

A novel approach to bind graphene oxide to polyamide for making high performance Reverse Osmosis membrane

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Abstract. We report the novel thin film composite RO membrane modified by graphene oxide. The thin film composite RO membrane was exposed to 2000 mg/l sodium hypochloride; thereafter it was subjected to different graphene oxide concentration ranging from 50 mg/l to 1000 mg/l in water. The resultant membrane was crosslinked with 5000 mg/l N-hydroxysuccinimide. The performance of different membranes were analysed by solute rejection and water-flux measurement. It was found that 100 mg/l graphene oxide exposure followed by 5000 mg/l N-hydroxysuccinimide treatment resulted in the membrane with the highest solute rejection of 97.78% and water-flux of 4.64 Liter per sqm per hour per bar g. The membranes were characterized by contact angle for hydrophilicity, scanning electron micrographs for surface morphology, energy dispersive X-Ray for chemical composition of the surface, Atomic force microscope for surface roughness, ATR-FTIR for chemical structure identification. It was found that the graphene oxide modified membrane increases the salt rejection performance after exposure to high-fouling water containing albumin. Highly hydrophilic, antifouling surface formation with the nanomaterial led to the improved membrane performance. Moreover, the protocol of incorporating nanomaterial by this post-treatment is simple and can be applied to any RO membrane after it is manufactured.

Keywords: thin film composite RO; graphene oxide; N-hydroxysuccinimide; antifouling; hydrophilic

1. Introduction

Water is an essential resource depleting on account of rapid industrialisation and growth in population leading to water- scarcity like conditions (Shannon *et al.* 2008). The abundant source of water is sea water which constitutes of more than 97% of the total presents on the earth. Desalination of the sea water is one of the most pragmatic options to fulfil the ever-increasing demand of water (Buonomenna 2013). Development in membrane technology in the last decade has made desalination so affordable that it can also be an option to generate water from seawater as compared to laying the long distance pipeline. Reverse Osmosis is an established technology with widespread application in desalination and water reuse; expanding at the rapid rate.

Thin Film Composite RO membrane technology is very efficient and economical in converting saline water into potable water or reusing the wastewater. Thin Film Composite RO membrane has

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an advantage that the each layer can be independently tuned for improvement in overall membrane performance (Petersen and Cadotte 1990). The base layer of the membrane is the fabric, the layer above that is poly sulfon of thickness 25-45 μm with pore size of 50-100 nm, the top most layer is a layer of polyamide of thickness 100-200 nm with pore size less than 1 nm (Raval and Gohil 2009, Khorshidi *et al.* 2016, Rangarajan *et al.* 2011).

It has been demonstrated that the water-flux of TFC RO membrane can be increased by controlled sodium hypochlorite treatment (Raval and Gohil 2010). It has been reported that nanotechnology plays an important role in water treatment (Raval *et al.* 2012). Improvement in water-flux can be achieved by incorporating nanomaterials in the top polyamide layer of the membrane in order to make the membrane process energy efficient. The nanoparticles which have been used are zeolite (Duan *et al.* 2015, Jeong *et al.* 2007, Dong *et al.* 2015), silica, MCM-41, Graphene oxide/TiO₂ and carbon nanotubes (Lee *et al.* 2014, Holt *et al.* 2006) to tailor the top polyamide layer for improved performance (Zhang *et al.* 2011, Lind *et al.* 2009, Fathizadeh *et al.* 2011, Dong *et al.* 2015, Jadav and Singh 2009, Yin *et al.* 2012). It has been shown that graphene and other 2-dimensional materials lead to novel functionality in the membrane (Gugliuzza *et al.* 2017). Zeolite nanoparticles were incorporated by interfacial polymerisation and by dispersing it in *m*-Phenyldiamine (MPD) and trimesoylchloride and coating it on a porous polysulfon membrane as stated by Fathizadeh *et al.* (2011), Jadav and Singh (2009) prepared silica nanoparticles and dispersed them in MPD solution and exposed it to Polysulfon base with immediate exposure of TMC solution in *n*-Hexane. Hydrophilic, anti-fouling membrane surface formation has been reported by incorporating reduced graphene oxide and TiO₂ in top barrier layer (Safarpour *et al.* 2015). Yin *et al.* (2012) prepared MCM-41 silica nanocomposite by in situ interfacial polymerisation with the use of MPD and TMC with nanoparticle dispersed. Carbon nanotubes can also be used as nanomaterials, as stated by Song *et al.* (2016). They dissolved Poly sulfone (PSf) and poly ethelene glycol into dimethylacetamide (DMAc) .They prepared nanocomposite dispersing Carbon nanotubes in DMAc before adding PSf into it. They then casted the solution on a glass sheet followed by treating it with a coagulating solution. The formed membrane was treated with MPD solution followed by TMC/*n*-Hexane solution (Song *et al.* 2016).

One of the most fascinating materials is Graphene Oxide. Containing plenty of oxygenous functional groups like carboxyl, epoxy and hydroxyl groups, it has super hydrophilic nature (Hu and Mi 2013, Park *et al.* 2015) and also possesses good anti-fouling property (Choi *et al.* 2013). Graphene Oxide can be used for surface modification of TFC-RO membrane as it produces stable bonds on the composite membrane with better interaction (Stankovich *et al.* 2006). The present paper demonstrates the novel and easier approach to bind graphene oxide over the polyamide layer of Thin Film Composite RO membrane by post-treatment with no requirement to alter the set process of making membrane. The novel membrane demonstrated the step change in performance i.e., salt rejection and water-flux.

2. Experimental

2.1 Materials and reagents

Graphene Oxide nanoparticle powder was supplied by Sigma-Aldrich with 4-10% edge oxidised. The Base TFC-RO membrane was prepared at CSIR-CSMCRI Bhavnagar by the method reported (Rangarajan *et al.* 2011). The active chlorine solution was made from Sodium

Hypochlorite, which was purchased from Rankem containing 4-6% (w/v) Chlorine in it. The cross linking agent N-Hydroxysuccinimide(NHS) was bought from Sigma-Aldrich with 98% purity. Albumin was used for testing the membrane fouling performance.

2.2 Synthesis of GO-TFC membranes

Base Thin Film Composite membrane was soaked in Deionised (DI) water over night. A Solution of Sodium Hypochlorite was prepared with concentration of 2000ppm with proper mixing of the solution. The concentration of sodium hypochlorite was verified by iodometric titration. The membrane was placed on a glass plate and taped properly on its sides. The membrane containing glass-plate was then dipped into the Sodium hypochlorite solution for one hour. The exposed membrane was then taken out form the hypochlorite solution and cut into two pieces. One of the two pieces was perfectly washed with plenty of water, exposed to sodium m-bisulfite to neutralize the active chlorine and preserved. Graphene oxide solution was prepared by dispersion of GO nanoparticles in DI water. The GO solution was properly stirred for 30 minutes followed by 30 minutes of sonication. The remaining part of the membrane was then exposed to GO solution and kept for one hour. Different sets of membranes were prepared starting from 50 ppm of GO to 1000 ppm of GO. N-Hydroxysuccinimide (NHS) was used as the crosslinking agent for binding of the GO particles on the surface of the membrane. After removal of the membrane from GO solution it was exposed to a solution containing 5000ppm of NHS for one hour. The membrane was taken out of NHS solution and treatment was done by keeping it in oven at 50° C for 30 minutes. Then permeation studies were done on the prepared membranes at various GO concentrations.

2.3 Characterisation of the GO-TFC membranes

The membranes were characterised using different characterisation methods. Scanning Electron Microscope (SEM) was used for imaging the surface morphology of the membranes. The cross-sectional view of the membranes was also taken using SEM. Energy-dispersive X-ray (EDX) of all the membranes was done for elemental analysis of the membrane. Atomic Forced Microscopy (AFM) was done for knowing the membrane surface roughness. Attenuated total reflectance (ATR)- Fourier transform infrared spectroscopy(FTIR) was done for all the samples i.e.; the base membrane, the membrane treated with Sodium Hypochlorite and GO membranes for analysis of the active functional groups present. Contact angle of all the membranes were done in order to find the membrane hydrophilicity. Glass transition temperature of Thin Film Composite RO membrane and Graphene oxide treated RO membrane were found by differential scanning calorimetry (DSC).

2.4 Salt rejection performance of the membrane

NaCl solution of 2000 mg/l concentration was prepared for performing rejection experiment; circular coupons of the membrane were cut whose performance has to be studied. The coupons were fitted in a RO testing kit and were tested at 250psig pressure.

2.5 Interaction of Graphene oxide treated membrane with Albumin

Graphene oxide treated membrane (GO-1000) was subjected to 5000 mg/l albumin solution in

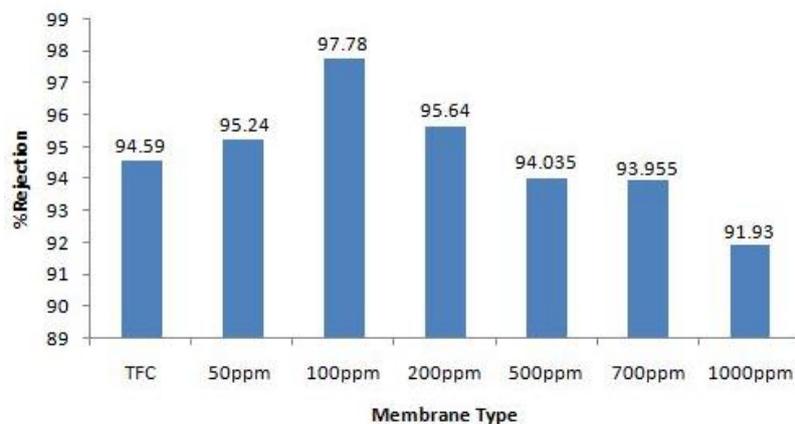


Fig. 1 Salt rejection of different membranes

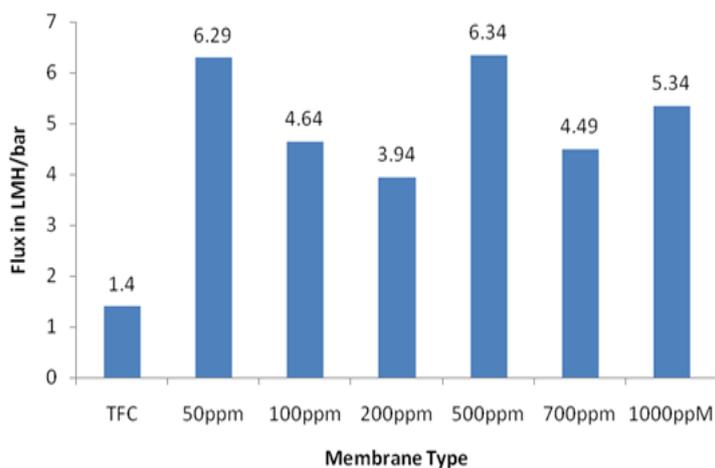


Fig. 2 Water-Flux obtained from different membranes

recirculation mode for 12 hours. The resultant membrane was taken out, dried and kept for scanning electron micrographs.

3. Results and discussions

The x axis of the plot represents the concentration of the Graphene Oxide solution, in which the membrane was exposed.

50ppm: TFC RO membrane with 50 mg/L graphene oxide post-treatment

100ppm: TFC RO membrane with 100 mg/L graphene oxide post-treatment

200ppm: TFC RO membrane with 200 mg/L graphene oxide post-treatment

500ppm: TFC RO membrane with 500 mg/L graphene oxide post-treatment

700ppm: TFC RO membrane with 700 mg/L graphene oxide post-treatment

1000ppm: TFC RO membrane with 1000 mg/L graphene oxide post-treatment

The rejection percentages of different membrane are shown in Fig. 1 and the corresponding flux are shown in Fig. 2.

The x axis of the plot represents the concentration of the Graphene Oxide solution, in which the membrane was exposed.

50ppm: TFC RO membrane with 50 mg/L graphene oxide post-treatment

100ppm: TFC RO membrane with 100 mg/L graphene oxide post-treatment

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500ppm: TFC RO membrane with 500 mg/L graphene oxide post-treatment

700ppm: TFC RO membrane with 700 mg/L graphene oxide post-treatment

1000ppm: TFC RO membrane with 1000 mg/L graphene oxide post-treatment

It can be seen from Fig. 1 that salt rejection of the TFC RO membrane increased from 94.59% to 97.78% when the membrane was treated with 100 mg/l graphene oxide solution. Thereafter, with increase in Graphene oxide concentration; there was a steady decline in salt rejection. This shows that Graphene oxide could bind polyamide layer after activation with sodium hypochlorite followed by N-Hydroxy succinimide crosslinking. However, on increasing concentration of graphene oxide, agglomerates form and they do not bind the membrane and the membrane salt rejection declines due to oxidative treatment of sodium hypochlorite. Thus, a decline in salt rejection after 100 mg/l was observed. Fig. 2 shows that the water-flux increased significantly with Graphene oxide; with the same 100 mg/l GO concentration, the water flux increased to 4.64 LMH/bar as compared to 1.4 LMH/bar for TFC RO membrane. The highest water-flux achieved with 500 mg/L GO treatment being 4.5 times the virgin TFC RO membrane; the treatment achieved superior membrane performance. Water-flux increased from 1.4 to 6.29 LMH/bar for 50 mg/l Graphene oxide treated membrane; however with increasing the concentration of Graphene oxide further upto 200 mg/l, water-flux declined because of aggregates formation. Further, increasing concentration of Graphene oxide to 500 mg/l, water absorption due to hydrophilic surface increased the water-flux, which declined further in case of 700 and 1000 mg/l because of resistance due to agglomeration.

As can be seen from Fig. 3(e) and 3(f), the SEM images show that Graphene oxide nanomaterial has embedded on the surface of the TFC RO membrane. The surface morphology of the top layer can be clearly viewed and the changes are remarkable as we go on increasing the Graphene oxide concentration. The agglomeration of the GO nanoparticles can be seen as we go to the maximum GO concentration concluding the saturation of accumulation.

Table 1 shows Energy dispersive X-Rays data. It indicates that with increase in GO concentration the carbon percentage goes on increasing. The Graphene oxide powder has a Carbon percentage of 88.67%. The percentage goes on increasing as we go from 100 PPM GO membrane to 1000ppm GO membrane from 64.92% to 87.29%.

Table 1 EDX data

Sample	C%	O%
TFC	57.46	39.27
GO nano particles	88.67	8.86
GO 100 ppm	64.92	9.32
GO200 ppm	65.07	9.00
GO 1000ppm	87.29	10.37

Scanning Electron Micrographs and Energy dispersive X-Rays

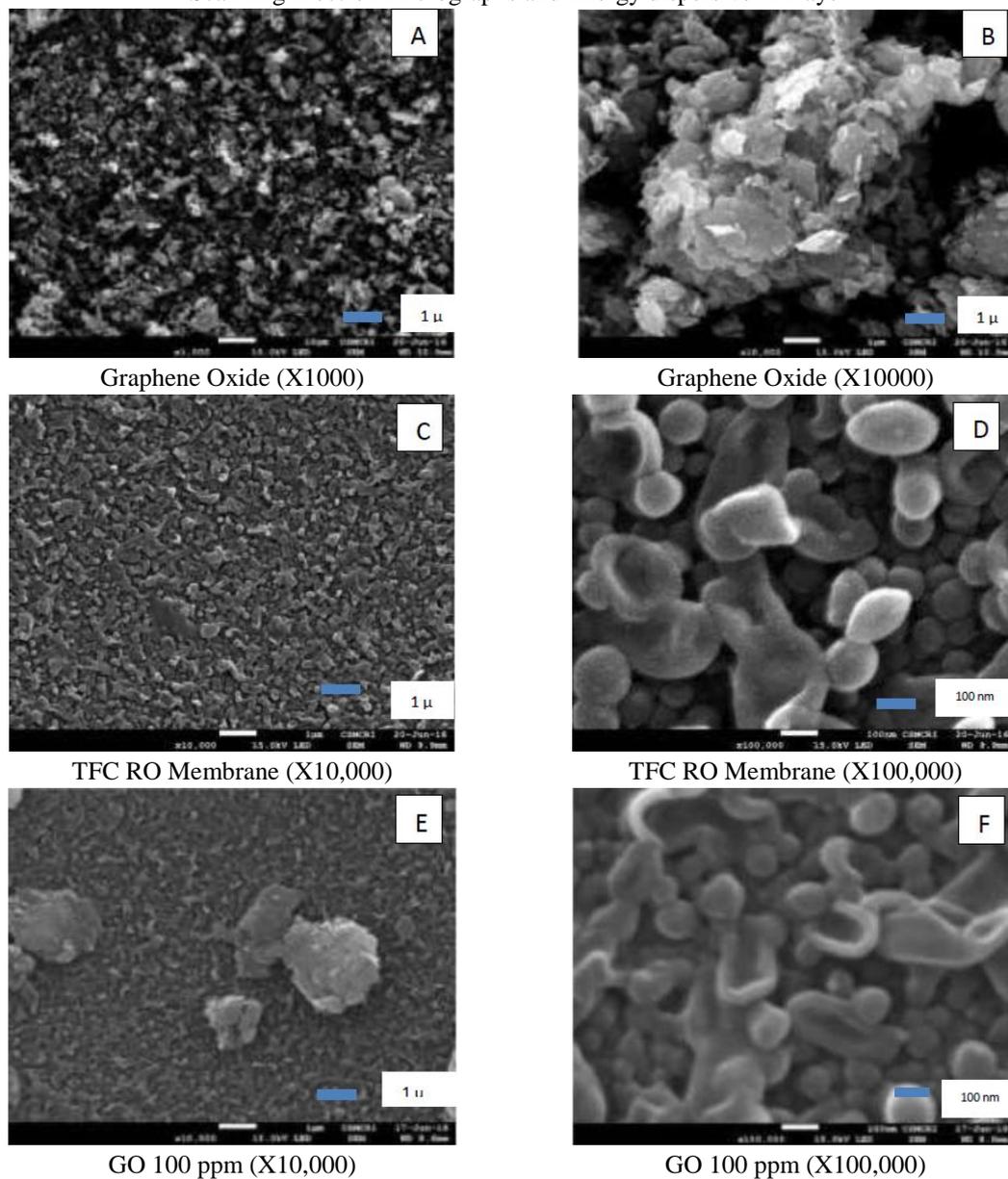


Fig. 3 Scanning Electron Micrographs of membrane samples

Table 2 AFM data of membranes

Membrane	Roughness Average (nm)	Surface skewness	Surface area ratio
TFC	49.7	0.527	14.863 %
TFC-Hypo	45.2	0.274	27.972 %
TFC-GO 100ppm	57.1	0.289	55.306 %
TFC-GO 1000 ppm	103	1.192	250.4%

Atomic Forced Microscopy Images and data

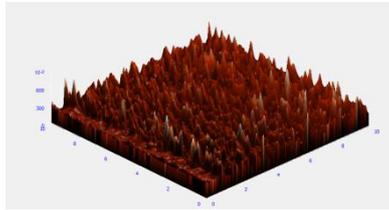


Fig. 4(a) TFC RO membrane

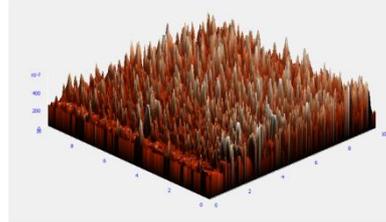


Fig. 4(b) TFC - HYPO (2000 mg/l - 1 hour)

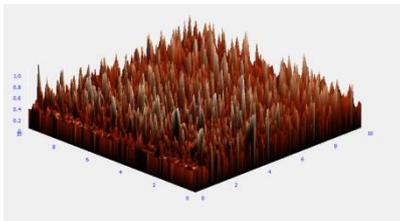


Fig. 4(c) 100 ppm GO nanocomposite

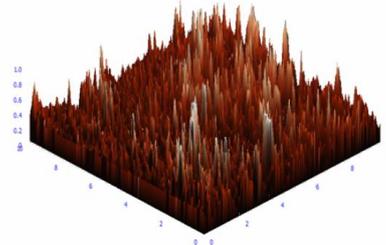
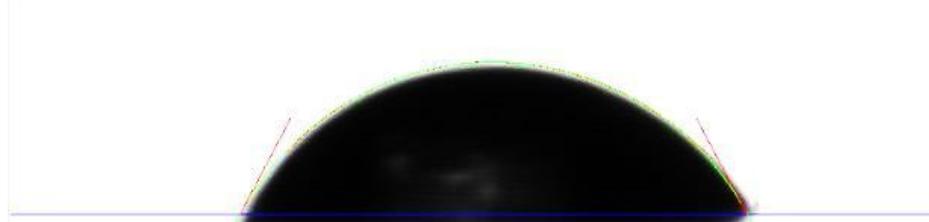


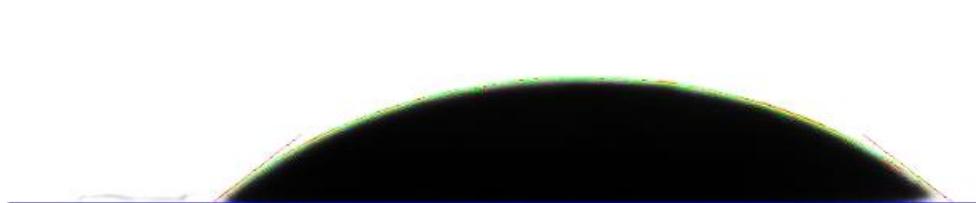
Fig. 4(d) GO-1000 ppm GO nanocomposite

CA [L] 62.2
CA [R] 62.2



(a) Base TFC

CA [L] 37.6
CA [R] 37.6



(b) 100ppm GO membrane

Fig. 5(a) and 5(b) Contact angles to understand hydrophilicity of the membrane

Atomic Force Microscope images in Fig. 4(a), 4(b) and 4(c) and data in Table 2 suggest that with increase in Graphene oxide concentration the value of Surface area ratio increases from 14.863% to 55.306%, which means that the effective surface area for water flow increases. This property results in increasing the flux of the membrane. Increasing Graphene oxide concentration further to 1000 ppm, it can be seen that the average roughness increases to 103 nm and surface area ratio increases dramatically. This is because of agglomeration of nanomaterial as can be seen

from Fig. 4(d).

Contact angle measurements of different membranes: Fig. 5(a) and 5(b) shows the contact angle measurement. Contact angle is a measure of the surface hydrophilicity of any surface, from contact angle studies it can be clearly seen that Graphene oxide treated membrane have lower contact angles implying more hydrophilic nature.

Fig. 6 shows dynamic light scattering of Graphene oxide nanomaterial. It shows that the average hydrodynamic radius of Graphene oxide material is 100 nm.

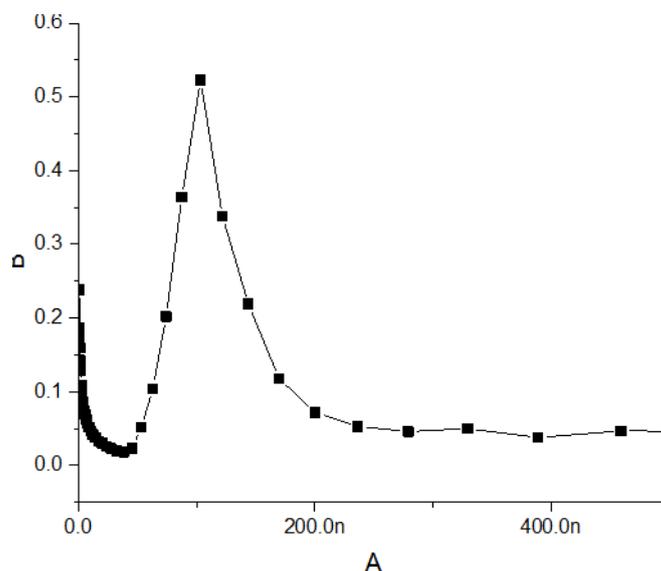


Fig. 6 Dynamic light scattering image of Graphene oxide nanomaterial

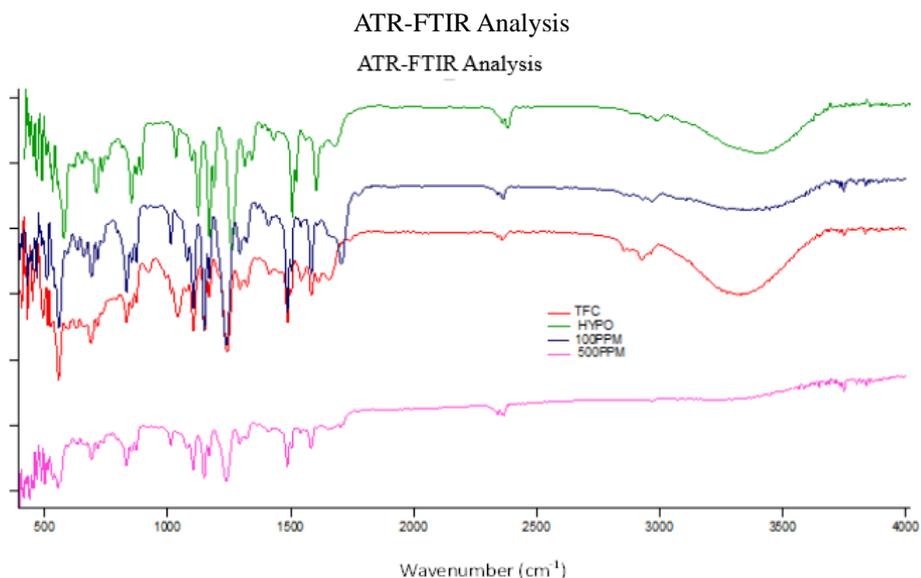


Fig. 7 ATR-FTIR Spectra of membranes

Study of membrane performance against fouling

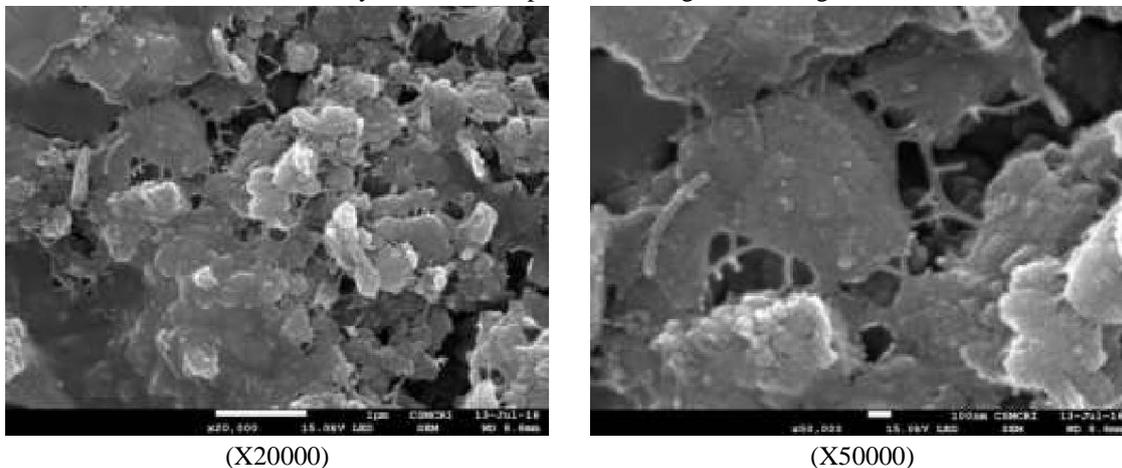


Fig. 8 SEM images of GO-1000ppm fouled membrane

Fig. 7 demonstrates the chemical structural modification on account of binding with graphene oxide. As we can see the peak corresponding to hydroxyl group present in polyamide layer of Thin Film Composite RO membrane at wave number 3400 cm^{-1} disappears for 500 mg/l graphene oxide composite RO membrane. This shows that hydroxyl group of polyamide layer has been utilized in binding with graphene oxide. Moreover, the chemical structural changes in ester and ether linkages are visible from the spectra.

Fig. 8 shows the Albumin fouled membrane (GO-1000). As visible from the SEM images in Fig. 8, there has been an interaction between Albumin and Graphene oxide over the membrane surface; this may be instrumental in retaining salt rejection performance of the membrane. It can be investigated in a future study.

4. Conclusions

It has been observed from the experimental results that graphene oxide can be used for surface modification of Thin Film Composite RO membrane. GO modified RO membrane exhibited significant improvement in in water-flux and solute rejection. The surface hydrophilicity has increased as visible from decline in contact angle. ATR-FTIR spectra suggested that the graphene oxide has chemically attached to polyamide barrier layer of RO membrane. Scanning electron micrographs have clearly demonstrated the presence of graphene oxide on the membrane layer and increase in pore-density on account of graphene oxide. Energy dispersive X-Ray confirmed the presence of graphene oxide by increase in carbon concentration of the membrane samples with increasing concentration of GO. Atomic force microscope images have demonstrated that the increase in surface area ratio from 14.86% to 55.3% increased the effective surface area available for flow of water; that justified increase in water-flux.

In this way, graphene oxide modified RO membrane demonstrated the improved overall performance with better antifouling performance and opens the possibilities for future work in this area.

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