



## Polysulfone nanocomposite membrane embedded by Graphene Oxide for removal of humic acid from water

N. Ranjbaran<sup>1,2</sup>, R. Yegani<sup>1,2,\*</sup>, A. Akbari<sup>1,2</sup>, M. Chapalaghi<sup>1,2</sup>

1. Faculty of Chemical Engineering, Sahand University of Technology, Tabriz, Iran

2. Membrane Technology Research Center, Sahand University of Technology, Tabriz, Iran

ryegani@sut.ac.ir

### Abstract

This study was performed to investigate effect of different concentrations of graphene oxide (GO) nanosheets on fouling of polysulfone (PSf) membranes applied in humic acid filtration. The GO was prepared from graphite and characterized by FTIR and XRD. The mixed matrix membranes were prepared with different percentages of GO. The membranes were characterized using a set of analyses and the results showed that the addition of GO up to 0.3 wt.% resulted in an increase in hydrophilicity, mechanical properties and water flux of membranes. Antifouling properties of the membrane was also investigated in filtration of humic acid solution and the results showed that reversible fouling and flux recovery of membranes were increased at the presence of GO.

**Keywords:** : Polysulfone, Graphene Oxide, Antifouling, Nanocomposite membrane

### Introduction

Humic acid (HA) is the major constituent of dissolved natural organic matter (NOM) which is found in surface and ground water. HA has been implicated in bacterial growth in water [1]. The presence of HA in surface water causes health problems because it reacts with disinfectants during the water treatment process and form toxic and carcinogenic disinfection by-products (DBPs) [2]. Therefore, it is necessary to remove HA from water using effective treatment processes. Electrocoagulation [3], adsorption [4], oxidation [5], and membrane filtration [1, 6] have been used to minimize concentration of HA in aqueous solution, surface and ground water. Among these processes, membrane filtration has been considered as an efficient method because of its low cost, high efficiency and less energy requirement and ease of operation [7]. For membrane filtration, polysulfone (PSf) based membranes are used most extensively because of its excellent thermal, mechanical, chemical compatibility and resistance over wide range of pH [8]. The major drawback of PSf membranes is their hydrophobic nature which causes them to suffer from fouling and possess low membrane life time [7].

So, all over the world, researchers are looking for a membrane with finely-balanced characteristics. The most widely employed method for increasing the surface hydrophilicity is to blend the PSf with some surface modifiers. Shokri et al. showed a technique of increasing hydrophilicity by blending PSf with Organoclay and witnessed enhanced performance of the resulted product[9]. In this direction, Tizchang et al. successfully increased hydrophilicity and antifouling properties of the membrane by preparing polysulfone composite membrane with silanized nanodiamond [10]. Among different nanoparticles, Graphene Oxide (GO) has



attracted much attention due to its unique characteristics such as hydrophilic properties, high surface area, hardness and the presence of different functional groups on the surface which makes the functionalization process much more convenient [11].

In this study, GO was prepared from expanded graphite through modified Hummers method. Then novel GO modified PSf membranes were prepared by blending of GO (0-0.5 wt.%) via non-solvent induced phase separation method. The synthesized PSf/GO Nanocomposite membranes were comprehensively characterized, in terms of the membrane morphology, mechanical and antifouling properties.

## **Experimental**

### **Materials**

Polysulfone (PSf, Udels P-1700, Solvay Advanced Polymer LLC) was used as the membrane material. N-methyl-2-pyrrolidinone (NMP) was purchased from Merck, Germany, and used as a solvent and polyethylene glycol (PEG) ( $M_w = 20,000$  (g/gmol)) was used as poreforming to prepare cast solution. Graphite (Aldrich) was used to manufacture graphene oxide for modification of a PSf membrane. potassium permanganate ( $KMnO_4$ , Sigma-Aldrich, 99%), sodium nitrate ( $NaNO_3$ , SigmaAldrich, 99%), sulfuric acid ( $H_2SO_4$ , Merck) and hydrogen peroxide ( $H_2O_2$ ) were used to oxidize graphite to graphene oxide for exfoliation.

### **Preparation of GO by oxidation of graphite**

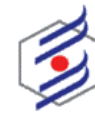
GO was prepared by oxidation of graphite using Modified Hummer's method [12]. Graphite (1.0 g) and  $NaNO_3$  (0.5 g) were mixed with  $H_2SO_4$  (60 mL) for 15 min. After slow addition of  $KMnO_4$  (3.0 g) and stirring for 7 h, the second part of  $KMnO_4$  (3.0 g) was added and stirring was continued for 12 h. By completion of oxidation, DI water (200 mL) and  $H_2O_2$  (30 v%, 10 mL) were added for reduction of remained  $KMnO_4$ . Graphite oxide was obtained by centrifugation, washing the paste with HCl solution (10 v %), and repeated washing of the product with DI water. Exfoliation of graphite oxide dispersion by probe ultrasonication, filtration, and finally drying the product in vacuum at 65°C give GO powders.

### **Preparation of neat and nanocomposite membranes**

Neat and nanocomposite PSf membranes were prepared by using NIPS method. The composition of each casting solution is given in Table 1. In the case of composite membrane, different amounts of GO were dispersed into NMP by applying sonication by probe system (Sonopuls HD 3200, Bandelin) for 15 min. Then, polymer was added to the suspension at 60°C and stirred for 6 h. After solution degassing, membrane was cast at thickness of 150  $\mu m$  using a doctor blade (CoaTest, Taiwan) on a glass plate. The film was immersed in DI water bath which was refreshed three times to complete NMP exchange.

**Table 1: Casting solution composition of neat and nanocomposite PSf membranes**

Membrane	GO/PSf ratio (wt/wt%)	NMP (%)	PEG (%)	PSf (wt%)
PSf	-	75	10	15
PSf/GO/0.1	0.1	75	10	14.985
PSf/GO/0.3	0.3	75	10	14.955
PSf/GO/0.5	0.5	75	10	14.925



### **Characterization of GO FT-IR and XRD**

Fourier transform infrared spectroscopy (FTIR) was carried out on a Bruker spectrometer at a resolution of 4 cm<sup>-1</sup>. An average of 24 scans was taken from the samples dispersed in KBr pellets. X-ray diffraction (XRD) was performed at the step scan mode by a D5000 X-ray diffractometer (Siemens, Germany) equipped with a Cu K $\alpha$  radiation ( $\lambda=0.1540$  nm) at an accelerating voltage of 35 kV and a current of 20 mA.

### **Characterization of membranes Pure water flux (PWF)**

Pure water flux of membranes was determined using a fabricated dead-end filtration system with 5cm<sup>2</sup> of effective membrane area. The feed was pressurized by nitrogen gas cylinder connected to the feed tank. To avoid any compaction, the membranes were compacted for 30 min at 1.5 bar. Then permeation experiment was subsequently carried out at 1 bar and after reaching steady state, water flux was calculated through the Eq. (1):

$$J_0 = \frac{M}{A \cdot t} \quad (1)$$

where  $J_0$  (Kg/m<sup>2</sup> .h) is pure water flux,  $M$  is collected mass of water (Kg),  $A$  is effective membrane area (m<sup>2</sup>) and  $t$  is sampling time (h).

### **Contact angle and mechanical properties**

Hydrophilicity of the membranes was evaluated by a contact angle goniometer (PGX, Thwing-Albert Instrument Co., USA) in a sessile drop technique at room temperature. The average of 5 measurements was reported to minimize the experimental errors. Tensile stress and elongation at break of hollow fiber membranes were evaluated using a tensile testing machine (Santam STM-5, Iran) at an extension rate of 10mm/min. Three samples of each membrane with length of 150mm were tested and the average values were reported.

### **Filtration experiment**

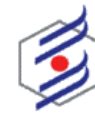
In order to evaluate the effect of GO on the membrane fouling behavior, filtration of HA solution was performed by using the dead-end filtration system. HA solution was prepared by dissolving 0.5 g of HA in 500 ml of DI water at the pH of 6 and stored in the refrigerator (4°C) before use. After measuring pure water flux ( $J_0$ ), the filtration system was filled with prepared HA solution and the permeate flux profile was recorded every 10 min. After 180 min of HA filtration and fouling, PWF was measured and recorded as  $J_1$ . Then, the cake layer on the membrane was rinsed and mechanically removed by a sponge. Afterward, pure water was again passed through the membrane and PWF ( $J_2$ ) was calculated. To investigate the fouling behavior of the fabricated membranes, the flux recovery ratio (FRR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and total fouling ratio (TFR) of the membranes were calculated by using the following equations:

$$FRR(\%) = \left( \frac{J_2}{J_0} \right) \times 100 \quad (2)$$

$$RFR(\%) = \left( \frac{J_2 - J_1}{J_0} \right) \times 100 \quad (3)$$

$$IFR(\%) = \left( \frac{J_0 - J_2}{J_0} \right) \times 100 \quad (4)$$

$$TFR(\%) = \left( \frac{J_0 - J_1}{J_0} \right) \times 100 \quad (5)$$



In order to measure the membrane rejection, the HA concentrations of feed and permeate solutions were determined by using a UV spectrophotometer (Bio Quest CE2501) and the HA rejection of membrane was calculated by using Eq (6):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (6)$$

where R(%) is the rejection percentage,  $C_p$  and  $C_f$  are permeate and feed concentrations, respectively.

### Results and discussion

#### Characterization of GO

As shown in Fig.1. , an apparent peak appeared at  $2\theta=10.6^\circ$ , which is the characteristic peak of GO. The result indicated that the structure of graphene was greatly altered after oxidation. Therefore, the XRD analysis confirmed that GO has been successfully prepared. In the FTIR spectrum of GO, stretching vibrations of C-OH, C-O, epoxy C=O groups, and C=C of aromatic rings are observed at 1219, 1716, 1051, and 853  $\text{cm}^{-1}$ , respectively [13].

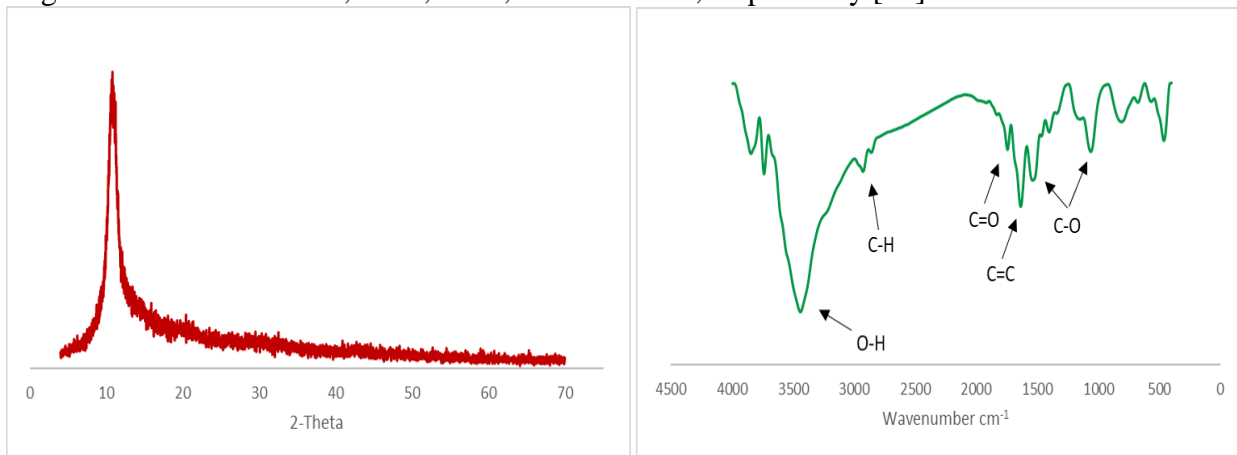


Figure 2: XRD patterns of GO.

Figure 1: FTIR spectrum of the GO.

#### Characterization of membranes Contact angle and mechanical properties

The surface hydrophilicity is one of the significant properties of membranes, which can affect the flux of membrane. Membranes with lower water contact angle exhibits better hydrophilic properties. Fig.3. displays the surface contact angles of the prepared membranes as a function of GO content. Results indicated that the surface hydrophilicity of the membranes was enhanced by the addition of GO into the PSf membrane. Water contact angle of neat PSf membrane was about  $81.4^\circ$ , while it was decreased to  $62.4^\circ$  for PSf/GO/0.3 membrane. However, when the GO content was increased to 0.3 wt%, contact angle was increased which may be attributed to the agglomeration of the particles and less presence of hydrophilic nanoparticles on the surface of the membrane.

Fig.4. shows the tensile strength of neat and nanocomposite membranes. The tensile strength of the PSf/GO membranes are also increased from 5.3 MPa to 7.71MPa when the concentration of GO was reached up to 0.3 wt%. This implies that GO with strong mechanical strength has an excellent interface compatibility in PSf polymer matrix, which can enhance the mechanical stability of the PSf/GO membranes. However, when the PSf/GO membranes was blended with a higher concentration of GO (i.e., 0.5 wt%), the high possibility of GO aggregation occurs, resulting in the decreasing of tensile strength. In this case, the optimal concentration of GO incorporated in PSf polymer is 0.3 wt%.

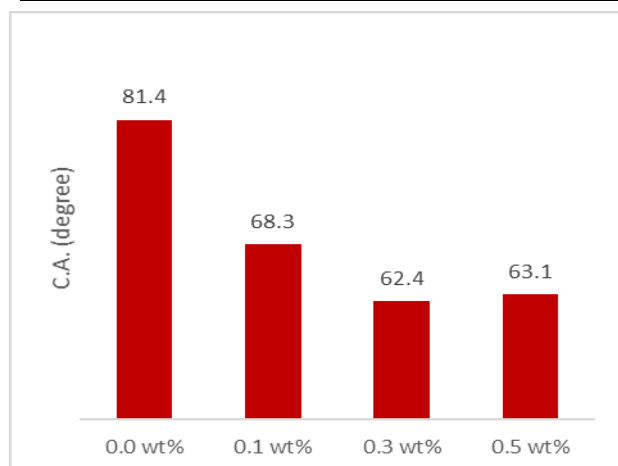


Figure 4: Variation of contact angle of neat and nanocomposite PSf membranes.

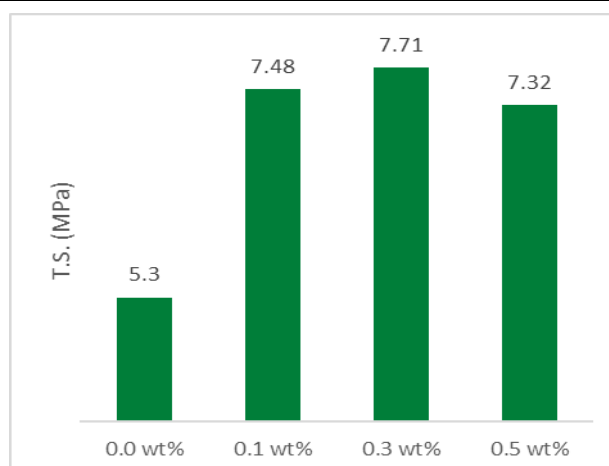


Figure 3: variation of mechanical strength of neat and nanocomposite PSf membranes.

### Membrane performances

As depicted in Table 2, neat PSf exhibited the lowest PWF among the fabricated membranes and for PSf/GO/0.3, water flux reached its peak value. The increase of PWF can be related to the hydrophilicity of the membranes. Hydrophilic surfaces tend to absorb water on the membrane surface that improves pure water flux of the membrane. Any further increase in GO contents up to 0.5 wt % reduces the PWF due to the agglomeration of GO on the membrane surface [14].

In order to evaluate antifouling properties of the membranes, fouling parameters including TFR, RFR, IFR and FRR of membranes were calculated. Table 2 shows a summary of these parameters for neat and nanocomposite membranes. The results show that neat PSf has the highest TFR, indicating that this membrane was easily fouled by HA. Addition of GO in casting solution up to 0.3 wt% decreased the TFR. The lower TFR values represent the better antifouling properties of the membranes. Moreover, lower values of IFR for nanocomposite membranes exhibit that adsorbed foulants on the membrane surface or its pores can be treated by physical treatment. On the other hand, hydrophilic surfaces make stronger bands with water molecules, so the formation of thin water layer on the membrane surface will reduce the hydrophobic adsorption of HA [10].

Table 2: Fouling and rejection parameters of prepared membranes during HA filtration.

Membrane	PWF (Kg/m <sup>2</sup> .hr)	TFR(%)	RFR (%)	IFR (%)	FRR (wt%)	R(%)
PSf	203.41	74.50	17.64	56.84	41.8	89.91
PSf/GO/0.1	275.72	75.40	27.86	47.54	55.73	90.20
PSf/GO/0.3	310.71	73.91	44.92	28.99	71.04	91.31
PSf/GO/0.5	265.64	74.68	37.98	36.70	63.29	91.02

### Conclusion

In this study, PSf/GO nanocomposite membranes were fabricated via NIPS method. The antifouling behavior of neat and nanocomposite PSf membranes during the filtration of HA in the dead-end system was investigated. The successful perpration of GO was confirmed by XRD, FTIR analyses. Improvement in hydrophilicity, porosity, PWF and mechanical strength of nanocomposite membranes were achieved. Eventually, the PSf/GO (0.3 wt%) had the highest values in pure water flux, antifouling properties, hydrophilicity, which was due to the presence of more hydrophilic groups on the surface of the membrane. However addition of more



than 0.3 wt% GO to the polymeric matrix did not represent much improvement in membrane performance because of agglomeration of particles in the composite materials.

## References

- [1] J. Shao, J. Hou, and H. Song, "Comparison of humic acid rejection and flux decline during filtration with negatively charged and uncharged ultrafiltration membranes," *Water Res.*, vol. 45, no. 2, pp. 473–482, 2011.
- [2] M. R. Esfahani, V. L. Pallem, H. A. Stretz, and M. J. M. Wells, "Humic acid disaggregation with/of gold nanoparticles: Effects of nanoparticle size and pH," *Environ. Nanotechnology, Monit. Manag.*, vol. 6, pp. 54–63, 2016.
- [3] N. Han et al., "Removal of sulfonated humic acid through a hybrid electrocoagulation–ultrafiltration process," *Ind. Eng. Chem. Res.*, vol. 54, no. 21, pp. 5793–5801, 2015.
- [4] R. Bai and X. Zhang, "Polypyrrole-coated granules for humic acid removal," *J. Colloid Interface Sci.*, vol. 243, no. 1, pp. 52–60, 2001.
- [5] Y. Wu, S. Zhou, X. Ye, R. Zhao, and D. Chen, "Oxidation and coagulation removal of humic acid using Fenton process," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 379, no. 1–3, pp. 151–156, 2011.
- [6] P. D. Peeva, A. E. Palupi, and M. Ulbricht, "Ultrafiltration of humic acid solutions through unmodified and surface functionalized low-fouling polyethersulfone membranes—effects of feed properties, molecular weight cut-off and membrane chemistry on fouling behavior and cleanability," *Sep. Purif. Technol.*, vol. 81, no. 2, pp. 124–133, 2011.
- [7] M. Kumar, Z. Gholamvand, A. Morrissey, K. Nolan, M. Ulbricht, and J. Lawler, "Preparation and characterization of low fouling novel hybrid ultrafiltration membranes based on the blends of GO-TiO<sub>2</sub>nanocomposite and polysulfone for humic acid removal," *J. Memb. Sci.*, vol. 506, pp. 38–49, 2016.
- [8] J. Mulder, *Basic principles of membrane technology*. Springer Science & Business Media, 2012.
- [9] E. Shokri, R. Yegani, B. Pourabbas, and N. Kazemian, "Preparation and characterization of polysulfone/organoclay adsorptive nanocomposite membrane for arsenic removal from contaminated water," *Appl. Clay Sci.*, vol. 132, pp. 611–620, 2016.
- [10] A. Tizchang, Y. Jafarzadeh, R. Yegani, and E. Shokri, "Polysulfone nanocomposite membrane embedded by silanized nanodiamond for removal of humic acid from water," *J. Water Environ. Nanotechnol.*, vol. 4, no. 3, pp. 213–226, 2019.
- [11] M. Sun and J. Li, "Graphene oxide membranes: Functional structures, preparation and environmental applications," *Nano Today*, vol. 20, pp. 121–137, 2018.
- [12] D. C. Marcano et al., "Improved synthesis of graphene oxide," *ACS Nano*, vol. 4, no. 8, pp. 4806–4814, 2010.
- [13] R. Azimi, H. Roghani-Mamaqani, and M. Gholipour-Mahmoudalilou, "Grafting poly (amidoamine) dendrimer-modified silica nanoparticles to graphene oxide for preparation of a composite and curing agent for epoxy resin," *Polymer (Guildf.)*, vol. 126, pp. 152–161, 2017.
- [14] Z. Xu, J. Zhang, M. Shan, Y. Li, B. Li, and J. Niu, "Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultra filtration membranes," *J. Memb. Sci.*, vol. 458, pp. 1–13, 2014.