

Desalting enhancement for blend polyethersulfone/polyacrylonitrile membranes using nano-zeolite A

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Abstract. Thin film composite membranes incorporated with nano-sized hydrophilic zeolite -A were successfully prepared via interfacial polymerization (IP) on porous blend PES/PAN support for water desalination. The thin film nanocomposite membranes were characterized by SEM, contact angle and performance test with 7000 ppm NaCl solution at 7bar. The results showed that the optimum zeolite loading amount was determined to be 0.1wt% with permeate flux 29LMH. NaCl rejection was improved from 69% to 92% compared to the pristine polyamide membrane where the modified PA surface was more selective than that of the pristine PA. In addition, there was no significant change in the permeate flux of the thin film nanocomposite membrane compared with that of the pristine PA in spite of the formation of the dense polyamide layer. The stability of the polyamide layer was investigated for 15 days and the optimized membrane presented the highest durability and stability.

Keywords: salting water; permeability; TFNCM; zeolite -A; interfacial polymerization

1. Introduction

The successful use of membrane performance depends on the proper choice of membrane materials. Ideally, a membrane should have a high permeate flux, high contaminant rejection, great durability, good chemical resistance, and low cost (Zhou and Smith 2002). A major challenge of the membrane technology is membrane fouling and the inherent trade-off between membrane selectivity and permeability (Geise *et al.* 2011).

Application of asymmetric membranes had some drawbacks since; polymeric membranes are limited by permeability and selectivity tradeoff while inorganic membranes are expensive, brittle and difficult to upscale. Recently, thin film composite (TFC) membranes were developed as an alternative approach to overcome these drawbacks (Sólon 2013).

Thin film composite membranes are formed by interfacial polymerization (IP) process using two monomers on the surface of the porous substrate to get a very thin active layer. Meanwhile; when nanomaterial dispersed in the active polyamide layer a thin film nanocomposite is formed (TFNC) (Low *et al.* 2015).

The concept of nanocomposite membranes was originally developed to overcome the Robeson upper boundary in the field of gas separation (Chung *et al.* 2007). Beside gas separation (Cong *et al.* 2007), many other

applications have been examined using nanocomposite membranes, such as direct methanol fuel cells (Chen *et al.* 2006), proton exchange membrane fuel cells (PEMFCs) (Serpil *et al.* 2012), sensor applications (Lu *et al.* 2007), lithium ion battery (Li 2008), pervaporation (PV) (Peng *et al.* 2007; Yang *et al.* 2009), organic solvent nanofiltration (OSN) (Soroko and Livingston 2009; Sorribas *et al.* 2013), and water treatment (Li and Wang 2013).

Due to their advantage over the conventional asymmetric membranes, TFNC membranes gained considerable attention and are considered as the cutting edge of creating the next generation of high performance membranes in water treatment (Yin *et al.* 2014).

In general, TFNC membranes are prepared via IP process using m-phenylenediamine (MPD) and trimesoyl chloride (TMC) as the two main active monomers for the PA layer formation (Kong *et al.* 2011). Then it follows by loading of nanomaterials in the PA layer either in the aqueous phase of amine or in the organic phase of acyl chloride. In addition, different derivatives of amines and acyl chloride were used to develop TFC membranes with different properties (Lau *et al.* 2012). A significant number of studies on membrane nanotechnology have focused on creating synergism or multifunction by using additives in membranes. Earlier, additives were used in the substrate layer to increase the force to draw water, but recently additives are used both in the thin film as well as in the substrate (Lau *et al.* 2012).

The addition of metal oxide nanoparticles including alumina (Maximous *et al.* 2010), TiO₂ (Bae *et al.* 2005) to polymeric ultrafiltration membranes had been shown to increase membrane surface hydrophilicity and water

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permeability, also the addition of $\text{CeO}_2/\text{Ce}_7\text{O}_{12}$ to the polymeric matrix increased the fouling resistance (Tarek *et al.* 2018). These inorganic nano-particles also enhance the mechanical and thermal stability of polymeric membranes; reduce the negative impact of compaction and heat for membrane permeability (Ebert *et al.* 2004, Tarek *et al.* 2018).

Usage of nano - zeolite as additives in TFNC enhanced the membrane performance by increasing permeability, negative charge, and the thickness of the polymeric active layer (Dong *et al.* 2011). On the other hand, zeolites-A in sodium form have pore diameters of approximately 4.2 Å that is between the water diameter (2.7 Å) and the hydrated sodium and chloride ion diameters (8–9 Å); therefore these particles provide preferential flow paths only for water (Jeong *et al.* 2007). Jeong reported that water permeability increased up to 80% over the TFNC membrane and the salt rejection was largely maintained ($93.9 \pm 0.3\%$) [Loading NP 0.4%W/V with permeability $3.8 \times 10^{-12} \text{ mpa}^{-1}\text{s}^{-1}$]. As well, the addition of 0.2 wt % nano-zeolites (250 nm size) caused moderately higher permeability and better salt rejection (> 99.4%) compared to commercial RO membranes (Lind *et al.* 2010).

The role of zeolite in TFNC was to create a preferential path for water by the small, hydrophilic pores of nano-zeolite (Lind *et al.* 2009). Whenever, the pores loaded with zeolites, the water permeability increased than non-loaded pores (Rakhi *et al.* 2016). Also, nano-zeolites were used as carriers for antimicrobial agents such as Ag^+ , which imparts anti-fouling property to the membrane (Dong *et al.* 2012).

The aim of this study is to develop a simple and low-cost method to prepare membranes with high permeability and high selectivity by fabrication of polyamide layer incorporated with lab prepared and fully characterized zeolite-A. The optimized TFC membrane was introduced for desalination of water.

2. Materials and methods

2.1 Materials

The rock was obtained from natural Egypt waste. Sodium hydroxide NaOH was obtained from (Modern Lab chemicals, Egypt). Piperazine hexa-hydrate (PIP) and isophthaloyl dichloride (IPC) were purchased from Sigma-Aldrich and Merk - Germany respectively which are used to establish the PA active layer on the substrate. N-hexane was obtained from Acros Organics. Sodium dodecylsulphate was purchased from Merk – Germany.

2.2 Methods

2.2.1 Preparation of Zeolite -A

Based on the similarity in Si/Al ratio for both kaolinite and zeolite-A, close to unity, Zeolite-A is directly prepared from meta-kaolinite without any additional silica, following the method of (Youssef *et al.* 2008). In a typical synthesis, 10 g of the rock were added to a 100 ml solution made of 3.0 M NaOH. The solution was stirred mildly for 30 min at 550 rpm. About 15-25 ml of the resulting slurry was then

charged into the CEM microwave vessels of express type of 100 ml capacity and heated for 2h at 80°C for the microzeolite samples, meanwhile, the nanoform zeolite-A is heated at the same temperature but for a period of 30 min up to 1h. The synthesized product was then collected, washed several times with distilled water till pH=7, and dried overnight at 80°C in an electric oven.

2.2.2 Membrane fabrication

2.2.2.1 Fabrication of UF blend membranes Pristine TFC membrane

UF PES/PAN membrane with ratio PES: PAN (12:2 wt.%) was prepared via inversion process according to Abdallah *et al.* 2017 and used as a substrate to produce TFC membranes by surface coating through IP process.

TFC membrane was synthesized on the previous fabricated 2% UF PES/PAN membrane through interfacial polymerization. The monomer solutions were prepared with ratio 1:0.3:0.3:0.3 wt.%/v comprising of piperazine: sodium hydroxide: dodecylsulfate: isophthaloyl dichloride respectively with amine soaking time 40 min, interfacial polymerization time 10 min, annealing temperature 80°C and curing time 10 min (Jamil *et al.* 2018).

2.2.2.2 Zeolite –A filled TFC membranes

Preparation of TFC zeolite-filled membranes was prepared identically to the TFC membranes. The organic phase was prepared by adding 0.3wt%IPC in hexane. The composition of amine solution was 1wt.% PIP, 0.3 wt.%NaOH, and 0.3wt.% SDS in water. The synthesized zeolite was first dispersed in water to prepare 0.5wt% concentrated solution under ultrasonication. Then, a predetermined amount of this concentrated zeolite solution was dispersed in the aqueous amine solution to make the mass fraction of zeolite in the aqueous phase ranging from 0.02wt.% to 0.2wt.%. The zeolite was dispersed in the aqueous phase due to its better dispersion in water than hexane. Homogeneous zeolite dispersion in the amine solution could be obtained by ultrasonication for 2 h at room temperature immediately prior to use in the interfacial polymerization reaction.

2.2.3 Characterization of zeolite -A

The prepared zeolite was characterized by X-ray diffraction (XRD), the XRD patterns were performed using Philips powder diffractometer in the reflection mode (Cu KR radiation, $\lambda=1.5418 \text{ \AA}$) and a scan rate of 2°C/min. DTA [STERAMLabsys™ TG-DSC1600°C] apparatus with heating rate 5 °C. TEM measurement (JEOL) was used to investigate the shape of zeolite. The surface charge and the mean diameter were determined by NICOMP nano-380ZLS, PSS Co., USA.

2.2.4 Membrane characterization

Morphologies of TFC membranes and thickness of PA were observed by QUANTA FEG250 Scanning Electron Microscope (SEM). The contact angle of the prepared TFNC membranes was obtained by (SCA 20, OCA 15EC) using the sessile drop method. The volume and contact time were 10µL and 10 sec. respectively with five times for each

membrane measured. The surface charge of the prepared membranes was measured using an electrokinetic analyzer - SurPASS, Anton Paar GmbH.

2.2.5 Performance evaluation

The separation performance of the synthesized TFC / TFNC membranes was evaluated in terms of water flux (F) and salt rejection (R) using a dead-end membrane testing cell. The membrane sample was loaded into the stainless cell with an effective area of 12.7 cm². The feed solution was prepared using 7000 ppm NaCl to simulate the brackish water. After the membranes were compacted for 2 h to reach the steady state at 7bar; the water flux was calculated using Eq.(1) (Abdallah *et al.* 2017)

$$F = \frac{V}{AT} \quad (1)$$

Where F is the permeate water flux (L m⁻² h⁻¹), V is the volume of permeate (L) collected over a period of time t (h), and A is the effective area of the membrane (m²). The salt rejection (R) was achieved according to Eq.(2) (Zhao *et al.* 2013)

$$R = 1 - \left(\frac{C_p}{C_f} \right) \times 100 \quad (2)$$

Where C_p and C_f are permeate and feed salt concentrations, respectively, which were determined by a conductivity meter.

3. Result and discussion

3.1 Characterization of zeolite-A

The crystal structure of zeolite-A nanoparticle was characterized by XRD. As shown in Fig.1, the synthesized nano- particles could be determined to be pure zeolite by comparison with the standard XRD powder patterns. Where the recorded major peaks at 2θ: 7.1, 10.0, 12.6, 16.3, 21.4, 24, 26.1, 26.5, 27.1, 30.0, 32.5 and 34.5°. The compound name and chemical formula of Zeolite A (Na) is given as Sodium Aluminum Silicate Hydrate (Na₉₆Al₉₆Si₉₆O₃₈₄ · 216H₂O). The diffraction pattern was matched with that of literature (Treacy and Higgins 2001) and this was identified to be of Zeolite A with Linde Type A (LTA) structure. The 2θ peak positions of the as-synthesized zeolite corresponded with that of Zeolite LTA (Nyankson *et al.* 2018).

Fig. 2 show the TEM image of zeolite-A . It can be seen that the zeolite nanoparticles had plate-like shapes and most of them exhibited particle size ranging in 100 nm. From surface charge measurement zeolite -A has a negative surface charge equal to -41.36mv with mean diameter 447 nm.

3.2 Characterization of TFNC membranes

3.2.1 Morphology characterization

The surface and cross-section morphology of both TFC and TFC loaded with zeolite - A membranes were analyzed using SEM to investigate the effect of zeolite incorporation. The SEM images of the top surface of TFC and TFNC (0.05 and 0.1 wt.% zeolite loading) membranes are shown in Fig. 3 at different magnifications.

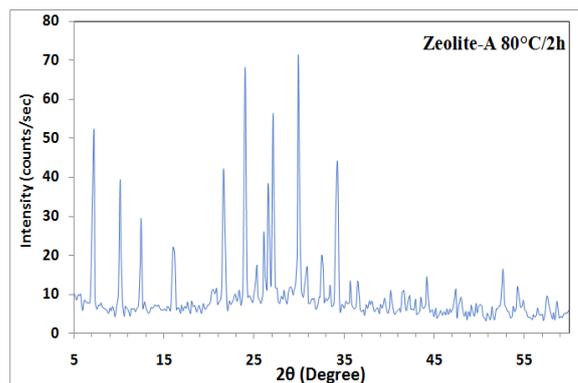


Fig. 1 XRD pattern for the prepared zeolite A

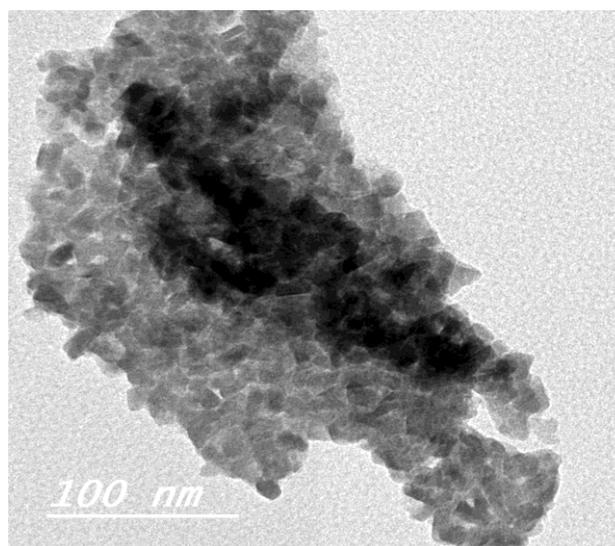
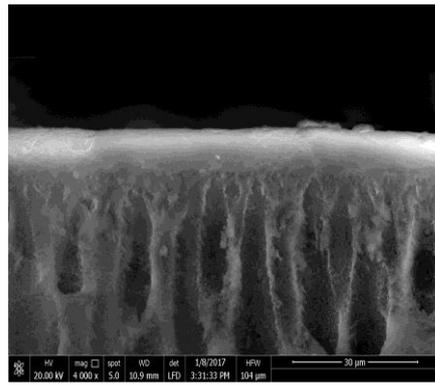


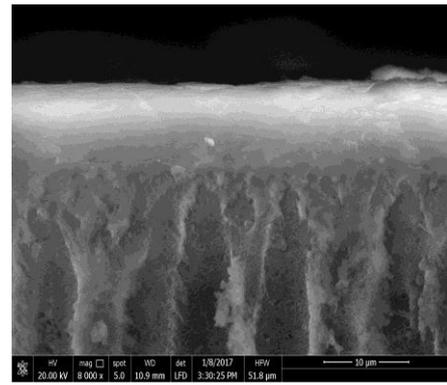
Fig. 2 SEM images for the Zeolite A

For the pristine TFC membrane, the typical polyamide morphology formed through interfacial polymerization also, the produced layer is exhibited a smoother surface that observed in Fig. 3(A). In Fig. 3 (B and C), there are some plate and cubic shapes on the polyamide surface that correspond to zeolite -A nanoparticles. So the incorporation of zeolite nano- particles affected the overall morphology of the polyamide thin film layer. Nevertheless, a few plate-like features could be observed on the surface of TFNC membrane in Fig. 3(B). A more cubic structure could be observed on the surface of 0.1 TFNC membrane in Fig. 3(C) (Zhao 2013), which was matched with the morphology of zeolite -A that are most covered with PA. SEM images emphasized that TFC was different from TFNC membrane surface and this difference reveal the presence of zeolite nanoparticles in the PA thin layer. This enhanced thickness which is expected to enhance the free volume (Ghanbari *et al.* 2015).

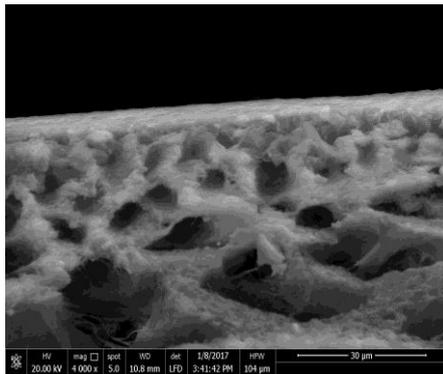
As well the pristine interfacial polymerization between Di amine and Mesoyl chloride is generally believed to be diffusion -limited: PIP diffuses into the organic phase to react with IPC (Xie *et al.* 2012). Their action only stops when no PIP is able to further penetrate across the barrier layer formed in the reaction zone. For TFN membranes



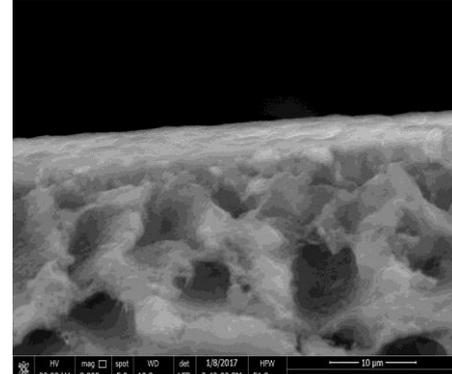
(a) pristine TFC



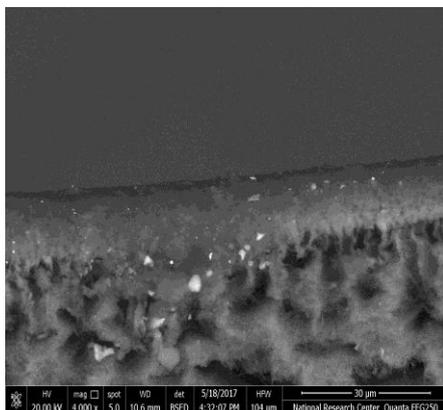
(a) pristine TFC at high magnification



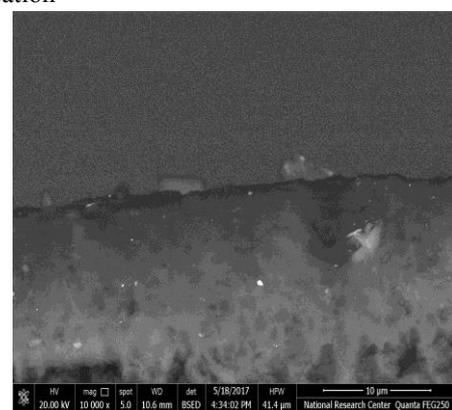
(b) 0.05 wt.% Zeolite- A TFC membrane



(b) 0.05 wt.% Zeolite- A TFC membrane at high magnification



(c) 0.1 wt.% Zeolite- A TFC membrane



(c) 0.1 wt.% Zeolite- A TFC membrane at high magnification

Fig. 3 SEM images for the prepared membranes

prepared with fillers in the aqueous solution, fillers were pre-deposited on the support; most of the fillers incorporated reside at the bottom region of the selective layer (Zhao *et al.* 2014), showing no features induced by filler morphologies on the membrane surfaces.

The dense selective layer of the prepared TFNC membranes in this work showed a two-layered structure that supposed by (Freger 2003). This double layer structure is owed to the different kinetic of zone reaction. It is theorized that the dense polyamide sub-layer perhaps constitutes the true separation barrier (Freger 2003; Freger 2005; Pacheco 2010) when zeolites are incorporated into amine through the aqueous phase. On the other hand the TFNC membrane also possesses a dense surface layer containing a low

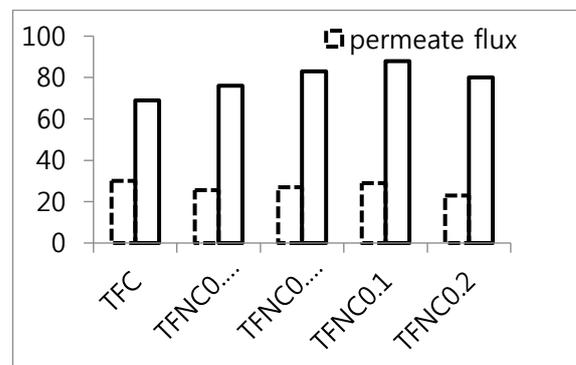


Fig. 4 Effect of zeolite –A amounts on separation performance of 7000 ppm NaCl at 7 bar

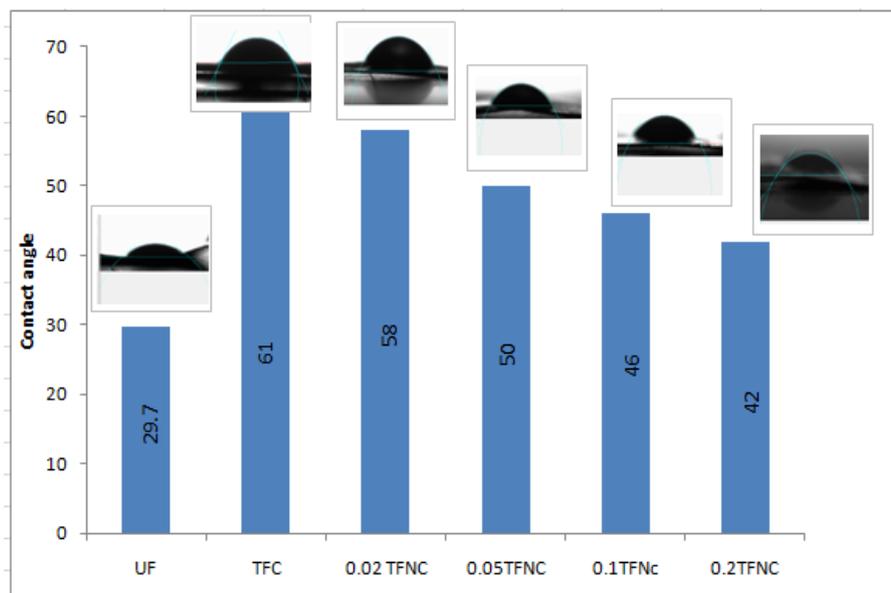


Fig. 5 Effect of zeolite –A amounts on membrane hydrophilicity

concentration of zeolites (Freger 2003, Freger 2005, Pacheco 2010). Here, the authors have selected blend membranes PES/PAN due to their high mechanical (compaction resistance and strength) and chemical stabilities. In addition to their hydrophilic natures that lead to a higher soaking with the reactive monomers and resulting suitable dense polyamide layer capable of loading zeolite - A.

3.2.2 Effect of zeolite –A amount on separation performance

The addition of inorganic fillers has key impacts on the interfacial void formation, aggregation, pore blockage of the morphology, and the transport phenomenon. Consequently, the impregnation of zeolites has a significant influence on the overall performance of the newly developed TFNCMs. The formation of these interfacial voids is attributed to two main phenomena, the interaction between the polymer phase and the filler and the stress exerted during preparation (Mahajan *et al.* 2002). The presence of interfacial voids creates additional channels that allow the solvent to pass through the membrane. However, mechanical strength and rejection rate are also concerned by the channel density (Chung *et al.* 2007).

The effect of zeolite ratio in the aqueous phase from 0.02 wt. % to 0.2 wt.% on membrane separation process was presented in Fig.4. The water flux of the typical TFC membrane decreased gradually from 30 LMH to 25 LMH at the lowest zeolite loading (0.02 wt%), respectively and with more loading amount 0.05 wt % - 0.2 wt%, the water flux increased again. The salt rejection increased gradually from loading (0.02wt % to 0.1 wt.%) of zeolite-A and decreased with 0.2 wt.% ratio. Where, the salt rejection reached 92% with loading ratio of 0.1wt.%, and then showed a significant decrease of about 85% with 0.2 wt %. The results indicated that the TFNC membrane filled zeolite improved the separation performance with loading ratio 0.1 wt. %.

However, with 0.2 wt.% loading ratio the zeolite-A nanoparticles were easily aggregated at high concentrations, which lead to the creation of interstitial defects during the membrane synthesis process. Thus, perfect salt rejection could not be achieved (Zhao *et al.* 2013). The interstitial on selective defects formed at the interfaces could displace the favorable nano-gaps and molecular sieve effects. Therefore, the optimal fillers loading were about 0.1wt.%. In addition, nano sized zeolite A can make the surface of the membrane smoother and decrease the tendency of fouling (Chung *et al.* 2007).

3.2.3 Contact angle and surface charge

Fig. 5 shows Contact angle of the support membrane, the pristine TFC and the TFNCM filled with zeolite –A. As can be seen from Fig. 5, UF PES/PAN, TFC and TFNC filled with zeolite -A have different contact angle values. The results indicate that the TFNCMs are much hydrophilic than TFC this can be attributed to the existence of zeolite nanoparticles. Also, the TFC contact angle is higher than UF PES/PAN due to the formed dense layer. The decrease in the contact angle normally indicates the increase in hydrophilicity, and more hydrophilic membrane surface typically produce better water permeability. The enhanced hydrophilicity of the TFN membranes could be due to the hydrophilic property of zeolite-A nanoparticles.

Also, improvement of the membrane permeability could be owed to the change of kinetics affected by the existence of zeolites-A nanoparticles during the IP process. Lind *et al.* proposed that zeolite nanoparticles might affect the polyamide structure as a result of the interaction between the zeolites and the monomer (Ma *et al.* 2012).

Fig. 6 shows the zeta potential value of the membrane surface, the pristine TFC and the TFNCM filled with zeolite –A, were measured at different pH values. The obtained values were different and all of these had a specific IEP (isoelectric point).

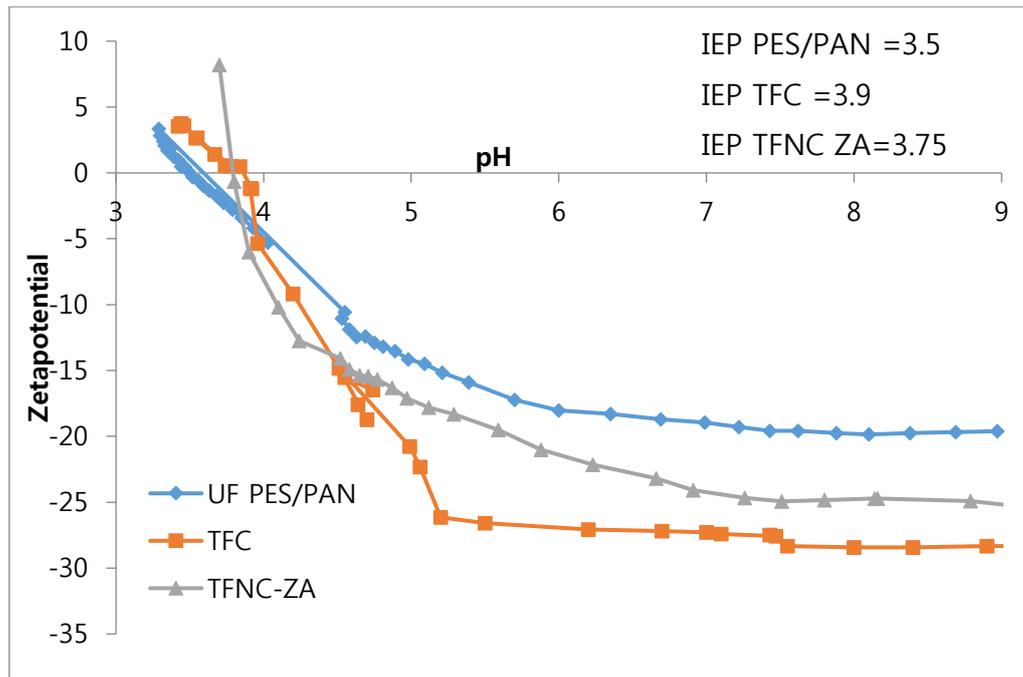


Fig. 6 surface charge values of the prepared membrane

The prepared membranes have positive zeta potentials at pH 3.5–3.9 because of the protonation of the amine functional groups. However, with the increase in pH, deprotonation of amine and carboxylic acid groups and the dissociation of carboxylic acid groups caused the membrane surfaces to become negatively charged. As shown in Fig. 6 For the UF PES/PAN membranes, the zeta potential values were similar at pH 5.5–9 with IEP = 3.5. The zeta potential value of pristine TFC was between 1 and –28 mV at pH 3.7–9 and the zeta potential value of TFNC filled with zeolite-A was highly positive charges than the pristine membrane where the values are between 8 and –25 mV at pH 3.7–9. That discrepancy between the zeta potential of prepared membranes may arise from the zeolite filled the dense layer and the degree of cross-linking (Mansor *et al.* 2018).

Electromigration is controlled by the membrane charge density and charge polarity, which are both characterized by the zeta potential (ZP) of the membrane surface. This parameter is usually evaluated from streaming potential analyses (Tay *et al.* 2002). The solution pH has a significant effect on ZP because it dictates the charge on the functional groups of the membrane material and of the molecules in solution. Moreover, the pH of the system may affect the “openness”, *i.e.*, pore size, of the membrane (Childress and Elimelech 2000), thus impacting on the size exclusion rejection mechanism. The solution pH at which the net membrane charge is zero is the iso-electric point (IEP). The membrane surface is negatively charged, *i.e.*, negative ZP, when the solution pH is higher than the IEP and positively charged otherwise.

A thorough understanding of the membrane performance (*i.e.*, water flux and solute rejection) as a function of the feed pH is mandatory because pH affects several of the system characteristics (Childress and

Elimelech 2000). Many studies focusing on the relationship between feed pH, membrane charge and ion rejection agree on the significant effect of feed pH, with abrupt changes and minimum rejections being expected at the IEP (Qin *et al.* 2004) Minimum rejections at the IEP are explained as a consequence of the fact that size exclusion is the only active separation mechanism at the IEP (Ferreira-Esmi *et al.* 2013). In the case of a NaCl solution, Childress and Elimelech found that water flux was maximal and salt rejection minimal at the membrane pore IEP, primarily due to decreased electrostatic repulsion and increased pore size.

Studies have been done to characterize the passage of salts through RO and NF membranes (Szabolcs *et al.* 2002). The effect of performance through these membranes varies at different pH due to the corresponding variation in membrane charge is presented in (Fig.7A).

At low pH, the hydrogen ion attaches to the membrane’s negative carboxyl groups and neutralizes the charge of the membrane. The absence of a negative charge at low pH reduces the membrane’s ion rejection. At pH more than 6, the absence of the hydrogen ion attached to the membrane’s carboxyl groups results in a negatively charged membrane. The presence of a negative charge improves the membrane rejection.

However, as pH increases and the hydroxyl ion concentration increases, the carboxyl groups on membranes surface are repelled or opened and the membrane “swells”. This “swelling” effect increases the passage of certain ions. Hydroxyl ions (OH⁻), for example, pass through the membrane more readily than chloride ions (Cl⁻). This is evidenced by a negligible decrease in pH in permeate of a produced water RO when running at high pH. At one site running at pH greater than 10, the pH in permeate of the RO actually increased to more than 11.

Along with the high passage of hydroxyl ions, an

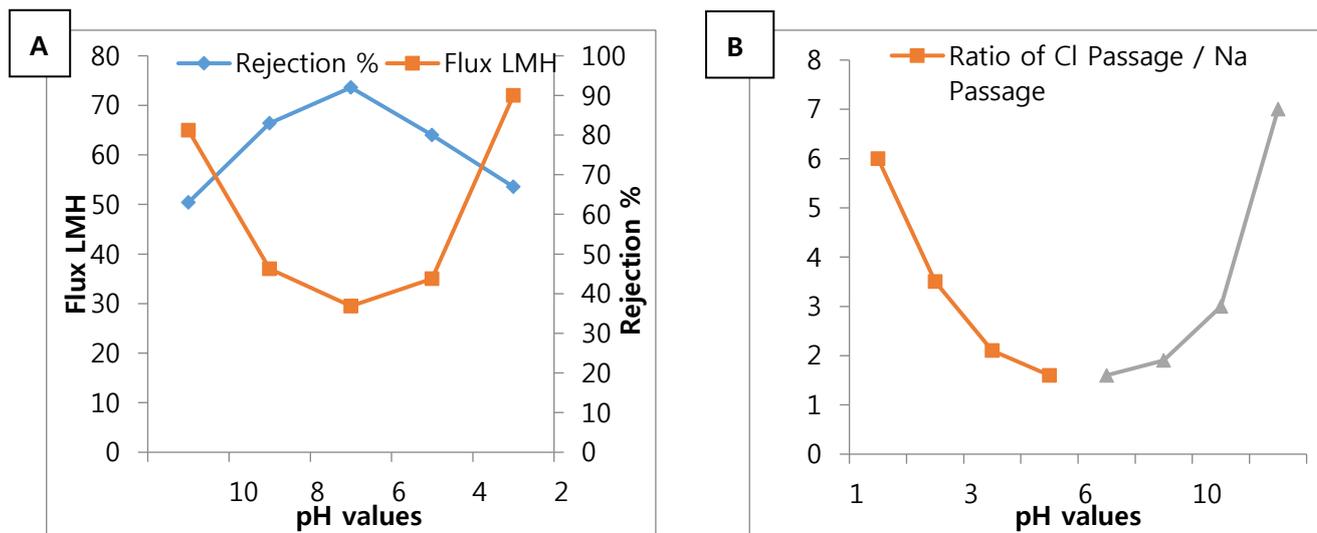


Fig. 7A Salt rejection and permeate flux at different feed pH values
 Fig. 7B Ratio of sodium passage to chloride passage as a function of pH

increase in the passage of sodium is also seen. The sodium acts as the counter ion to the hydroxyl ions in order to maintain charge neutrality in permeate. Controlled studies used optimized TFNC membrane treating a 7000 ppm sodium chloride solution with caustic soda injected to increase pH. Fig. 7B shows the significant increase in sodium passage relative to chloride passage as pH is increased above pH=10. The sodium passage was 7 times that of the chloride passage. In the case of, injection with hydrochloric acid to decrease pH, the chloride passage was 6 times that of the sodium passage when the solution pH =2.

On the other hand, in previous work the effect of pH over the efficiency of zeolite Na - A in the process of water softening has no considerable effect is observed, which indicates a high efficiency of the zeolite in a broad range of pH values. Again, better results are observed for the synthesized zeolite (Loiola *et al.* 2012).

3.2.3 Performance evaluation for the TFNC membrane

The efficiency of the polyamide layer was done by separation test of 7000 ppm NaCl solution at 7 bar for the prepared TFC and TFNCMs filled with zolite - A (0.1 wt.%) through determining the Permeate flux and percent of salt rejection. The pristine TFC membrane rejected NaCl with 69 % that is greatly higher than the salt rejection of the PAN/PES support layer (data not presented). This due to the IP process, the pores were covered by a PA thin layer, which acted as a dense layer on the porous support PES/PAN and capable of salt ions rejection.

For the TFNC membranes with zolite - A (0.1 wt.%), the permeate flux had no significant change meanwhile. the rejection of salt increased. The salt rejection of the TFNC membrane reached to 92% which is higher than the TFC pristine membrane. This is attributed to the zeolite-A properties that facilitates the diffusion of water molecules

into the membrane and the complete uniform filling of the Z-A powders in the polyamide layer that covers the porous support membrane. On the other hand, lower performance of pristine TFC was due to the incomplete coating of its pores (Mansor *et al.* 2018). So, the TFNC membrane filled with 0.1 wt.% zeolite-A had suitable permeability and selectivity.

3.3 Stability of the TFC membrane

For studying the availability of using TFNC membranes in laboratory applications, the performance and the mechanical stabilities should be investigated. Therefore, permeation tests were performed at 7 bar for 7000 ppm NaCl aqueous solution for definite time. Fig. (8) showed that the performance stability for the optimized TFNC membranes in terms of permeate flux and salt rejection rates during 15 days. Also the cross SEM image for the tested membrane is inserted in Fig. (8).

The tested membrane provides a steady permeate flux during the period of testing, which confirms the highest durability and term performance stability. In addition, the optimized TFC membrane exhibits the stable fitting structure of the polyamide layer. The measured water flux of the optimized membrane was around 29 LMH with salt rejection 92%. Here, without any doubt this method is applicable on laboratory level due to the low costs of nanoparticles used.

Table .1 illustrates the comparison of the performance of TFNC membranes prepared in this work with other TFNC loaded with other zeolites and meso fillers in previous works (Huang *et al.* 2013, Bao *et al.* 2013, Yin *et al.* 2012, Fathizadeh *et al.* 2011, Dong *et al.* 2015). This table displays fillers type, loading amount, monomers, feed concentration, the flux and the percent of rejection. The other TFNC membranes provided flux from 20 -74 LMH with rejection from 91.4 -98% compared to our prepared TFNCM in this study, which needs lower operating pressure.

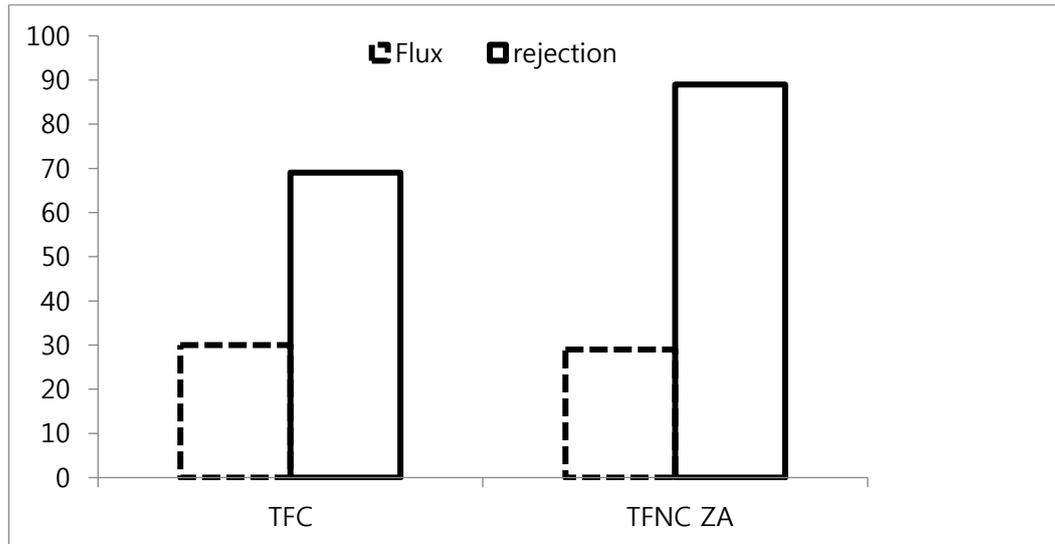


Fig. 8 Performance evaluation for the optimized TFNC membrane

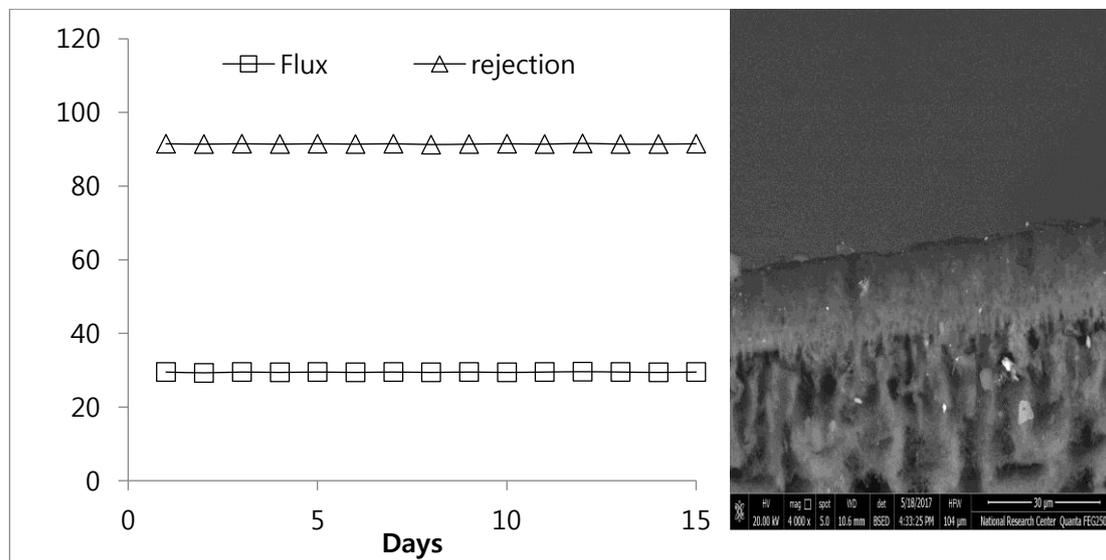


Fig. 9 Stability Performance for the optimized TFNC membrane

Table 1 TFNC membranes filled with zeolite-A and other meso-fillers

| support | Polymer matrix | Filler | Filler loading | Monomer | Dispersed phase | Feed concentration | Performance | | REF |
|---------|----------------|------------------|----------------|---------|-----------------|--------------------|-------------|-------------|---------------------------------|
| | | | | | | | Flux LMH | Rejection % | |
| PSf | PA | Z-A | 0.10 | MPD&TMC | Hexane | 2000 | 20.2 | 91.4 | (Huang <i>et al.</i> 2013) |
| PSf | PA | SiO ₂ | 0.10 | MPD&TMC | Hexane | 2000 | 53.0 | 96.0 | (Bao <i>et al.</i> 2013) |
| PSf | PA | MCM-41 | 0.10 | MPD&TMC | Hexane | 2000 | 46.6 | 97.9 | (Yin <i>et al.</i> 2012) |
| PES | PA | Z-X | 0.20 | MPD&TMC | Hexane | 2000 | 29.7 | 98.0 | (Fathizadeh <i>et al.</i> 2011) |
| PSf | PA | Z-Y | 0.15 | MPD&TMC | aqueous | 2000 | 74.2 | 98.8 | (Dong <i>et al.</i> 2015) |
| PES/PAN | PA | Z-A | 0.10 | PIP&IPC | aqueous | 7000 | 29.0 | 92.0 | This work |

4. Conclusion

Selective polyamide thin film layer was prepared via interfacial polymerization for piperazine with sonicated isophthaloyl dichloride over porous blend Polyethersulfone / Polyacrylonitrile substrate to form NF TFC membrane. The fabricated polyamide layer was incorporated with hydrophilic zeolite - A. The loading amount of zeolite A in the polyamide layer was optimized.

The fabricated TFNC membranes were characterized and evaluated by salt separation for prepared synthetic solution of NaCl. The suitable thickness and cross-linking degree as well the best flux and salt separation for TFCN membrane were achieved with 0.1wt. % zeolite - A. The contact angle results indicate that the TFNCMs are much hydrophilic than TFC due to the existence of zeolite nanoparticles. Zeta potential test indicates that the prepared membrane carried negative charge on its surface due to the negative charge of the nano- zeolite- A.

Generally, the flux of the neat TFC in this study is close to the flux with the prepared TFNC membranes with high salt separation from 69% to 91.5% for TFC and TFNC membrane respectively with high tendency of antifouling due to the nano-sized zeolite A. The prepared membrane provides a steady permeate flux during the period of 15 days, which confirms the highest durability and term performance stability.

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