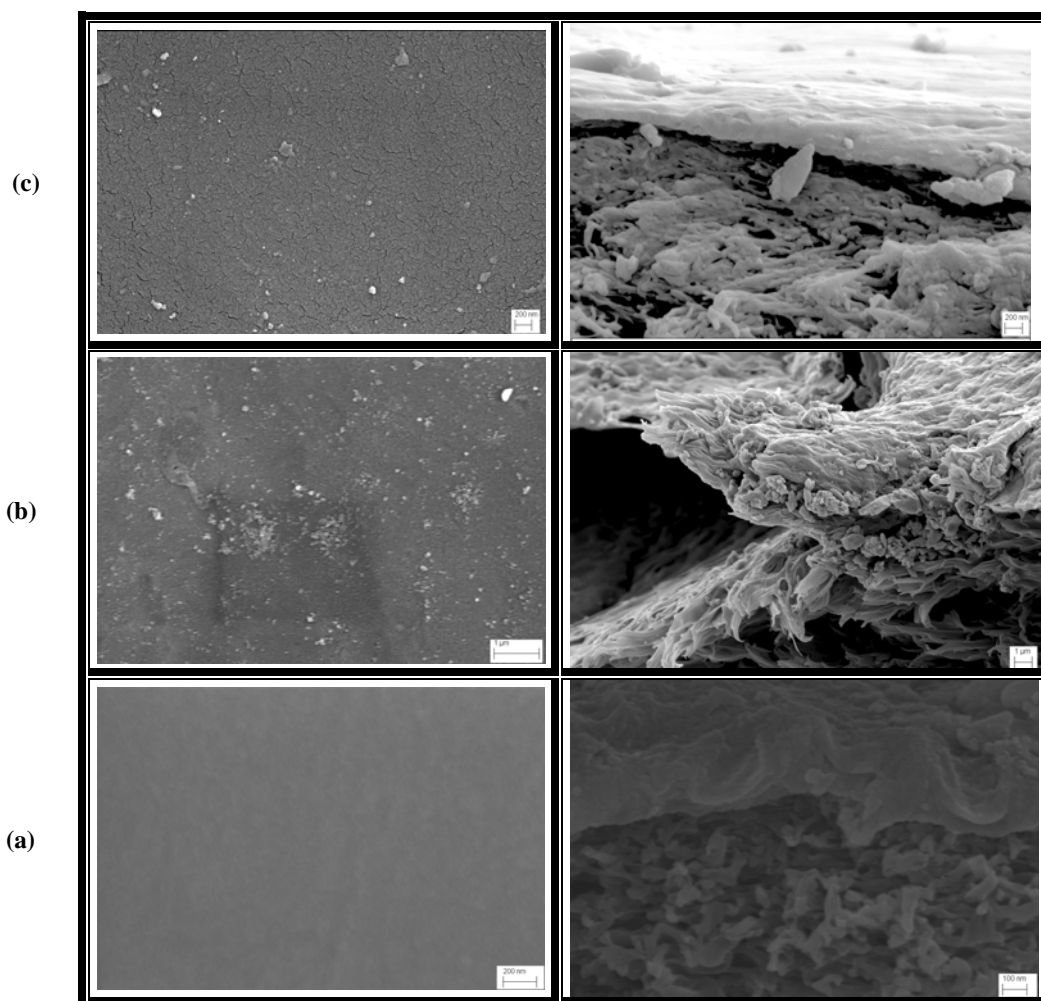
For PS/PVA-TFC membrane, the ATR-FTIR was studied using PS membrane as background, the spectrum shows the characteristic peaks of OH, C-H, C=O, CH<sub>2</sub> and CH<sub>3</sub>, and C-O at 3480, 3043, 1754, 1373-1519, 1051-1253cm<sup>-1</sup>, respectively, as shown in Fig. (3-a). Also, by doping TiO<sub>2</sub> nanoparticles with PS/PVA, no significant change was observed except a very small peak at 750 cm<sup>-1</sup>, as shown in Fig. (3-b).



**Fig. 3:** ATR-FTIR of (A) PS/PVA-TFC and (B) PS/PVA-TiO<sub>2</sub> TFNC membranes using PS as background.

Also, in order to investigate the morphology and confirm the formation of composite thin layer over the PS support, the surfaces and cross sections of PS and synthesized thin film composite membranes were

characterized using SEM, as shown in Fig. (4). The PVA barrier layer appeared as non-porous, but it is hard to discriminate from the polysulfone skin layer suggesting a good bond formed between the PS support and PVA barrier layer. From the SEM micrograph (4c), the thickness of PVA barrier layer was estimated usually to be about  $220\pm 40$ .



**Fig. 4:** SEM images of (a) PS support layer, (b) PS-TiO<sub>2</sub>, and (c) PS/PVA-TiO<sub>2</sub>-TFNC membrane; for both top surface (left) and cross section (right).

### 3.2. Reverse osmosis performance of the synthesized membranes:

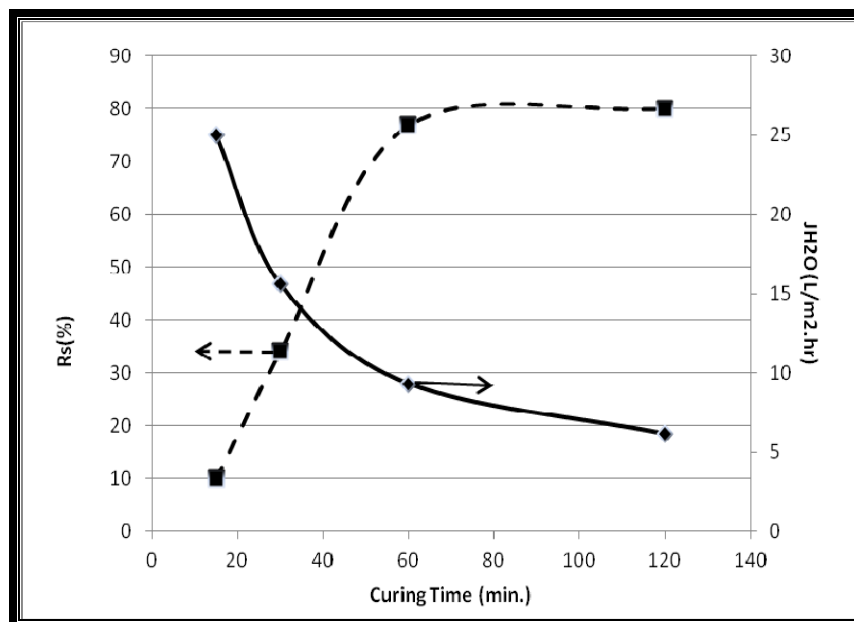
Several parameters are known to influence the salt rejection and permeate flux. These parameters include the membrane characteristics, operation conditions and feed solution (Bartels *et al.*, 2005).

The studied parameters included cross-linker concentration, curing time and temperature during the membrane formation as well as TiO<sub>2</sub> concentration in PVA barrier layer. The effect of these parameters on water flux and salt rejection are presented as follows: -

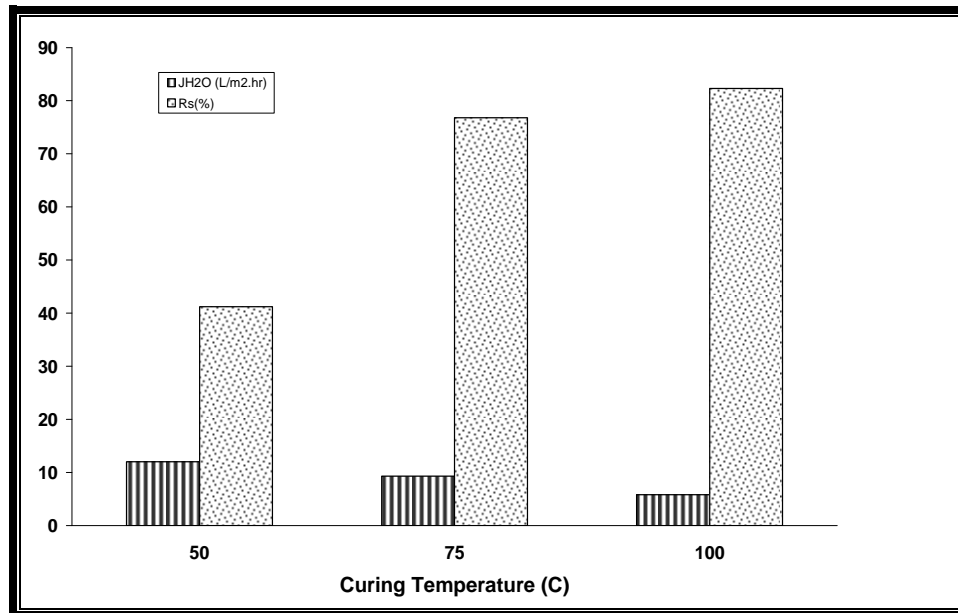
For low cross-linker concentration, there are high fluxes without any observed salt rejection (%) up to cross-linker concentration of 3wt. % which possesses the reasonable results of reverse osmosis performance. The permeation flux was (9.32 L/m<sup>2</sup>.hr) with salt rejection of (76.79%), so it was selected as the best GA concentration. Further increasing in GA concentration, the water flux sharply decreases.

It is well known in the membrane industry that the transport characteristic for a membrane can be controlled by adjusting the solvent evaporation temperature and oven exposure time which influence the rate of solvent evaporation leading to the formation of the pore structure (Joshi and Rao 1990). Therefore, the effects of both curing time (15-120min) and curing temperature (50-100°C) on reverse osmosis performance were studied, as shown in Figs. (5) and (6), respectively. Evidently, both of curing time and temperature have similar effect, i.e., increasing both of curing time and temperature increase salt rejection (%) with a decrease in water flux. The

increase of the curing temperature at fixed time leads to the formation of much smaller pores, which increases salt rejection efficiency and vice versa of water flux. In contrast, low evaporation temperature results in a membrane of high solvent content and the possibility of existence of large pores on the membrane becomes high; this leads to high water flux with low salt rejection.



**Fig. 5:** Effect of curing time on reverse osmosis performance of PS-PVA/TFC membrane using 2000 ppm feed NaCl solution and 15.5 bar applied pressure

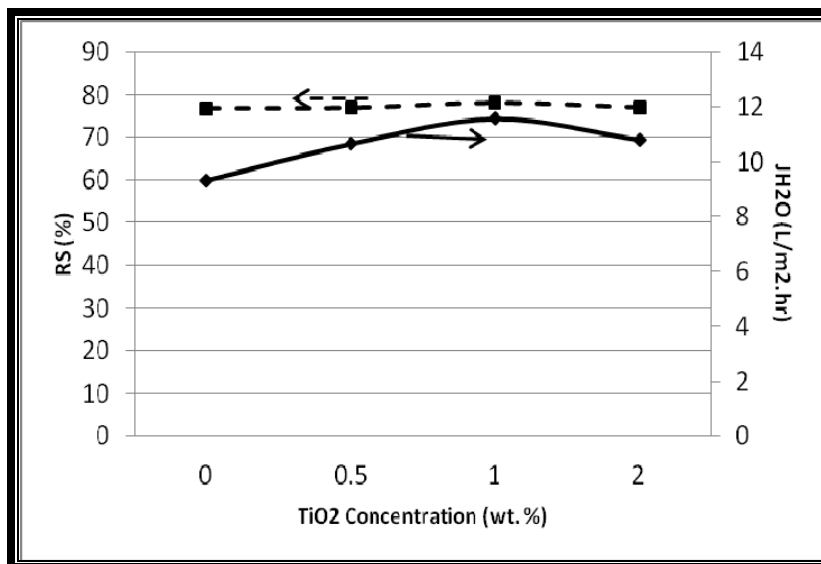


**Fig. 6:** Effect of curing temperature on reverse osmosis performance of PS-PVA/TFC membrane using 2000 ppm feed NaCl solution and 15.5 bar applied pressure.

A similar trend was noticed with respect to time of solvent evaporation. However, the increase in evaporation time at fixed temperature leads to a decrease in water flux with increasing salt rejection (%). This behavior can be explained on the basis that longer exposure time leads to more solvent loss (lower residual

solvent content), forms a denser structure and reduced the porosity in the membrane. So, the water flux decreases with increasing salt rejection (Mohamed and Al-Dossary 2003).

On the other hand, the effect of  $\text{TiO}_2$  nanoparticles concentration (0.5, 1, 2 wt. %) related to PVA concentration on barrier layer was studied, Fig. (7). It is obvious that as  $\text{TiO}_2$  concentration increases the water flux improves with a slight increase in salt rejection (%) up to  $\text{TiO}_2$  concentration of 1 wt. % which was considered as the best concentration. After that, any increase leads to a decrease in permeate flux; this may be due to the aggregation of  $\text{TiO}_2$  nanoparticles and decreasing of hydrophilicity.



**Fig. 7:** Effect of  $\text{TiO}_2$  concentration on reverse osmosis performance of PS-PVA/TFNC membrane using 2000 ppm feed NaCl solution and 15.5 bar applied pressure.

From the above studies, the membrane prepared from PS coated with  $\text{TiO}_2$  of 0.25 wt. % for 30 min, 0.1% PVA crosslinked with GA solution concentration of (3% wt. %) and cured at a temperature of  $75 \pm 2^\circ\text{C}$  for 60 min gave the optimum performance for neat PS/PVA TFC membranes. Also, this TFC membrane modified with 1 wt.% of  $\text{TiO}_2$  membrane possessed the best reverse osmosis performance, so, it was selected to evaluate the water desalination process. The study included the effect of feed water salinity and the applied pressure on membrane performance.

The effect of applied pressure onto  $J_{\text{H}_2\text{O}}$  and  $R_s$  was studied for the selected synthesized TFNC membrane, as shown in Table (2). It can be seen that, by increasing the applied pressure the values of both  $J_{\text{H}_2\text{O}}$  and  $R_s$  increase simultaneously. The analogy of high flux-high salt rejection can be explained by the fact that the produced water flux is directly proportional to the net applied pressure. On the other hand, solute diffusion is not affected by any change in applied pressure. It is expected that  $R_s$  may decrease at high applied pressure. This is confirmed by the fact that  $J_{\text{H}_2\text{O}}$  is high, thus decreases of  $R_s$  and vice versa. These obtained results agree with the results of previous studies (Rao *et al.*, 1997).

**Table 2:** The effect of applied pressure onto  $J_{\text{H}_2\text{O}}$  and  $R_s$

Pressure (psi)	$J_{\text{H}_2\text{O}}$ (L/m <sup>2</sup> .hr)	$R_s$ (%)
75	4.13	45
15	7.35	69
225	11.56	78

Also, reverse osmosis properties (salt rejection and water flux) for the selected membrane were investigated at different salinity feed solution, using constant applied pressure (15.5 bar), Table (3).

**Table 3:** Effect of feed concentration on reverse osmosis parameters.

Feed concentration		$R_s$ (%)	$J_{\text{H}_2\text{O}}$ (L/m <sup>2</sup> .hr)
EC ( $\mu\text{s}$ )	TDS (ppm)		
3780	2000	78	11.56
9500	5000	57	6.98
19000	10000	48	4.82



From Table (3), it is obvious that, both water flux and salt rejection increase with the decrease of feed concentration. The decrease in permeate flux ( $J_{H_2O}$ ) with increasing the feed water concentration can be explained as, the water flux through the membrane is proportional to the effective pressure ( $P_{eff}$ ), which can be defined as:  $P_{eff} \propto P - \Delta\Pi$

Where  $P_{eff}$  and  $P$  are the effective and applied pressures,  $\Delta\Pi$  is the osmotic pressure. The increase of the feed concentration at constant applied pressure leads to an increase in its osmotic pressure. Thus, the decrease in the effective pressure leads to a decrease in water flux.

In case of salt rejection, the decrease of salt rejection by increasing feed concentration can be explained as the reported in previous works (Bartles et al., 2005; McCurley and Seitz 1991, Flory 1953, Wong et al., 2012), the passage of salt through the membrane in terms of several interacting mechanisms including convection, diffusion, and charge repulsion. Specifically, the combined influence of membrane charge and feed ionic strength is known to play a significant role in salts rejection. Possible explanation for the observed trends is the swelling of the polymer in ionic solutions. The driving force for swelling is dependent on the difference between the charge density of the polymer and the ionic strength of the solution (McCurley and Seitz 1991). Therefore, at higher solution ionic strength, there is a greater ability of the solution to equalize the charge densities in the polymer, reducing electrostatic repulsion between polymer chains and minimizing the swelling (Flory 1953).

### 3.3 Application of synthesized PS/PVA-TiO<sub>2</sub> TFNC membranes in desalination of groundwater samples:

Attempts were performed aiming desalination of both brackish and saline water samples using the selected synthesized TFNC membrane. The chemical analyses data of feed water and permeate samples after 6hr operation times are illustrated in Table (4).

For brackish water sample, the selected membrane showed salt rejection (71.87 %) with permeate flux of 10.25 L.m<sup>-2</sup>.hr<sup>-1</sup>. The sequence of salts rejection related to initial concentration of each salt can be arranged as follows: R Na<sub>2</sub>SO<sub>4</sub> > Mg(HCO<sub>3</sub>)<sub>2</sub> > Ca(HCO<sub>3</sub>)<sub>2</sub> > MgSO<sub>4</sub> > NaCl, as shown in Table (5).

**Table 4:** Chemical analysis before and after desalination of both brackish and saline water samples using selected TFNC membrane.

Sample	TDS (ppm)	unit	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total cations	CO <sub>3</sub> <sup>--</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>	Total anions	Salts (%)				
													NaCl	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	Mg(HCO <sub>3</sub> ) <sub>2</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub>
Brackish Before	2380	ppm	28.56	81.79	678	12	37.93	0	404.32	800	578	39.56	41	37	5	13	4
		epm	1.425	6.726	29.48	0.3		0	6.62	16.64	16.3						
		%	4	18	77	0.8		0	17	42	41						
Brackish After	669	ppm	12.1	20.40	195	9	10.99	0	101	130	252.3	11.474	62	17	7	9	5
		epm	0.60	1.67	8.48	0.23		0	1.65	2.70	7.11						
		%	5	15	77	2		0	14	24	62						
Sample	TDS (ppm)	unit	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Total cations	CO <sub>3</sub> <sup>--</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>	Total anions	Salts (%)				
			NaCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>	CaSO <sub>4</sub>		Ca(HCO <sub>3</sub> ) <sub>2</sub>									
Saline Before	8608	ppm	255	469.1	2100	8	142.82	0	305.00	2100	3523	148.0	64	3	24	6	3
		epm	12.73	38.58	91.31	0.20		0	4.999	43.68	99.35						
		%	9	27	64	0		0	3	30	67						
Saline After	4192	ppm	87.7	210.7	1050	3	67.43	0	130	900	1730	69.63	68	2	24	3	3
		epm	4.37	17.32	45.65	0.07		0	2.13	18.72	48.78						
		%	6	26	68	0		0	3	27	70						

**Table 5:** The salts rejection before and after desalination of brackish water sample using selected TFNC membrane.

parameter	Salts				
	NaCl	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	Mg(HCO <sub>3</sub> ) <sub>2</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub>
Sample before: 2380 (ppm)	915.8	880.6	119	309.4	95.2
Sample after: 669 (ppm)	414.78	113.73	46.83	60.21	33.45
Rejected salts (ppm)	561.02	766.87	72.17	249.19	61.75
Rejected salts (%)	57.49	87.08	60.64	80.54	64.86
RS (%) related to TDS: (71.87)	23.57	32.22	3.03	10.47	2.59

On the other hand, it showed 51.72 % salt rejection with 5 L.m<sup>-2</sup>.hr<sup>-1</sup> permeate flux. The sequence of salts rejection related to initial concentration of each salt can be arranged as follows: R CaSO<sub>4</sub> > MgCl<sub>2</sub> > MgSO<sub>4</sub> = Ca (HCO<sub>3</sub>)<sub>2</sub> > NaCl, as shown in Table (6).

**Table 6:** The salts rejection before and after desalination of saline water sample using selected TFNC membrane.

parameter	Salts				
	NaCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>	CaSO <sub>4</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub>
Sample before: 8608 ppm	5509.12	258.24	2065.92	516.48	258.24
Sample after: 4192 ppm	2751.28	80.92	971.04	121.38	121.38
Rejected salts (ppm)	2757.84	177.32	1094.88	395.1	136.86
Rejected salts (%)	50.05	68.66	52.99	76.49	52.99
RS (%) related to TDS (51.72)	32.03	2.06	12.72	4.59	1.58

These results suggest that each ion could have an individual contribution to the membrane charge by the means of adsorption. In other words, the charge density and sign are not constant but depend very much on the

salt type and its concentration; this phenomenon is attributed to ionic adsorption at the interface membrane/solution.

Generally, the selected membrane could be acceptable for practical uses in reverse osmosis desalination especially for brackish water as compared with saline water because the water flux of brackish groundwater is about 1.5 time that of saline water.

#### 4- Conclusion:

This study developed new types of PS/PVA TFNC membranes using TiO<sub>2</sub> nanoparticles. These types were synthesized by ex-situe coating TiO<sub>2</sub> on PS support layer and/or in-situe crosslinked PVA barrier layer. The synthesized membranes were characterized using contact angle, ATR-FTIR, and SEM.

The optimum conditions of membrane synthesis were investigated. It included TiO<sub>2</sub> nanoparticles (0.25 wt. %) for 30 min soaking time for ex-situe coating of PS support layer. Also, for improvement the cross-linked PVA barrier layer, the optimum conditions included 3 wt.% of GA which was used as cross-linker, curing time 60 min and curing temperature of 75°C as well as 1 wt.% TiO<sub>2</sub> nanoparticles concentration. The modification using 1 wt. % TiO<sub>2</sub> leads to improve the water flux from 9.32 to 11.56 (L.m<sup>-2</sup>.hr<sup>-1</sup>) with slightly increase in salt rejection (%) which increased from 76.79 to 78 (%). Also, the effect of applied pressure and feed water salinity on reverse osmosis performance was studied. The increase in applied pressure increases the values of both J<sub>H<sub>2</sub>O</sub> and R<sub>S</sub> simultaneously and vise versa of water salinity; i.e., both water flux and salt rejection increase with the decrease of feed concentration.

Also, attempts aiming desalination of two water (brackish and saline) samples were carried out using best synthesized TFNC membrane. The results showed acceptable performance for selected membranes in water desalination processes especially for brackish water with salt rejection (71.87 %) and permeate flux of 10.25 L.m<sup>-2</sup>.hr<sup>-1</sup> as compared with that of saline water with 51.72 % salt rejection with 5 L.m<sup>-2</sup>.hr<sup>-1</sup> permeate flux.

#### Acknowledgements

The author is grateful for financial support for his scientific visit to chemical Engineering Dept., Texas University at Austin, Texas, USA, where this work was achieved, provided by Science and Technology Development Fund (STDF) through USA-Egypt Science and Technology collaboration program.

#### References

- Bae, T.H. and T.M. Tak, 2005. "Effect of TiO<sub>2</sub> nanoparticles on fouling mitigation of ultra filtration membranes for activated sludge filtration", *J. Membr. Sci.*, 249: 1-8.
- Bartels, C., R. Franks, S. Rybar, M. Schierach and M. Wilf, 2005. "The effect of feed ionic strength on salt passage through reverse osmosis membranes", *Desalination*, 184: 185-195.
- Bezuidenhout, D., M.J. Hurndall and R.D. Sanderson, 1998. "Reverse osmosis membranes prepared from potassium peroxy disulphate-modified poly(vinyl alcohol)", *Desalination*, 116: 35-43.
- Bolto, B., 2009. "Cross linked poly(vinyl alcohol) membranes, *Prog. Polym. Sci.*, doi:10.1016/j.progpolymsci.2009.05.003.
- Bottino, A., G. Cappannelli, O. Monticelli and P. Piaggio, 2000. "Poly (vinylidene fluoride) with improved fictionalization for membrane production", *J. Membr. Sci.*, 166: 23-29.
- Bottino, A., D. Cappannelli, V. Asti and P. Piaggio, 2001. "Preparation and properties of novel organic-inorganic porous membranes, *Sep. Purif. Technol.*, 22/23: 269-275.
- Cadotte, J.E. and A.F. Turbak, 1981. "Synthetic Membranes, ACS Symposium Series 153, American Chemical Society, Washington, D.C., 305-326.
- Cadotte, J.E., R.S. King, R.J. Majerle and R.J. Peter-sen, 1981. "Improved porous support for thin-film composite reverse osmosis membranes", Office of Water Research and Technology, Washington, D.C., Report No. PB82-197997, 6-7.
- Cao, X., J. Ma, X. Shi and Z. Ren, 2006. "Effect of TiO<sub>2</sub> nanoparticle size on the performance of PVDF membrane", *Applied Surface Science*, 253: 2003-2010.
- Chu, T.J. and M.H. Yang, 1992. "Hydraulic permeation of water through heat-treated PVA membrane", *J. Chem. Eng. Jpn.*, 25: 660-665.
- Fishman, M.J. and L.C. Friedman, 1985. "Methods for determination of inorganic substances in water and fluvial sediments", U.S. Geol. Surv., Book 5, Chapter A1. Open file report 85-495, Denver, Colorado, U.S.A.
- Flory, P.J., 1953. "Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, USA.
- Gancarz, I., G.P. Zniak, M. Bryjak and W. Tylus, 2002. "Modification of polysulfone membranes 5. Effect of n-butylamine and allylamine plasma", *Eur Polym J.*, 38: 1937-1946.

- Gohil, J.M. and P. Ray, 2009. "Polyvinyl alcohol as the barrier layer in thin film composite Nanofiltration membranes: preparation, characterization, and performance evaluation", *J. Colloid Interface Sci.*, 338: 121-127.
- Hester, J.F., S.C. Olugebefola and A.M. Mayers, 2002. "Preparation of pH-responsive polymer membranes by self-organization", *J. Membr. Sci.*, 208: 375-388.
- Immelman, E., R.D. Sanderson and E.P. Jacobs, 1993. "Poly(vinyl alcohol) gel sub-layers for reverse-osmosis membranes. 1. In-solubilization by acid-catalyzed dehydration", *J. Appl. Polym. Sci.*, 50: 1013-1034.
- Jegal, J. and K.H. Lee, 1999. "Nanofiltration membranes based on poly(vinyl alcohol) and ionic polymers", *J. Appl. Polym. Sci.*, 72: 1755-1762.
- Jegal, J., N.W. Oh and D.S. Park, 2001. "Characteristics of the nanofiltration composite membranes based on PVA and sodium alginate", *J. Appl. Polym. Sci.*, 79: 2471-2479.
- Jegal, J., N.W. Oh and K.H. Lee, 2000. "Preparation and characterization of PVA/SA composite Nanofiltration membranes", *J. Appl. Polym. Sci.*, 77: 347-354.
- Joshi S.V. and A.V. Rao, 1990. "Synthesis and evaluation of poly (m-phenylene isophthalamide as a reverse osmosis membrane", *Desalination*, 78: 355-362.
- Kim, S.H., S.Y. Kwak, B.H. Sohn and T.H. Park, 2003. "Design of TiO<sub>2</sub> nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem", *J. Membr. Sci.*, 211: 157-165.
- Koops, G.H., and C.A. Smolders, 1991. "Pervaporation Membrane Separation Processes", R.Y.M. Huang, ed., Elsevier, Amsterdam, 274.
- Kurihara, M., T. Watanabe and T. Inoue, 1982. U.S. Patent, 4,366,062.
- Lang, K., G. Chowdhury and T. Matsuura, 1994. "Reverse-osmosis performance of modified polyvinyl-alcohol thin-film composite membranes", *J. Colloid Interface Sci.*, 166: 239-244.
- Lang, K., T. Matsuura and G. Chowdhury, 1995. "Preparation and testing of poly vinyl alcohol composite membranes for reverse-osmosis", *Can. J. Chem. Eng.*, 73: 686-692.
- Lang, K., S. Sourirajan and T. Matsuura, 1996. "A study on the preparation of polyvinyl alcohol thin-film composite membranes and reverse osmosis testing", *Desalination*, 104: 185-196.
- Li, Y. and X.L. Lu, 2001. "Research progress of modification of poly (vinylidene fluoride) porous membrane", *J. Tianjin Poly tech. Univ.*, 20(5): 74-78.
- Li, J. S., Y. Liang, H. Y. Wang, X. Y. Sun and L. J. Wang, 2004. "Preparation and characterization of TiO<sub>2</sub>/PVDF composite hollow fiber membrane", *ACTA Polym.*, 5: 709-712.
- Lonsdal, H.K., V. Merten and R.L. Riley, 1965. "Transport properties of cellulose acetate osmosis membrane", *J. Appl. Polym. Sci.*, 9: 1341-1362.
- McCurley, M.F. and W.R. Seitz, 1991. "Fiber-optic sensor for salt concentration based on polymer swelling coupled to optical displacement", *Anal. Chim. Acta*, 249: 373-380.
- Mohamed, N.A. and A.O.H. Al-Dossary, 2003. "Structure-property relationships for novel wholly aromatic polyamide-hydrazides containing various proportions of para-phenylene and meta phenylene units II Perparation and properties of semi permeable membranes for water desalination by reverse osmosis separation performance", *Euro. Polym.J.*, 39: 1653-1667.
- Rainwater, F.H. and L.L. Thatcher, 1960. "Methods for collection and analysis of water samples", *U. S. Geol. Survey water Supply*, 1454.
- Ramesh, P.B. and V.G. Gaikar, 2001. "Membrane characteristics as determinant in fouling of UF membranes", *Sep Purif Technol.*, 24: 23-34.
- Rao, A.P., N.V. Desai and R. Rangarajan, 1997. "Interfacially synthesized thin composit RO membranes for seawater desalination", *J. Membrane Sci.*, 124: 263-272.
- Rozelle, L.T., J.E. Cadotte, K.E. Cobian and C.V. Kopp, 1977. "Reverse Osmosis and Synthetic Membranes", S. Sourirajan, ed., National Research Council Canada, Ottawa, 249-261.
- Sanderson, R.D., 1993. "Polyvinyl-alcohol and modified polyvinyl-alcohol reverse osmosis membranes", *Desalination*, 91: 114-1114.
- Sanderson, R.D., E. Immerman and D. Bezuidenhout, 1993. "Polyvinyl-alcohol and modified polyvinyl-alcohol reverse-osmosis membranes", *Desalination*, 90: 15-29.
- Yang, M.H., 1995. "Hydraulic permeation of NaCl solution through sulfonated polysulfone-poly vinyl alcohol/polysulfone composite reverse osmosis membrane", *Polym. Test.*, 14: 415-424.
- Yang, Y. and P. Wang, 2006. "Preparation and characterizations of a new PS/TiO<sub>2</sub> hybrid membranes by sol-gel process", *Polymer*, 47: 2683-2688.
- Yoo, Y.E., J.H. Kim, Y. Kim and C. K. Kim, 2003. "Novel ultrafiltration membranes prepared from the new miscible blends of polysulfone with poly(1- vinylpyrrolidone-co-styrene) copolymers", *J Membr Sci.*, 216: 95-106.
- Wang, Z., Y.W. Lu and S.M. Wang, 2002. "Study on the preparation and characteristics of PVDF/CA blend ultra filtration membrane", *J. Membr. Sci. Technol.*, 22 (6): 4-8.

Wong, M. C.Y., K. Martinez, G.Z. Ramon and E. M.V. Hoek, 2012. "Impacts of operating conditions and solution chemistry on osmotic membrane structure and performance", *Desalination*, 287: 340-349.