

Synthesis and optimization of co-polymerized graphene oxide spin-coated over nylon for efficient water desalination

Abbas Jorsaraei Talar^a, Taghi Ebadi^{a,*}, Reza Maknoon^a, Alimorad Rashidi^b

^aDepartment of Civil and Environment Engineering, Amirkabir University of Technology, Tehran, Iran, Tel. (+98) 21 6454 303; email: Tebadi@aut.ac.ir (T. Ebadi), Tel. (+98) 21 48252092; email: Jorsaraei.Abbas@aut.ac.ir (A. Jorsaraei), Tel. (+98) 21 8878 8015; email: Maknoon@aut.ac.ir (R. Maknoon)

^bNanotechnology Research Centre, Research Institute of Petroleum Industry (RIPI), Tel. (+98) 21 48252092; email: Rashidiam@gmail.com

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ABSTRACT

Freshwater is indeed the main need of humans which can be prepared from saline water sources. Herein, in order to prepare an optimized nanocomposite membrane, graphene oxide (GO) nanosheets were cross-linked by N-isopropylacryl amide (NIPAM) and N,N-methylenebis (acrylamide) monomers in the presence of ammonium persulfate. In following, the cross-linked GO which had lower spacing between nanosheets and higher hydrophilicity, was spin coated on nylon substrate with two different pore sizes. During the synthesis procedure, effects of factors including pore size of nylon substrate, GO loading%, and draw solution concentration on desalination performance were studied. To characterize the prepared samples, FESEM, AFM, and X-ray diffraction methods were used. Desalination performance of the membranes was studied through forward osmosis and dead end processes. The results showed that by increasing the GO loading, desalination performance is enhanced. Furthermore, it was observed that the nylon substrates possessing larger pores are more suitable for desalination of draw solutions with higher NaCl concentration. The significantly better desalination performance of the GO cross-linked nanocomposite on nylon can be attributed to its optimized interlayer spacing and higher hydrophilicity.

Keywords: Desalination; Graphene oxide; Tuning the GO d-spacing; Nylon; Forward osmosis

1. Introduction

Supplying freshwater is indeed vital for humanity and societies, which has driven tremendous efforts to provide drinkable water. Along with growing population in the world, more fresh water would be required to satisfy the peoples' needs. However, fresh water resources have been significantly lowered which has become an important environmental challenge. Researchers have pursued novel technologies to provide freshwater from saline water resources [1–8]. Among different techniques, using membranes to remove ions from water has been of great interest [9–13].

In preparation of efficient membranes to remove ions, carbon-based materials (e.g., graphene or CNT) have attracted widespread attention. Graphene as a wonder material which possesses outstanding properties has been a practical candidate for this application. Different experimental and theoretical studies have proved the suitability of graphene in desalination [14–19]. Several techniques have been followed by using graphene in desalination, including functionalization [14,20,21], preparation of nanocomposites [10,11,22,23], incorporating other nanocarbons such as CNT [24,25], and using metal oxides [26] which were aimed to modify the graphene for better desalinating performance. In following, some of the most prominent researches are reviewed.

* Corresponding author.

Molecular dynamics is commonly used to predict the activity of novel membranes in desalination [20,27]. Wang et al. [20] studied the effect of functionalization by hydrogen or hydroxyl groups on water desalination of nanoporous graphene for which excellent salt rejection and water permeance of 785.6 LMH bar⁻¹ was obtained. Yuan et al. [21] studied the desalination activity of carboxyl functionalized graphene oxide (GO) which could improve hydrophilicity and indicated better salt rejections due to electrostatic repulsion by negative charge. In another research, Kaveh and Azar [28] synthesized GO by reaction between octylamine and carboxyl groups followed by dispersing in (trimesoyl chloride)/*n*-hexane solution in which the membrane was prepared by interfacial polymerization and displayed better salt rejection.

In a research performed by Choi et al. [15], GO layers were deposited over polyamide thin film composite which could increase the surface hydrophilicity and enhance the antifouling performance. Hu and Mi [29] deposited GO over polydopamine coated polysulfone support, where the GO was cross linked by 1,3,5-benzenetricarbonyl trichloride. It is reported that the cross linking improves the dispensability in water and also modifies the interlayer spacing of the GO nanosheets for which the flux of 276 LMH MPa⁻¹ and relatively low rejection of monovalent and divalent salts was observed [29]. Zeng et al. [16] synthesized reduced GO (rGO)-composite hydrogels to increase the water flux in forward osmosis (FO). They have observed that in FO process, small amounts of rGO and composite hydrogels, water flux increases significantly. Akin et al. [30] studied the salt rejection performance of GO/polyaniline composite which provided maximum salt rejection of 82% at 10 bar. Song et al. [31] studied the effect of osmotic pressure on water flux through molecular dynamics simulation and showed that graphene leads to higher water flux compared with CNT.

Regarding the fact that interlayer spacing of the graphene sheets plays a vital role in desalination, most of the recent works have concentrated on modifying the spacing of graphene sheets through cross linking. Qian et al. [32] have used diamine monomers to enhance the desalinating activity of the GO through cross linking which displayed the water flux of 20.1 kg m⁻² h⁻¹ along with ion rejection of 99.9% in pervaporation method. Lai et al. [11] have synthesized GO incorporated thin film nanocomposites through interfacial polymerization in which the GO was placed within cross-linked polyamide; this nanocomposite membrane showed higher surface hydrophilicity and 95.8% and 97.7% removal of Na₂SO₄ and MgSO₄, respectively. Recently, Shi et al. [18] have proposed a new method of interfacial polymerization to prepare ultra-thin polyamide membranes where the negatively charged GO was used and polymerization between meta-phenylene diamine and trimesoyl chloride was conducted at void regions of GO. This novel membrane resulted salt rejection of 99.7% and large permeance of 3.0 L m⁻² h⁻¹ bar⁻¹ in reverse osmosis method.

Herein, synthesis procedure and factors including GO loading, pore size of substrate and draw solution concentration were optimized toward obtaining the best desalination performance by GO/cross-linked nanocomposite over nylon membrane. Furthermore, as the membranes should be versatile in order to be used in different processes, two different

evaluation methods (i.e., forward osmosis (FO) and dead end) were considered to assess the desalination performance of the prepared membranes.

2. Experimental

2.1. Materials and methods

In synthesis procedure, analytical grade of graphite, sulphuric acid, N-isopropylacrylamide (NIPAM), N,N'-methylenebisacrylamide (MBA), ammonium persulfate (APS), potassium permanganate, urea, nitric acid, hydrogen peroxide were used to prepare the membranes, which were purchased from Sigma-Aldrich, Germany.

2.2. Synthesis procedure

In the synthesis procedure, GO was synthesized through a fast and facile solvothermal method [33] in which mixture of graphite powder, potassium permanganate, concentrated sulfuric acid and nitric acid was introduced to Teflon bottle which was held in stainless steel autoclave followed by heating at 135°C for 1.5 h. Then the mixture was cooled to room temperature and slowly added to a mixture of DI water and H₂O₂ which yielded a light yellow solution. The resulting solution was centrifuged and neutralized by DI water and after performing the freeze-drying process, GO was obtained. Furthermore, sonication was carried out to exfoliate the GO flakes (125 W for 10 min) to prepare monolayer or multilayer GO in two concentrations (i.e., 2 and 6.3 mg mL⁻¹).

In following, for fabrication of the nanocomposite membrane, copolymerization of GO into two monomers of NIPAM and MBA in presence of APS as initiator was carried out by using spin-coater [34]. As a support layer, nylon microporous filter (purchased from Tianjin Navigator Lab Instrument, RPC, Tianjin, China) was used with two different pore sizes (0.22 and 0.45 μm). Then, coating of the nylon substrate on precursor solution was conducted for 30 s followed by setting on a spin coater and spanning for 30 s at 1,000 rpm and placing in a convection oven (Thermo Fisher, Waltham, Massachusetts, United States) at 80°C for 2 h for complete free-radical polymerization of the monomers. To ensure the preparation of a smooth nanocomposite of GO-polymer on nylon substrate, coating and polymerization were repeated for four times.

2.3. Desalination performance assessment

In the experiments, effects of various factors on desalination performance were studied. Different factors such as pore size of the nylon substrate (i.e., 0.22 and 0.45 μm), concentration of the draw solution (i.e., 0.5 and 1 M), and graphene oxide content (i.e., 6.3 and 20 mg) were investigated. To evaluate the performance of the membranes, a home-made FO setup was used. Also, a dead-end setup was employed to assess the performance of membrane in desalination. In FO experiments, the desalination performance is evaluated in terms of reverse salt rejection flux (RSR) which is based on concentration difference between two sides of the membrane.

RSR was calculated by multiplying the rate of change of feed concentration with time by the volume of the feed

solution and then dividing by the area of the membrane, expressed in units of $\text{g m}^{-2} \text{h}^{-1}$ or $\text{mol m}^{-2} \text{h}^{-1}$.

The RSR value is determined using the following equation:

$$\text{RSR} = \frac{V(C_t - C_0)}{A \times t} \quad (1)$$

where V is volume of feed solution, A is the effective area of the membrane, t is duration of the experiment, and C_t and C_0 show the concentration at t min after experiment and at beginning, respectively. The RSR_0 corresponds to reverse salt flux in first 30 min and the RSR_{15} represents the salt rejection in the last 30 min of the FO experiment. The reason for considering this equation for emulating the desalination performance is that it considers the most important factors of each membrane. In contrast to evaluation by removal percentage which considers only initial and final concentrations, here effects of effective area of the membrane and also time of experiments are also considered which gives a detailed result.

Retention mechanism in membranes is reliant on size sieving, electrostatic repulsion and adsorption [35,36], usually acting in tandem to affect separations.

Additionally, in the dead-end experiment the following equation was utilized to assess the membrane's performance:

$$\text{Rejection}(\%) = \frac{C_f - C_p}{C_f} \times 100 \quad (2)$$

where the C_f and C_p correspond to electrical conductivity (EC) of the feed and permeant concentration, respectively.

2.4. Characterization

To characterize the prepared membranes, different techniques were employed. To study the morphology of the samples, field emission scanning electron microscopy (FESEM) was used (MIRA3 Tescan, Kohoutovice, Czech Republic, FESEM with different magnifications). To determine the interlayer spacing of the graphene nanosheets, X-ray diffraction (XRD) was adopted by X-ray diffraction using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54\text{\AA}$) (Inel Equinox 3000 instrument, Artenay, France). Diffraction patterns were recorded in the 2θ range of 10° – 110° , with a scan rate of 0.02°s^{-1} . Furthermore, by capturing the contact angle images of the samples' droplet, hydrophilicity of the prepared membranes was investigated (by OCA 25 Dataphysics). Moreover, the atomic force microscopy (by ARA Research, Tehran, Iran) was adopted to study the topology of the synthesized GO/nylon membrane.

3. Results and discussion

3.1. Characterization

The XRD pattern of the GO is shown in Fig. 1. It can be observed that before adding monomers and polymerization, the main peak was emerged at 2θ of 12.46° . This implies that the interlayer spacing of the GO nanosheets was about 7.1\AA which is not suitable for efficient separation of the

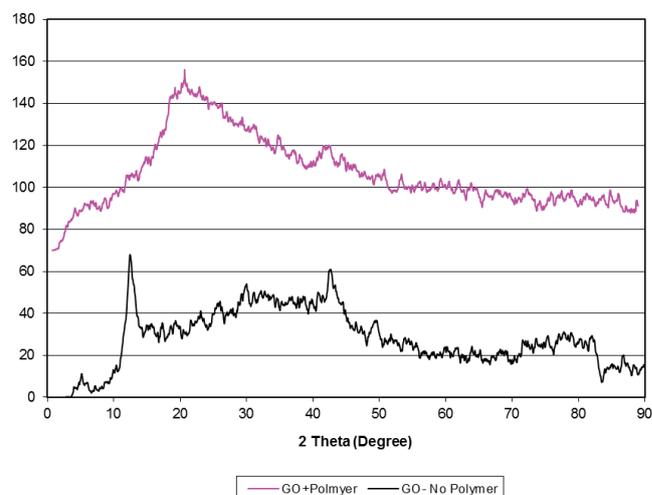


Fig. 1. XRD patterns of the prepared GO and GO/polymer nanocomposite.

target ions with smaller sizes. So it is essential to decrease the interlayer spacing of GO nanosheets to hinder the passage of the salt ions. One the most efficient alternatives for decreasing the d spacing and preparing GO membranes for enhanced water desalination is polymerization by appropriate monomers. The polymerization of the GO by monomers not only decreases the d spacing to favorite level but also improves the stability and strength of GO nanosheets against chlorine. The XRD pattern of GO after polymerization is shown in Fig. 1, in which, it is evident that the characteristic peak is shifted to 2θ of 19.71° reflecting the d spacing of the 4.5\AA . As it was expected, after polymerization the d spacing of the GO was decreased significantly. Actually by tuning and engineering the d spacing of the GO nanosheets, separation efficiency can be enhanced substantially.

Furthermore, the FESEM micrographs of the nylon substrate and GO/nylon nanocomposite membrane are shown in Fig. 2. Figs. 2(a) and (b) represent the nylon substrate before spin coating which is composed of uniform pores. After spin coating, a thin layer of modified GO was deposited over the nylon. It is of great importance to prepare a membrane with uniform structure to provide almost the same performance everywhere over the membrane. As the side view of the GO/nylon membrane shows that the nylon substrate is completely covered by co-polymerized GO which is effective in desalination. In addition, to study the topology of the deposited thin layer, AFM image was used. The AFM image in Fig. 3 indicates that almost a smooth layer is deposited through spin coating; however, a hill is also seen in this figure whose height is about 81.4 nm .

As the hydrophilicity of the membrane is an important factor in desalination process, it was determined for the synthesized sample. As shown in Fig. 4, the contact angle of the sample is about 11.73° which implies that the prepared membrane is hydrophilic [37]. It is reported that the hydrophilic membranes contribute to high flux permeability of the solution which is attributed to interaction of the molecules with polar groups of GO [38].

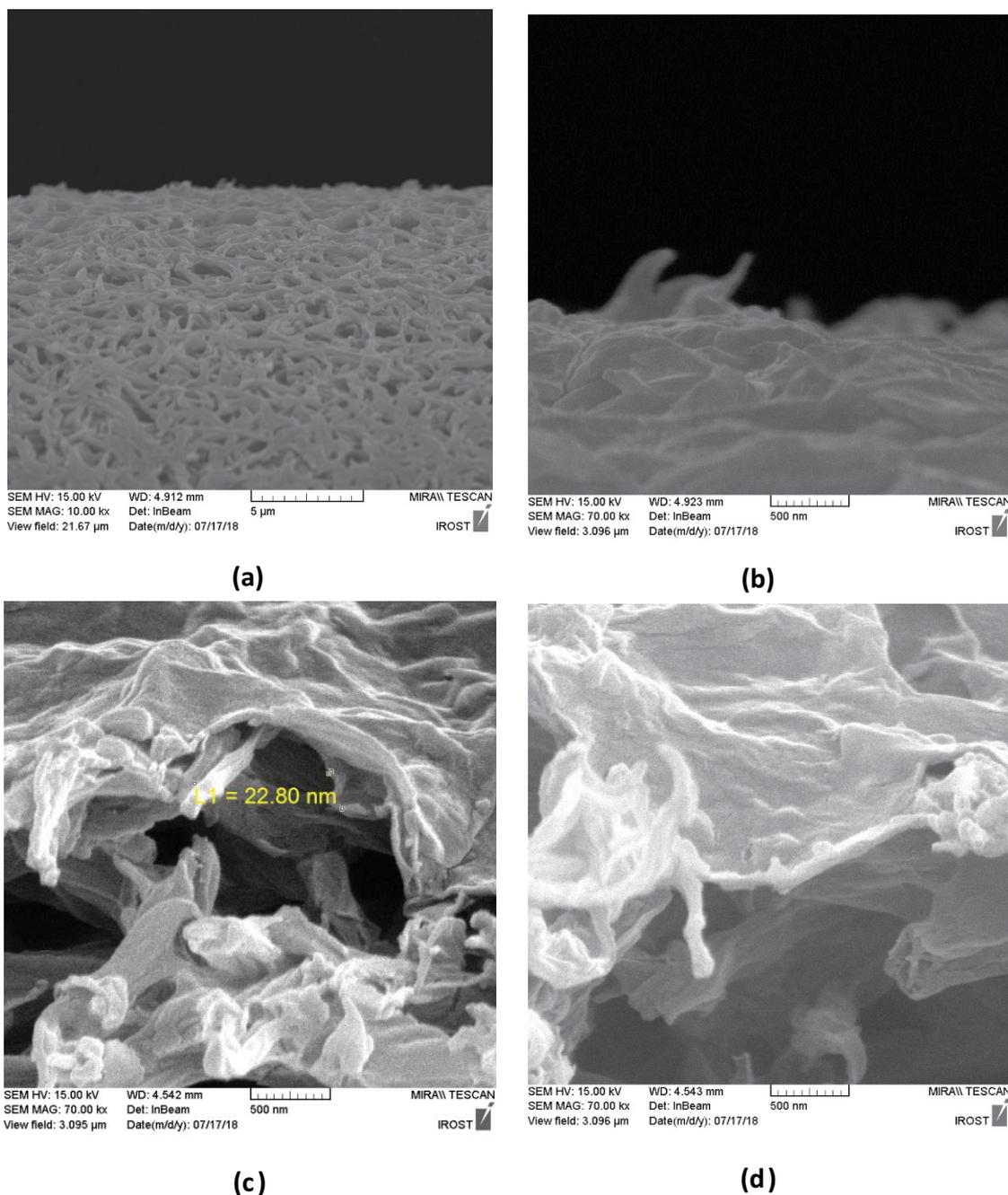


Fig. 2. FESEM micrographs of ((a) and (b)) nylon-66 substrate (side view), ((c) and (d)) GO/nylon membrane.

3.2. Desalination performance

Performance of the membranes is assessed in terms of permeability and salt rejection. The permeability of the nylon substrate and GO/nylon membrane for water and NaCl solution are shown in Fig. 5. For comparison, pristine nylon substrate was evaluated for which, at first, the pure water flux of $341 \text{ Lm}^{-2} \text{ h}^{-1}$ was obtained and then it was decreased to $129 \text{ Lm}^{-2} \text{ h}^{-1}$ at 1 bar. Then 1 h, the stable flux was observed and average flux of $133 \text{ Lm}^{-2} \text{ h}^{-1}$ was resulted after 1.5 h. In addition, for the GO/nylon membrane, the pure water flux was started by $144 \text{ Lm}^{-2} \text{ h}^{-1}$ and then decreased to

$55 \text{ Lm}^{-2} \text{ h}^{-1}$ at 1 bar. The stable flux was reached after 1 h and TM flux of $52 \text{ Lm}^{-2} \text{ h}^{-1}$ was acquired for this membrane after 1.5 h. Interestingly, Fig. 5 confirms that the compaction on GO/nylon membrane was almost negligible and difference between steady state and the third-hour flux was not significant (i.e., $0.3 \text{ Lm}^{-2} \text{ h}^{-1}$). In following, a 0.1 molar NaCl solution was used as feed for further permeability experiments. The filtration flux of the GO/nylon membrane for NaCl solution started by $62 \text{ Lm}^{-2} \text{ h}^{-1}$ and it was reduced to $24.7 \text{ Lm}^{-2} \text{ h}^{-1}$. The flux of NaCl solution through GO/nylon became stable and the average flux of $25.7 \text{ Lm}^{-2} \text{ h}^{-1}$ was obtained after 1.5 h.

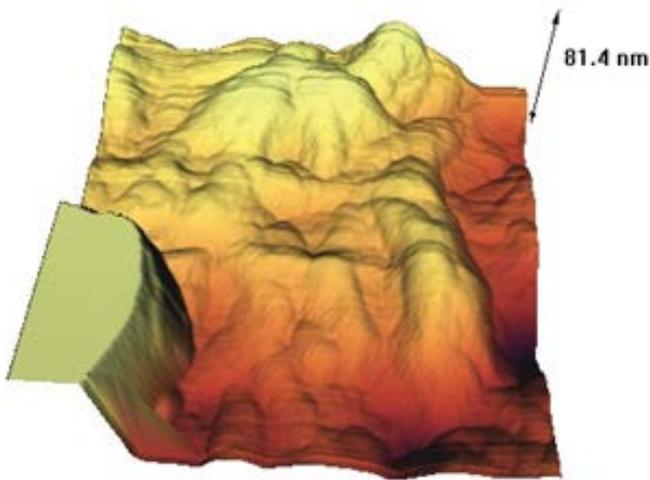


Fig. 3. AFM image of the co-polymerized GO which was spin coated over nylon.



Fig. 4. Contact angle results of the co-polymerized GO.

After reaching the steady state of the Go-nylon membrane by using pure water, feed solution experiments were carried out for an extended period. A 0.1 molar NaCl solution was chosen for the feed solution. The filtration flux of GO-nylon membrane using feed solution began with $62 \text{ Lm}^{-2} \text{ h}^{-1}$ and then decreased to $24.7 \text{ Lm}^{-2} \text{ h}^{-1}$. Stable flux after 1 h, averaging $25.7 \text{ Lm}^{-2} \text{ h}^{-1}$ was obtained after 1.5 h.

3.2.1. FO experiments

The FO experiment results are given in terms of RSR_0 and RSR_{15} which, as mentioned, are indicators of membrane performance in rejection of salt. In these experiments, when the 1 and 0.5 molar NaCl solutions were used as the draw solution, nylon substrate containing $22 \mu\text{m}$ pores provided average RSR_0 and RSR_{15} of 17.75 and 17.74, and 13.69 and 13.49, respectively. In addition, the nylon substrate possessing $45 \mu\text{m}$ pores showed RSR_0 and RSR_{15} of 17.78 and 17.81, and 13.78 and 13.25 for the draw solutions of 1 and 0.5 molar NaCl, respectively. In the next step, effect of sole polymerization through spin coating is investigated which had the RSR_0 and RSR_{15} of 9.29 and 9.47, and 8.74 and 8.91 when the draw solutions of 1 and 0.5 molar NaCl were used, respectively. This indicates the positive effect of polymerization through spin coating which enhanced the overall performance of nylon substrate in salt rejection; however, an acceptable performance was not obtained. For ease of the comparison between the samples, only RSR_0 curve of the membranes is shown. For these samples, the RSR_0 curve is shown in Fig. 6.

In following, the effects of graphene on salt rejection of spin coating over nylon substrate are studied. As stated previously, two different amounts of GO were added during polymerization process. These experiments were carried out on both nylon- $0.22 \mu\text{m}$ and nylon- $0.45 \mu\text{m}$, so that the configuration between substrate and the prepared

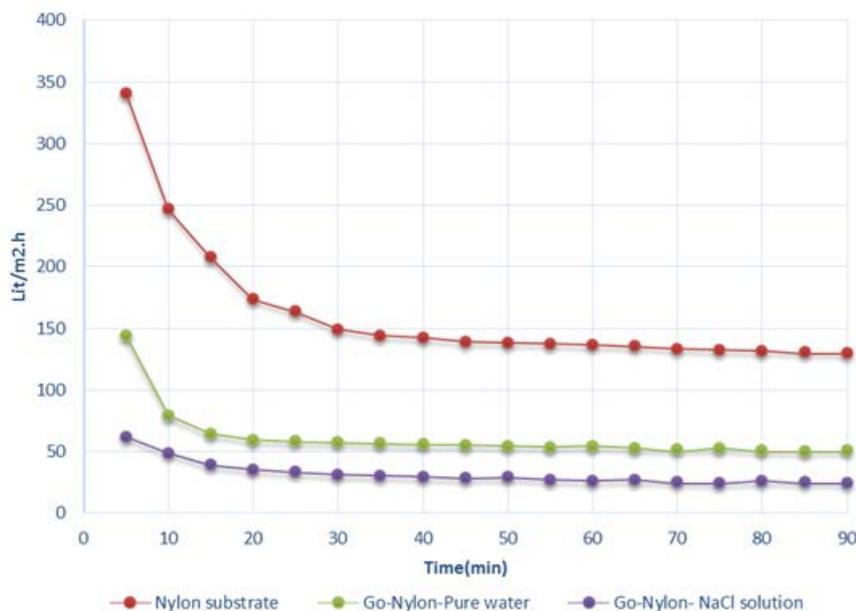


Fig. 5. Permeability of the nylon substrate and GO/nylon for water and GO/nylon membrane by NaCl solution.

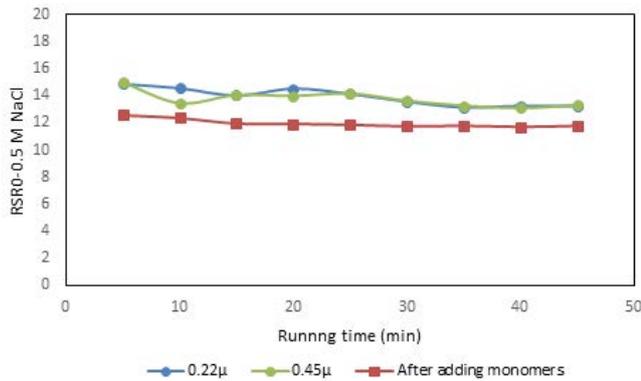


Fig. 6. RSR_0 curve of the nylon substrates containing pores of 0.22 and 0.45 μm along with RSR_0 of polymer over nylon-0.22.

nano-membrane can be studied. The results for membrane possessing 11 mg GO (LNA samples) showed that when the draw solution of 1 M NaCl is used, RSR_0 and RSR_{15} of 8.6 and 8.67 are observed, respectively. In addition, when the draw solution of 0.5 M NaCl is used for LNA sample, the RSR values are decreased significantly indicating the vital effect of draw concentration on overall desalinating performance of the membrane. Furthermore, for the membranes containing 33 mg GO, the RSR_0 and RSR_{15} were decreased by 0.16 and 0.35 for draw solution of 1 M NaCl and by 0.41 and 0.12 for draw solution of 0.5 M NaCl, respectively. Enhancement of the salt rejection activity by increasing the GO content can be attributed to more barriers which block the salts passage and thereby improving the overall desalinating performance. The results for these experiments are shown in Figs. 7 and 8.

The same experiments were performed on the membranes over the nylon-0.45 μm substrate which showed almost better results for draw solutions with higher concentration (Figs. 9 and 10), compared with that of the nylon-0.22 μm . The results showed that when the membrane possessing 11 mg GO is used, RSR_0 and RSR_{15} of 8.32 and 8.58 are obtained for draw solution of 1 M NaCl which are decreased to 6.72 and 6.27 for the draw solution of 0.5 M

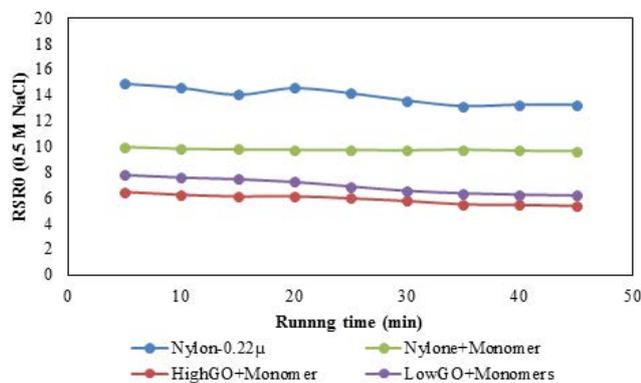


Fig. 7. RSR_0 curve of the co-polymerized GO/nylon-0.22 with different amounts along with those of the bare nylon and nylon/monomer for draw solution of 0.5 M NaCl.

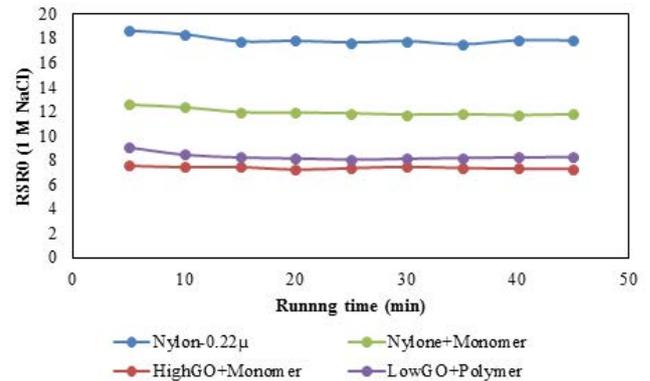


Fig. 8. RSR_0 curve of the co-polymerized GO/nylon-0.22 with different amounts along with those of the bare nylon and nylon/monomer for draw solution of 1 M NaCl.

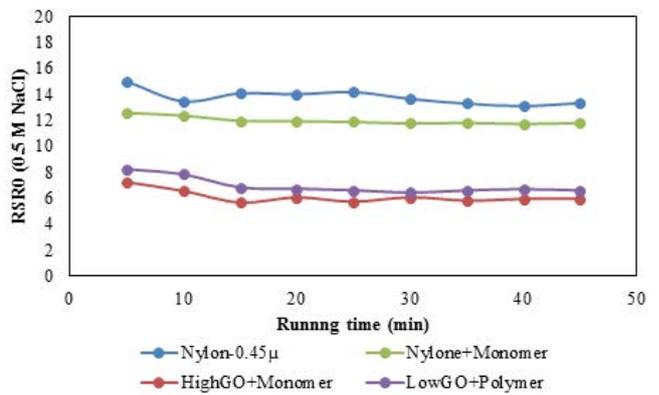


Fig. 9. RSR_0 curve of the co-polymerized GO/nylon-0.45 with different amounts along with those of the bare nylon and nylon/monomer for draw solution of 0.5 M NaCl.

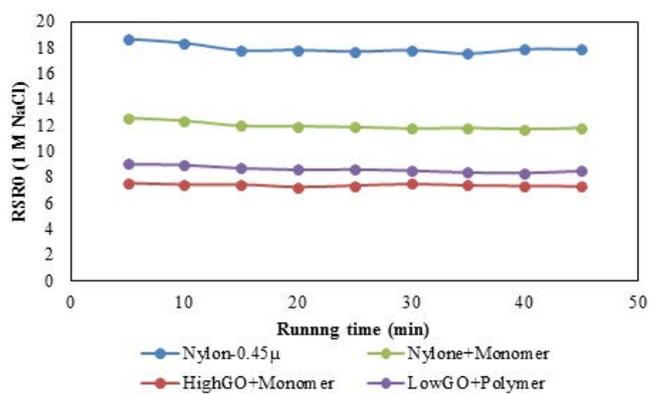


Fig. 10. RSR_0 curve of the co-polymerized GO/nylon-0.45 with different amounts along with those of the bare nylon and nylon/monomer for draw solution of 1 M NaCl.

NaCl, respectively. Additionally, the membranes which were prepared by 33 mg GO showed RSR_0 and RSR_{15} of 8.04 and 8.35 for draw solution of 1 M NaCl and 6.12 and 6.28 for draw solution of 0.5 M NaCl, respectively. In general, the salt

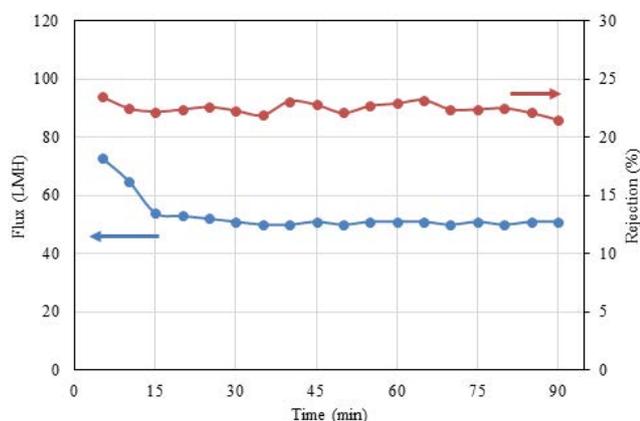


Fig. 11. Solution flux and salt rejection performance of the membrane in water desalination through dead-end experiment.

rejection results of the different membranes showed that by increasing the GO content, better desalinating performance is observed which can be due to more barriers against the salts passage. Also it was found that nylon substrate with smaller pores is more effective in salt rejection of the draw solutions with lower NaCl concentration; however, the nylon substrate possessing larger pores showed better performance for draw solution with higher concentration. As the best results were obtained for the membrane containing 33 mg GO over nylon-0.45 μm substrate, this sample was chosen for dead-end experiments.

The optimized performance of the co-polymerized GO over nylon substrate can be the result of different factors. By adding the monomers to GO, d spacing of the GO nanosheets was engineered to reach the optimal level for rejection of salt ions. This is evident from the results, which confirmed the significantly better results for modified GO/nylon membrane. The other factor, which can contribute to better performance, is the configuration between modified GO and nylon substrate which was clarified in the experiments. Additionally, the effect of GO content was also elucidated for which positive proportion between GO content and desalination performance was observed.

3.2.2. Dead-end experiments

The flux performance and salt rejection activity of the co-polymerized GO over nylon is shown in Fig. 11. In this experiment, a descending trend was obtained which indicates that the GO/nylon membrane shows slightly fouling behavior during the filtration of the NaCl containing solution. It is well known that the membrane compaction is essential for the NF and RO membranes which is a function of applied pressure and the type of membrane which is prepared for this purpose [39,40]. However, regarding the fibrous structure of the substrate and uniform coverage by modified GO, compaction was not significant. As the dead-end method is low-cost and has a simple operation, the sample which showed the best performance in FO experiments, was assessed in dead-end cell too. To perform the experiment

in dead-end cell, the feed solution of 1,200 ppm NaCl was used. Performance of the membrane in dead-end test is shown in Fig. 9. As can be observed, the average flux during the test was $45.6 \text{ L m}^{-2} \text{ h}^{-1}$ which is comparative with the results reported in literature. Furthermore, the average salt rejection of 23.4% was observed for this sample which is in an acceptable level; however, it should be enhanced in further researches. Accordingly, it is believed that the prepared membrane is better suited for FO operation and should be modified to yield better dead-end results.

4. Conclusion

In this research work, regarding the crucial importance of the drinking water for humanities, an efficient membrane was synthesized for water desalination. The membrane was prepared by tuning and engineering the interlayer spacing of GO which was carried out by co-polymerization of suitable monomers. Then, the modified GO was spin-coated over different types of nylon substrates. To assess the desalination performance of the co-polymerized GO/nylon nanocomposite membrane, the solution of NaCl was utilized in different experiments of FO and dead-end cell. The results indicated that co-polymerization of GO enhances the salt-rejection activity of the nylon substrate significantly while providing acceptable solution permeability. In addition, the activity of membranes was configured by pore size of the nylon substrate and it was found that the nylon substrate possessing larger pores is more suitable for desalination of the draw solutions with higher concentrations, and vice versa. Moreover, it was observed that the co-polymerized GO/nylon nanocomposite membrane is better suited for FO process which should be further optimized for better dead-end results.

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