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Preparation and Characterization of an Antifouling Polyethersulfone Nanofiltration Membrane Blended with Graphene Oxide/Ag Nanoparticles

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P A P E R   I N F O

A B S T R A C T

Graphene oxide/Ag nanoparticles (Ag/GO) was prepared and employed to synthesize antifouling polyethersulfone (PES) mixed matrix membranes. The performance of the membranes was evaluated in terms of flux, hydrophilicity and anti-biofouling properties. With increment of the Ag/GO from 0 to 0.1 wt.%, the pure water flux increased from 24.7 up to 54.1 kg/m^2 h. The flux recovery ratio (FRR) of the membranes was performed using milk powder solution and the results illustrated that the 0.1 wt.% Ag/GO membrane had the best fouling resistance with the FRR value of 95.45%. The performance of the nanofiltration was assessed using the retention of Direct Red 16. It was indicated that the Ag/GO-PES membranes have remarkable dye removal (98.38% rejection). The anti-biofouling activities of the 0.1 wt.% Ag/GO mixed matrix membrane was also investigated using activated sludge and the results showed a notable improvement.

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1. INTRODUCTION

Application of the membrane processes among the modern methods for separation is of high interest for scientists[1, 2]. Membrane separation has many advantages such as simplicity of operating conditions, low energy consumption, no phase shift, compact design and environmental friendliness. However, membrane fouling as a key constraint has limited its application. This limitation can surpass membrane performance and can bring huge damage in this type of separation [3-6]. Diverse polymers such as polysulfone (PSF), polyethersulfone (PES), polyvinylidene difluoride (PVDF) and polyacrylonitrile (PAN) have been used for membrane preparation [6-10]. The PES polymer, due to its physical and chemical properties such as thermal and hydrolytic stability as well as good mechanical and film forming properties is the most common type of used polymer in membrane processes [11-13]. The major problem of PES is its hydrophobic

characteristic that will lead to membrane fouling, reducing the membrane performance [14]. Membrane modification is the alternative mitigating the fouling and biofouling in the membrane through improving of hydrophilicity property [15]. Many strategies employed for developing antifouling membranes are including hydrophilic surface modification by coating [16-18], grafting [16], embedding and mixing hydrophilic nanoparticles [19].

Bio-fouling on membrane surface are formed by bacterial bio-films [20]. The common way to eliminate this type of fouling is the use of antibacterial agents. Silver nanoparticles (Ag NPs) exhibit very strong bactericidal activity against both Gram-positive and Gram-negative bacterial strains [21-23]. For instance, in a research work performed by Guzman and his colleagues, the Ag NPs was synthesized by agglomerates of grains with a fine size, showing reasonable bactericidal activity against Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus aureus [24]. Lee and coworkers have reported the Ag NPs immobilized on thin film composite polyamide membrane for anti-biofouling performance [25].

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Another finding on the Ag NPs shows a reduction in anti-biofouling properties due to its accumulation [7, 26]. For this reason, sufficient dispersion is needed which can be provided through placing on a carbon substrate. Graphene oxide (GO) due to the existence of hydroxyl groups, epoxy, carbonyl and carboxyl and covalently bonded oxygen-containing groups can create a good dispersion of silver on the surface and edge of the graphene oxide sheets and can be used as a carbon substrate for the nanoparticles [27-31]. Modified GO with silver nanoparticles can be used as an additive in the matrix of membrane that gives properties such as hydrophilicity, antibacterial, low toxicity and biological and chemical durability [32, 33]. The observed antibacterial effect of Ag ions has been associated to inactivation with the thiol group in biotic enzymes and DNA, resulting in the marked development of pyrimidine dimerization with photodynamic reaction and the possible obstacle of DNA proliferation. The structural changes in the cellular coverage and exchange of the hydrogen atom of the thiol group to form a S−Ag complex have also been confirmed in bacterial cells [34, 35].

Tang and his colleagues fabricated Ag/GO nanocomposites with different Ag NPs to GO ratios and carefully investigated their antibacterial activities against both the Gram-negative (G−) bacteria (Escherichia coli) and the Gram-positive (G+) bacteria (Staphylococcus aureus) [36]. Vatanpour and his coworkers have reported the addition of Ag/GO nanosheets to polyethersulfone mixed matrix membrane with anti-bacterial properties which increased membrane performance. Mahmoudi and his colleagues synthesized a novel nanohybrid polysulfone membrane blended with Ag nanoparticles on GO nanosheets that improved water contact angle and flux and also showed excellent antibacterial properties, which could prevent the organization of biofouling on the membrane surface [5]. And then, in another research, the Ag/GO nanocomposites modified PVDF membranes displayed an improvement in hydrophilicity, mechanical property, permeability, antibacterial properties and biofilm formation prevention [37].

In this work, the Ag/GO nanoparticle was used in the matrix of PES nanofiltration membrane. In order to investigate the effect of the Ag/GO nanoparticle on membrane performance removing dye, the surface hydrophilicity, antifouling capability, and permeability were measured and calculated. The membrane structure was evaluated by SEM images, water contact angle and AFM analysis. The antifouling capability of modified membranes was assessed during activated sludge filtration.

2. MATERIALS AND METHODS

2. 1. Materials   Solvent of dimethylacetamide (DMAc) and Ultrason E 6020P Mw=58000 g/mol Polyethersulfone (PES) polymer were provided by BASF Co., Germany. Polyvinyl pyrrolidone (PVP) with 25,000 g/mol molecular weight was obtained from Merck, Germany. Distilled water was employed in this work. All the chemical reagents used in our experimental work were obtained from Fluka, Aldrich, or Merck and used without further purification. To characterize the products, X-ray diffraction (XRD) patterns were recorded with a Riguka diffractometer (Japan, RINT 2500 V) using Cu-Ka radiation.

2. 2. Preparation of Ag/GO Nanocomposites
The Ag/GO nanocomposites were prepared in one step reaction. In a typical procedure, 200 mg GO powder was dispersed in 100 mL of water by ultrasonication for 1 h at room temperature, forming stable graphite oxide colloid;then, 230 mg AgNO3 was added while stirring. Then, 1 g sodium citrate was gradually added to the mixture with magnetic stirring for 30 min. Subsequently, the mixture was transferred to an oil bath and kept at 95°C for 1 h under constant stirring. Finally, the products were washed with ethanol and deionized water. The resulting Ag/GO nanocomposites were dried in a vacuum oven at 60 °C for 24 h [38].

2. 3. Preparation of Mixed Matrix Ag/GO/PES
The unfilled and mixed matrix asymmetric PES membranes were prepared by immersion precipitation phase inversion method. The composition of casting solutions for all membranes are presented in Table 1. The proper quantity of the Ag/GO was mixed into DMAc and well dispersed by sonication for 30 min to improve homogenous solutions using DT 102H Bandelin ultrasonic (Germany). Then, PES and polyvinylpyrrolidone (PVP) were dissolved in the dope solution by continuous stirring for 24 h. Finally, the prepared homogenous polymer solution was again sonicated for 20 min to remove air bubbles and impressive dispersing of the Ag/GO in the polymer matrix. After that, the solutions were casted using self-made casting knife with 150 μm thickness on glass plate and immediately moved to a non-solvent bath (distilled water) for immersion precipitation at room temperature (25°C) without any evaporation.
After primary phase separation and membrane formation, the membranes were stored in fresh distilled water for 24 h to guarantee complete phase separation. This will wash out the water-soluble components from the membrane.

TABLE 1. The compositions of casting solutions

Membrane type	PES (wt.%)	PVP (wt.%)	Ag-GO (wt.%)	DMAc (wt.%)
M1	20.0	1.0	0	79.0
M2	20.0	1.0	0.1	78.9
M3	20.0	1.0	0.5	78.5
M4	20.0	1.0	1.0	78

Finally, the membranes were sandwiched between two sheets of filter papers for 24 h at room temperature for drying.

2. 4. Characterization of the Synthesized Ag/GO and Prepared NF Membranes
The morphology of the membrane surface and cross-section was investigated using Philips-XL30 scanning electron microscope (The Netherlands) with an accelerating voltage of 20kV. The membranes were cut into small pieces and cleaned with filter paper for removal of probable attached contaminants. The pieces were immersed in liquid nitrogen for 60-90 s to freeze. Frozen pieces of the membranes were broken and held in air for drying. The dried samples were gold sputtered to make them electrically conductive. SEM images were taken under very high vacuum conditions at 20 kV.

The surface morphology and roughness of the prepared membranes was analyzed by atomic force microscopy (AFM). The AFM device was Nanosurf® Mobile S scanning probe-optical microscope (Switzerland) equipped with Nanosurf® MobileS software. Small squares of the prepared membranes were cut and pasted on specimen holder. The membrane surfaces were imaged in a scan size of $4.4\mu m \times 4.4\mu m$ The surface roughness parameters of the membranes which are reflected in terms of the mean roughness (Sa), the root mean square of the Z data (Sq) and the mean difference between the highest peaks and lowest valleys (Sz) were obtained by Nanosurf® MobileS software for quantitative analysis of images.

A current method to quantify the surface hydrophilicity is water contact angle measurement technique. Propensity of small water droplets to be extended on the membrane surface is related to the membrane surface hydrophilicity. For this measurement, a G10, KRUSS digital microscope (Germany) was applied to record the status of distilled water droplets injected on the membrane surface and to determine the prepared membranes hydrophilicity. All contact angle measurements were performed using 2µl of deionized water. To minimize the experimental error, the mean value of the contact angle was calculated using five random sites on each membrane.

2. 5. Porosity Measurements
The overall porosity (ε) was determined using gravimetric method, as defined in the following equation [39]:

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \tag{1}$$

where ω1 and ω2 are the weight of the wet and dry membranes, respectively. A is the membrane effective area (m^2), dw water density (0.998 g/cm^3) and L the membrane thickness (m).

Furthermore, in order to calculate the, mean pore radius (rm) of the membrane, Guerout–Elford–Ferry equation on the basis of pure water flux and porosity data was employed [39].

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \tag{2}$$

where, η is the water viscosity (8.9×10^{-4} Pa s), Q the volume of the permeate pure water per unit time (m^3/s), and ΔP the operation pressure (0.5 M Pa).

2. 6. Membrane Performance
2. 6. 1. Pure water flux and Antifouling Experiments
The permeate flux, separation and fouling tests of the Ag/GO PES nanofiltration membranes were carried out in a dead-end cell (150 ml volume) with a membrane surface area of 12.56 cm^2. The cell was equipped with a pressure gauge. Pressurized nitrogen gas was used to force the liquid through the membrane. Constant stimulation at a rate of 400 rpm was applied to decrease the concentration polarization of the membrane. The transmembrane pressure was compressed at 5 bar for 30 min to earn a constant permeate flow and after that, the pressure was reduced to the operating pressure of 4 bar. The pure water flux (PWF), $J_{W,1}$ (kg/m^2 h) was calculated using the equation:

$$J_{W.1} = \frac{M}{A \Delta t} \tag{3}$$

where, M (kg) is the weight of permeated water, A (m^2) the membrane area, and Δt (h) the permeation time.

To assess the antifouling properties of the prepared membrane, a milk powder solution with concentration of 8000 mg/L was rapidly replaced with the stirred cell after PWF tests. The flux for milk powder, JP (kg/m^2 h), was measured based on the water quantity permeated through the membranes at 4 bar for 90 min. The fouled membranes were washed with distilled water for 15 min after filtration of milk solution. Consequently, the water flux of cleaned membranes, $J_{W,2}$ (kg/m^2 h), was again measured. The flux recovery ratio (FRR) can be defined as follows:

$$FRR = \left(\frac{J_{W2}}{J_{W1}}\right) \times 100 \tag{4}$$

Generally, higher *FRR* shows better antifouling property of the ultrafiltration membranes. Furthermore, in order

to analyze the fouling process in detail, total fouling ratio (R_t), reversible fouling ratio (R_r) and irreversible fouling ratio (R_{ir}) were calculated using the following equations [39]:

$$R_t(\%) = \left(1 - \frac{j_p}{j_{W1}}\right) \times 100 = R_{ir} - R_r \qquad (5)$$

$$R_r (\%) = \left(\frac{j_{W2} - j_p}{j_{W1}}\right) \times 100 \qquad (6)$$

$$R_{ir}(\%) = \left(\frac{j_{W1} - j_{W2}}{j_{W1}}\right) \times 100 \qquad (7)$$

2. 7. Anti-biofouling Assessments   Distilled water and activated sludge were stirred together and finally a turbid solution (100 ppm activated sludge) was obtained. A sludge with concentration of 100 mg/l was used for biofouling test because the maximum possible effluent TSS concentration under unbalanced condition is less than 100 mg/l. The activated sludge solution separation test was carried out in a dead-end cell with effective separation area of 12.56 cm^2. The flux for turbid solution was measured based on the water quantity permeated through the membranes at 4 bar for 90 min. After filtration of turbid solution, the fouled membranes were washed with distilled water for 15 min and then the water flux of cleaned membranes was again measured.

2. 8. Dye Removal Experiments   In the present study, Direct red 16 was selected as a dye containing azo group. In order to evaluate the dye removal efficiency of the prepared membranes, filtration experiments were performed in the dead-end filtration cell for 120 min with driving force of 4 bar. In every run, 150 mL of synthetic dye solution (50 mg/L), which is within the range of typical concentration in textile wastewaters, was used and the flux and rejection were calculated from Equations (3) and (8). 35 UV–Vis spectrophotometer (JENWAY 6320D) at 526 nm was employed for dye concentration determination. The calibration standard curves with R250.999 was obtained. The following equation was used for assessment of dye removal (R) percent [19]:

$$(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100 \qquad (8)$$

where, Cp and Cf are dye concentration (mg/L) in feed and permeate, respectively.

3. RESULTS AND DISCUSSION

3. 1. Characterization of Ag/GO Nanocomposites
To identify the sample composition, XRD characterizations were performed (Figure 1). In the patterns of Ag/GO nanocomposites, there are only four

main diffraction peaks at 2θ values of 38.048, 44.53, 64.63, and 77.54 corresponding to (111), (200), (220) and (311) planes of face centered cubic (FCC) silver with a lattice parameter of a = 4.08 and compared with the standard powder diffraction card of JCPDS, Silver file NO. 98-006-2675.

Figure 2 (a–d) shows the morphology of the as-prepared Ag/GO composites according to FE-SEM. After the GO was doped with Ag particles and reduced, the Ag crystallites are deposited on graphene surfaces as spacers to keep the neighboring sheets separate, and a curled and corrugated morphology was observed. The average particle size of the spherical nanoparticles found to be in the range of 45–95 nm [38].

3. 2. Hydrophilicity and Pure Water Flux of the Ag/GO Membranes   Water contact angel measurement can be used to identify surface hydrophilicity of the prepared membrane. As illustrated in Figure 3, by adding nanofiller to the membrane matrix, a logical trend on reduction in the amount of water contact angles can be observed. It should be noted that presence of oxygenated functional groups on the graphene oxide surface can bring about a reduction in the contact angle, causing an increase in membrane permeability [40].

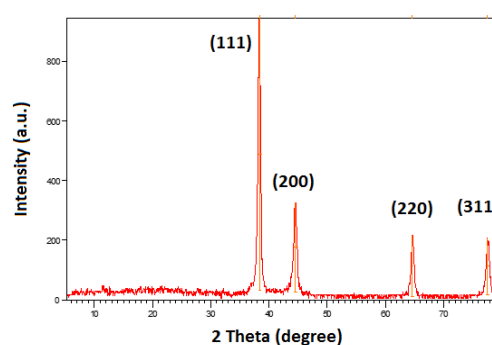Flux transmission depends on many factors, including hydrophilicity.

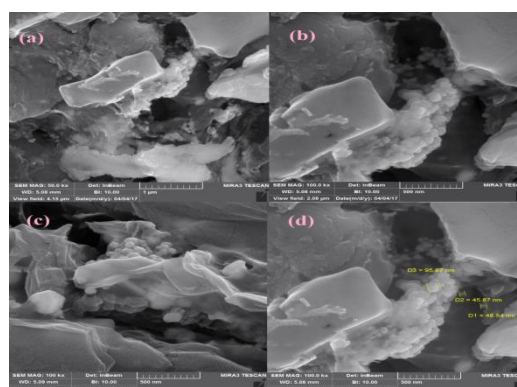**Figure 1.** XRD patterns of Ag/GO nanocomposite

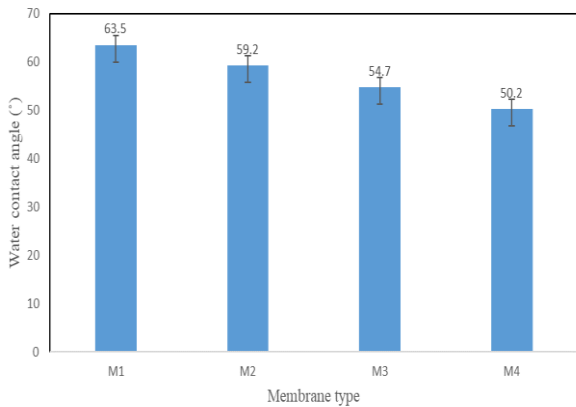**Figure 2.** SEM images of (a–d) Ag/GO nanocomposites

Figure 3. Water contact angle of the produced membranes

The hydrophilic functional groups on the membrane surface caused a change in the pure water flux (PWF) that established hydrogen bonds between membrane surface and water molecules (Figure 4).

Adding the nanoparticles up to 0.1wt%, led to an increase in PWF (M2). Also, with increasing concentration of the nanoparticles to more than 0.1wt.%, the reduction in PWF was observed (M3 and M4). That was due to the accumulation of nanoparticles and clogging the pores in the structure of the membrane. It should be noted that the rejection obtained for the milk powder solution is more than 98%, showing un-correlation between increase in flux and defects or cracks in the membrane due to poor bond between the Ag/GO and PES [5].

3. 3. Morphology Analysis   The digital images of membrane surface are shown in Figure 5. As seen in Figure 6, with increasing concentration of Ag/GO nanosheets, the membranes color becomes darker than unfilled membrane. This changes in color intensity can be attributed to migration of the NPs to membrane surface during phase inversion methods in coagulation bath.
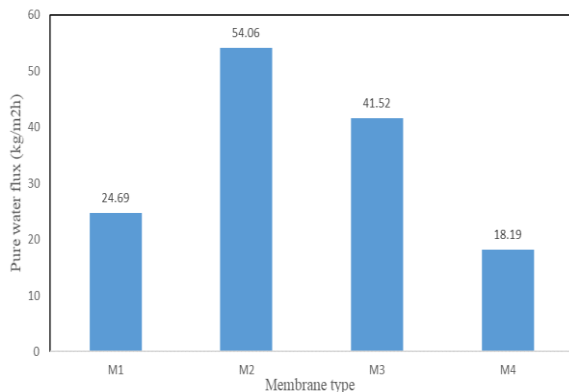

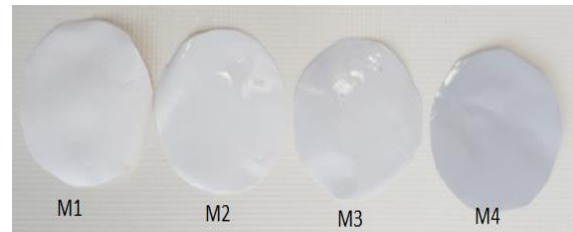**Figure 4.** Pure water flux of the Ag/GO blended PES membranes

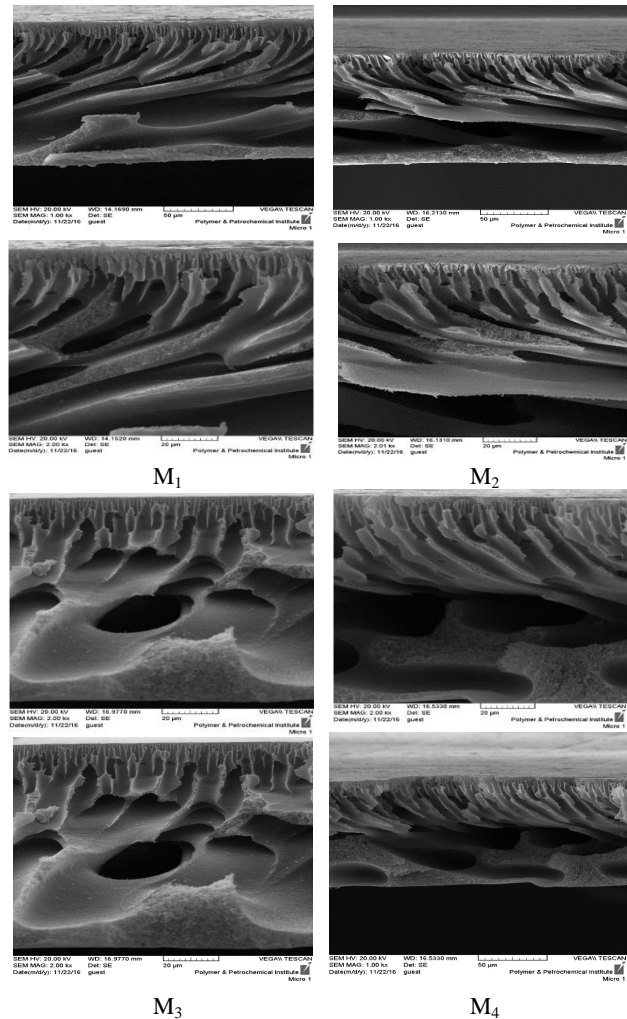**Figure 5.** The apparent of difference membranes in the effect of adding Ag/GO

Figure 6. Cross-section SEM images of the membrane in tow magnification with different mix compositions (M$_1$) Unfilled PES, (M$_2$) 0.1% Ag/GO-PES, (M$_3$) 0.5% Ag/GO-PES and (M$_4$) 1% Ag/GO-PES

To evaluate the effect of nanoparticles concentration on the structure and morphology of the membrane, SEM images are presented in Figure 6.

As shown in the picture, asymmetric structure with uniform dispersion of nanoparticles is visible and finger like pores with thin top layer and thick bottom layer can

be easily recognized. The identical building of the membranes, implies that the impact of nanoparticles on morphology was low.

So, this result shows there was not an important influence on the formation of mold membrane. Small differences in the structure of membranes at low concentrations was observed that described the increase in porosity and consequently increase the radius.

3. 4. Fouling Behavior of the Prepared Members

Figure 7 depicts the antifouling performance of prepared membrane. Figure 7 shows the effect of different concentrations of Ag/GO nanosheets on the membrane permeability during filtration. The results of 0.1 wt.% of Ag/GO were demonstrated the highest permeability compared to the other concentrations.

Flux recovery ratio (FRR) is one of the important parameters for antifouling assessment. The FRR diagram is displayed in Figure 8. The greatest FRR for membrane was achieved for membrane embedded with 0.1 wt.% of Ag/GO. Antifouling performance of Ag/GO mixed membrane could be related to hydrophilicity. Water contact angle declined due to remaining functional groups of Ag/GO on the membrane surface (Figure 3). Also, membrane fouling was considerably reduced as a result of the increase in hydrophilicity. Creating a layer of water molecules on the membrane surface due to the presence hydrophilic nanosheets, can inhibit the hydrophobic deposition attaching to the membrane surface. The results demonstrated that the addition of the Ag/GO nanosheets in the PES membrane was useful to improve the permeability [44].

According to the deposition phenomenon, resistance parameters such as reversible fouling resistance (Rr) and irreversible fouling resistance (Rir) were obtained as shown in Figure 9. Irreversible fouling resistance with 0.1wt.% nanoparticles has reached lowest value, but Rir has also increased with increasing concentration.
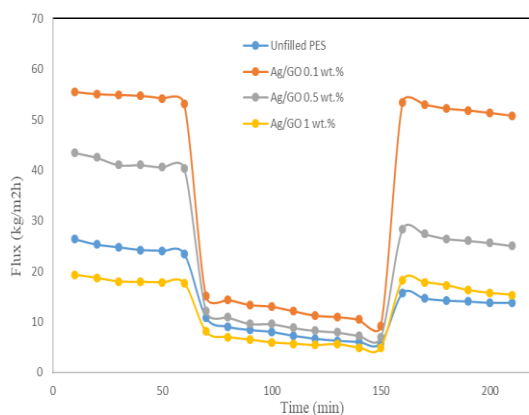

Figure 7. Flux against time of the membranes with different concentrations of Ag/GO nanosheets. The filtration process includes three phases: water flux, milk powder filtration and second water flux after washing fouled membranes
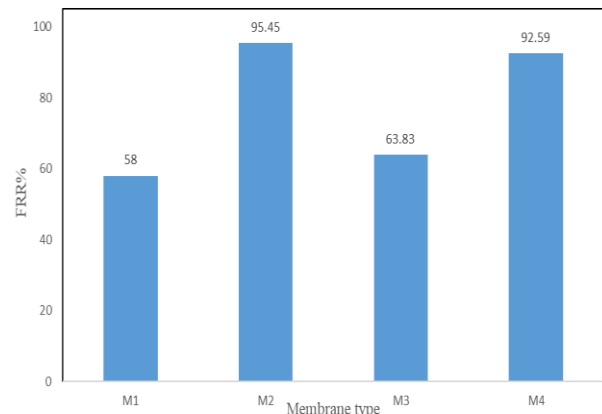

Figure 8. Flux recovery ratio (FRR) of the prepared nanocomposite membranes in filtration of milk powder solution
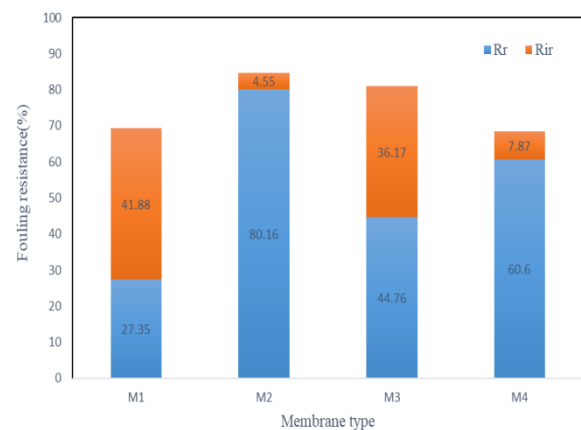

Figure 9. Fouling resistance ratio of Ag/GO-PES ultrafiltration membranes

The trapped residual foulants into the membrane pores and valley surface are responsible for irreversible aggregation, which noticeably can be removed by washing process. The M2 membrane (embedded with 0.1 wt.% Ag/GO) indicated the highest FRR.

AFM technique was used for measuring the surface roughness of membranes. It is believed that lower roughness and surface energy replies on stronger antifouling property. In addition, foulants may be absorbed in the valleys of membrane with unusual surfaces resulting in clogging of the valleys. The AFM images and its associated results are presented in Figure 10 and Table 2. The average roughness (Sa) of the unmodified PES membrane mitigated from 47.118 to 1.454 nm for the Ag/GO 0.1 wt.% embedded membranes, and then increased to 7.958 nm for the Ag/GO 1 wt.%. In low concentration of Ag/GO, due to little electrostatic interactions between the Ag/GO, they are symmetrically arranged in membrane, resulting in a smooth membrane surface.
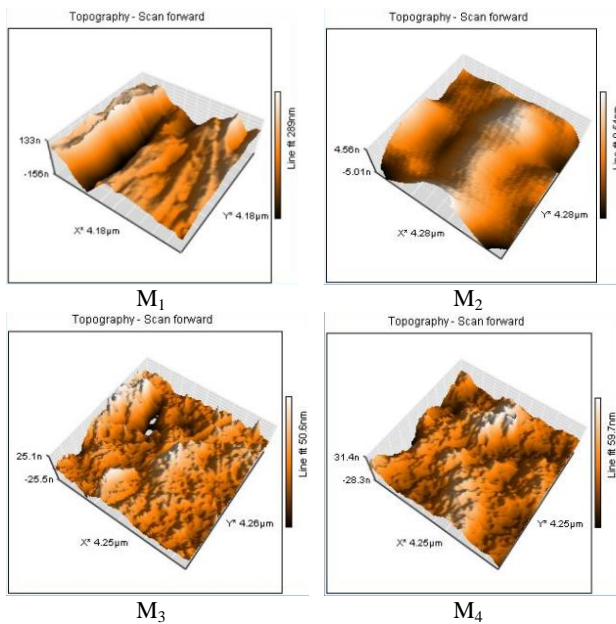
Figure 10. Surface AFM images of the Ag/GO mixed matrix PES membranes with different concentrations. (M_1) Unfilled PES, (M_2) 0.1 %, (M_3) 0.5 % and (M_4) 1 %

TABLE 2. Surface roughness parameters of Ag/GO embedded PES membranes resulted from analyzing three randomly chosen AFM images

Membrane	S_a (nm)	S_q (nm)	S_z (nm)
M_1	47.118	59.601	304.46
M_2	1.454	1.858	14.613
M_3	6.780	8.899	87.139
M_4	7.958	10.138	90.956

But, because of increment in pore size and agglomeration of Ag/GO, roughness of membrane surface was increased at high concentration of Ag/GO [9].

3. 5. Dye removal Efficiency   The results of dye rejection are shown in Figure 11. This figure describes the capability of the prepared membranes for Direct Red 16 removal from synthetic feed (50 mg/L) after 60 min filtration as a function of the Ag/GO percentage in the casting solution. The dye removal efficiency for the modified membrane was above 98%. This is due to the presence of nanoparticles in the membrane structures [19].

3. 6. Anti-biofouling Behavior   In order to specify the reproducibility of the membrane performance and anti-biofouling property, five cycles of activated sludge (100 ppm) fouling experiments were performed with the 0.1 wt.% Ag/GO membrane. Figure 12 describes that the flux for the 0.1 wt.% Ag/GO-PES membrane during five cycles examined showed rising trend.
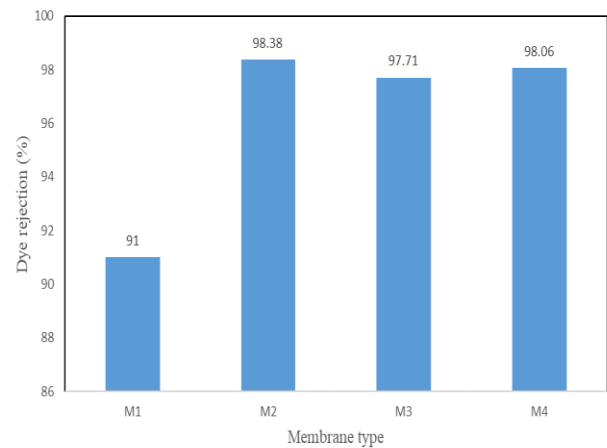

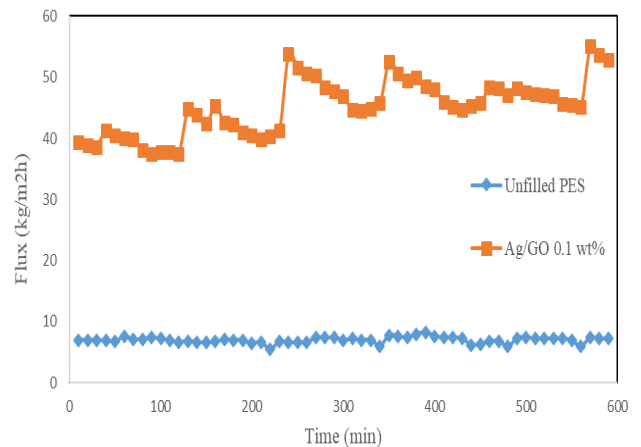**Figure 11.** Dye rejection performance of the prepared Ag/GO-PES nanofiltration membranes

Figure 12. Flux versus time for the membranes at 4 bar during five steps: water flux (30 min), activated sludge solution (100 ppm), flux (90 min), and water flux (30 min) after 15 min washing with distilled water

It was because of the anti-biofouling properties resulted from the presence of Ag nanoparticles on the membrane surface. The antibiofouling property is induced by the Ag/GO nanocompound on membrane surface, which alleviate fouling during filtration.

4. CONCLUSION

In this work, a hydrophilic nanofiller (Ag/GO nanocomposite) was successfully used and blended in to the PES membrane during the phase inversion to reclaim membrane flux, antifouling, antibiofouling and dye removal performance. The effect of Ag/GO in the casting solution were investigated and optimized in the 0.1 wt.% of Ag/GO. The fabricated Ag/GO-PES membranes exhibited better flux and dye rejection of

98.38% compared to the unmodified membranes. By embedding the Ag/GO, hydrophilicity of the membranes was remarkably improved. Antifouling experiments showed that addition of the Ag/GO in the casting solution led to an increase in flux recovery and a decrease in irreversible fouling to 4.55 %. Anti-biofouling property of the modified membrane was approved using activated sludge filtration.

6. REFERENCES

1. Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Mariñas, B.J. and Mayes, A.M., "Science and technology for water purification in the coming decades", *Nature*, Vol. 452, No. 7185, (2008), 301-310.

2. Liu, Y., Zhang, S. and Wang, G., "The preparation of antifouling ultrafiltration membrane by surface grafting zwitterionic polymer onto poly (arylene ether sulfone) containing hydroxyl groups membrane", *Desalination*, Vol. 316, (2013), 127-136.

3. Huang, J., Wang, Z., Zhang, J., Zhang, X., Ma, J. and Wu, Z., "A novel composite conductive microfiltration membrane and its anti-fouling performance with an external electric field in membrane bioreactors", *Scientific Reports*, Vol. 5, (2015).

4. Oktian, Y.E., Lee, S. and Lee, H., "Mitigating denial of service (dos) attacks in openflow networks", in Information and Communication Technology Convergence (ICTC), 2014 International Conference on, IEEE., (2014), 325-330.

5. Vatanpour, V., Shockravi, A., Zarrabi, H., Nikjavan, Z. and Javadi, A., "Fabrication and characterization of anti-fouling and anti-bacterial ag-loaded graphene oxide/polyethersulfone mixed matrix membrane", *Journal of Industrial and Engineering Chemistry*, Vol. 30, (2015), 342-352.

6. Safarpour, M., Vatanpour, V. and Khataee, A., "Preparation and characterization of graphene oxide/TiO_2 blended pes nanofiltration membrane with improved antifouling and separation performance", *Desalination*, Vol. 393, (2016), 65-78.

7. Zhao, C., Xu, X., Chen, J., Wang, G. and Yang, F., "Highly effective antifouling performance of PVDF/graphene oxide composite membrane in membrane bioreactor (MBR) system", *Desalination*, Vol. 340, (2014), 59-66.

8. Yu, L., Zhang, Y., Zhang, B., Liu, J., Zhang, H. and Song, C., "Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties", *Journal of Membrane Science*, Vol. 447, (2013), 452-462.

9. Zinadini, S., Zinatizadeh, A.A., Rahimi, M., Vatanpour, V. and Zangeneh, H., "Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates", *Journal of Membrane Science*, Vol. 453, (2014), 292-301.

10. Chong, J., Aba, N., Wang, B., Mattevi, C. and Li, K., "Uv-enhanced sacrificial layer stabilised graphene oxide hollow fibre membranes for nanofiltration", *Scientific Reports*, Vol. 5, (2015).

11. Thelen, H., Kaufmann, R., Klee, D. and Hoecker, H., "Development and characterization of a wettable surface modified aromatic polyethersulphone using glow discharge induced hema-graft polymerisation", *Fresenius' Journal of Analytical Chemistry*, Vol. 353, No. 3, (1995), 290-296.

12. Saleem, A., Frormann, L. and Iqbal, A., "High performance thermoplastic composites: Study on the mechanical, thermal, and electrical resistivity properties of carbon fiber-reinforced polyetheretherketone and polyethersulphone", *Polymer Composites*, Vol. 28, No. 6, (2007), 785-796.

13. Yan, L., Li, Y.S. and Xiang, C.B., "Preparation of poly (vinylidene fluoride)(PVDF) ultrafiltration membrane modified by nano-sized alumina (Al_2O_3) and its antifouling research", *Polymer*, Vol. 46, No. 18, (2005), 7701-7706.

14. Rahimi, Z., Zinatizadeh, A. and Zinadini, S., "Preparation of high antibiofouling amino functionalized mwcnts/pes nanocomposite ultrafiltration membrane for application in membrane bioreactor", *Journal of Industrial and Engineering Chemistry*, Vol. 29, (2015), 366-374.

15. Peyravi, M., Rahimpour, A., Jahanshahi, M., Javadi, A. and Shockravi, A., "Tailoring the surface properties of pes ultrafiltration membranes to reduce the fouling resistance using synthesized hydrophilic copolymer", *Microporous and Mesoporous Materials*, Vol. 160, (2012), 114-125.

16. Rahimpour, A., "Uv photo-grafting of hydrophilic monomers onto the surface of nano-porous pes membranes for improving surface properties", *Desalination*, Vol. 265, No. 1, (2011), 93-101.

17. Qin, H., Sun, C., He, C., Wang, D., Cheng, C., Nie, S., Sun, S. and Zhao, C., "High efficient protocol for the modification of polyethersulfone membranes with anticoagulant and antifouling properties via in situ cross-linked copolymerization", *Journal of Membrane Science*, Vol. 468, (2014), 172-183.

18. He, T., Frank, M., Mulder, M. and Wessling, M., "Preparation and characterization of nanofiltration membranes by coating polyethersulfone hollow fibers with sulfonated poly (ether ether ketone)(SPEEK)", *Journal of Membrane Science*, Vol. 307, No. 1, (2008), 62-72.

19. Baker, J. and Dudley, L., "Biofouling in membrane systems—a review", *Desalination*, Vol. 118, No. 1-3, (1998), 81-89.

20. Negm, N.A., Abd-Elaal, A.A., Mohamed, D.E., El-Farargy, A.F. and Mohamed, S., "Synthesis and evaluation of silver nanoparticles loaded with gemini surfactants: Surface and antimicrobial activity", *Journal of Industrial and Engineering Chemistry*, Vol. 24, (2015), 34-41.

21. Seil, J.T. and Webster, T.J., "Antimicrobial applications of nanotechnology: Methods and literature", *International Journal of Nanomedicine*, Vol. 7, (2012), 2767-2774.

22. Shrivastava, S., Bera, T., Roy, A., Singh, G., Ramachandrarao, P. and Dash, D., "Characterization of enhanced antibacterial effects of novel silver nanoparticles", *Nanotechnology*, Vol. 18, No. 22, (2007), 225103-225110.

23. Guzman, M., Dille, J. and Godet, S., "Synthesis and antibacterial activity of silver nanoparticles against gram-positive and gram-negative bacteria", *Nanomedicine: Nanotechnology, Biology and Medicine*, Vol. 8, No. 1, (2012), 37-45.

24. Lee, S.Y., Kim, H.J., Patel, R., Im, S.J., Kim, J.H. and Min, B.R., "Silver nanoparticles immobilized on thin film composite polyamide membrane: Characterization, nanofiltration, antifouling properties", *Polymers for Advanced Technologies*, Vol. 18, No. 7, (2007), 562-568.

25. Pugliara, A., Makasheva, K., Despax, B., Bayle, M., Carles, R., Benzo, P., BenAssayag, G., Pecassou, B., Sancho, M.C. and Navarro, E., "Assessing bio-available silver released from silver nanoparticles embedded in silica layers using the green algae

chlamydomonas reinhardtii as bio-sensors", *Science of the Total Environment*, Vol. 565, (2016), 863-871.

26. Ong, C., Goh, P., Lau, W., Misdan, N. and Ismail, A., "Nanomaterials for biofouling and scaling mitigation of thin film composite membrane: A review", *Desalination*, Vol. 393, (2016), 2-15.

27. Filice, S., D'Angelo, D., Libertino, S., Nicotera, I., Kosma, V., Privitera, V. and Scalese, S., "Graphene oxide and titania hybrid nafion membranes for efficient removal of methyl orange dye from water", *Carbon*, Vol. 82, (2015), 489-499.

28. Qin, D., Liu, Z., Sun, D.D., Song, X. and Bai, H., "A new nanocomposite forward osmosis membrane custom-designed for treating shale gas wastewater", *Scientific Reports*, Vol. 5, (2015).

29. Sun, X.-F., Qin, J., Xia, P.-F., Guo, B.-B., Yang, C.-M., Song, C. and Wang, S.-G., "Graphene oxide–silver nanoparticle membrane for biofouling control and water purification", *Chemical Engineering Journal*, Vol. 281, (2015), 53-59.

30. Shukla, A.K., Alam, J., Alhoshan, M., Dass, L.A. and Muthumareeswaran, M., "Development of a nanocomposite ultrafiltration membrane based on polyphenylsulfone blended with graphene oxide", *Scientific Reports*, Vol. 7, (2017).

31. de Faria, A.F., Martinez, D.S.T., Meira, S.M.M., de Moraes, A.C.M., Brandelli, A., Souza Filho, A.G. and Alves, O.L., "Anti-adhesion and antibacterial activity of silver nanoparticles supported on graphene oxide sheets", *Colloids and Surfaces B: Biointerfaces*, Vol. 113, (2014), 115-124.

32. Wang, X. and Dou, W., "Preparation of graphite oxide (GO) and the thermal stability of silicone rubber/go nanocomposites", *Thermochimica Acta*, Vol. 529, (2012), 25-28.

33. Feng, Q., Wu, J., Chen, G., Cui, F., Kim, T. and Kim, J., "A mechanistic study of the antibacterial effect of silver ions on escherichia coli and staphylococcus aureus", *Journal of Biomedical Materials Research*, Vol. 52, No. 4, (2000), 662-668.

34. Ma, Y., Zhou, T. and Zhao, C., "Preparation of chitosan–nylon-6 blended membranes containing silver ions as antibacterial materials", *Carbohydrate Research*, Vol. 343, No. 2, (2008), 230-237.

35. Tang, J., Chen, Q., Xu, L., Zhang, S., Feng, L., Cheng, L., Xu, H., Liu, Z. and Peng, R., "Graphene oxide–silver nanocomposite as a highly effective antibacterial agent with species-specific mechanisms", *ACS Applied Materials & Interfaces*, Vol. 5, No. 9, (2013), 3867-3874.

36. Li, J., Liu, X., Lu, J., Wang, Y., Li, G. and Zhao, F., "Anti-bacterial properties of ultrafiltration membrane modified by graphene oxide with nano-silver particles", *Journal of Colloid and Interface Science*, Vol. 484, (2016), 107-115.

37. Weiwei, W., Wenfang, W., Xiaoli, C., Yucheng, W. and Lingshu, D., "Synthesis and characterization of ag/graphene nano-composite", *Rare Metal Materials and Engineering*, Vol. 44, No. 9, (2015), 2138-2142.

38. Zinadini, S., Zinatizadeh, A., Rahimi, M., Vatanpour, V., Zangeneh, H. and Beygzadeh, M., "Novel high flux antifouling nanofiltration membranes for dye removal containing carboxymethyl chitosan coated Fe₃O₄ nanoparticles", *Desalination*, Vol. 349, (2014), 145-154.

39. Liu, F., Abed, M.M. and Li, K., "Preparation and characterization of poly (vinylidene fluoride)(pvdf) based ultrafiltration membranes using nano γ- Al₂O₃", *Journal of Membrane Science*, Vol. 366, No. 1, (2011), 97-103.

40. Vatanpour, V., Madaeni, S.S., Moradian, R., Zinadini, S. and Astinchap, B., "Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite", *Journal of Membrane Science*, Vol. 375, No. 1, (2011), 284-294.

Preparation and Characterization of an Antifouling Polyethersulfone Nanofiltration Membrane Blended with Graphene Oxide/Ag Nanoparticles

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چکیده

نانوذرات اکسید گرافن/نقره (Ag/GO) تهیه و برای تولید غشاهای زمینه مخلوط پلی‌مر پلی اتر سولفون(PES) با خاصیت ضد گرفتگی به کار گرفته شد. عملکرد غشاء تهیه شده از لحاظ شار عبوری و خواص آب‌دوستی و ضد زیست گرفتگی مورد بررسی قرار گرفت. با افزایش نانوذراتAg/GO از ۰ تا ۰/۱ درصد وزنیt، جریان آب خالص از۲۴/۷ از ۵۴/۱ کیلوگرم در متر مربع افزایش یافت. نسبت شار برگشتی (FRR) غشا با استفاده از محلول شیر خشک انجام شد و نتایج نشان داد که غلظت ۰/۱ درصد وزنی Ag/GO دارای بهترین مقاومت گرفتگی با مقدار FRR ۹۵/۴۵ درصد بود. عملکرد نانوفیلتراسیون با استفاده از عبور دادن رنگ Direct Red 16 بررسی شد. مشخص شد که غشاهای Ag / GO-PES دارای حذف رنگ قابل توجه (۹۸٫۳۸٪ پس دهی) هستند. فعالیت ضد زیست گرفتگی غشای زمینه مخلوط ۰/۱ درصد وزنی Ag/GO با استفاده از لجن فعال نیز مورد بررسی قرار گرفت و نتایج حاکی از بهبود قابل ملاحظه در عملکرد داشت.

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