#### RESEARCH ARTICLE

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# Graphene oxide, an effective nanoadditive for a development of hollow fiber nanocomposite membrane with antifouling properties

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#### Abstract

A series of hollow fiber (HF) membranes made from nanocomposites of polyethersulfone (PES) and graphene oxide (GO) at GO concentrations of 0.2%, 0.5%, and 1.0% were prepared by the dry-wet spinning process. The structure and the properties of as-prepared HF membranes were characterized by scanning electron microscopy (SEM); atomic force microscopy (AFM); measurements of contact angle, zeta potential, molecular weight cut-off (MWCO), and porosity; thermogravimetric analysis (TGA); and tensile testing. Long-term filtration tests were performed with the proteins bovine serum albumin (BSA), pepsin, trypsin, and lysozyme, which are common model organic foulants used in membrane fouling studies. The results showed that HF membrane made from PES/GO nanocomposite dope had a water permeability of  $30 \pm 1.5$  Lm<sup>-2</sup> hr<sup>-1</sup> bar<sup>-1</sup>, which is an increase of approximately 36% compared to that of a PES HF membrane. Among the membranes containing GO, the membrane with a 0.5 wt% GO loading exhibited the best antifouling performance, that is, this membrane recovered more than approximately 96% of its initial pure water flux, demonstrating a high resistance to the irreversible fouling. In addition, the same membrane showed an improvement in MWCO, an approximately 15% increase in porosity, along with optimum mechanical and thermal properties.

#### **KEYWORDS**

antifouling property, graphene oxide, hollow fiber membrane, nanocomposite

# **1** | INTRODUCTION

Polyethersulfone (PES) has been investigated intensely in the literature for preparing ultrafiltration membranes owing to its excellent properties which include (i) low protein adsorption; (ii) an ability to withstand exposure to high temperatures in water for prolonged periods, and a wide pH tolerances from pH 2 to 13; (iii) a superior ability to be functionalized with a wide range of molecules and polymers; (iv) an ability to form a membrane with reproducible properties and controllable pore size in a wide variety of configurations and modules; and (v) and a high degree of chemical and thermal stability due to its phenyl ether and phenyl sulfone group's availability.<sup>[1–5]</sup> Despite its outstanding physical and chemical properties, PES has one serious limitation related to its intrinsic hydrophobic nature, which precludes the use of PES membranes to some extent in aqueous liquid filtration applications due to membrane fouling. Therefore, research on PES membranes has often focused on hydrophilic modification approaches,

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which are (i) surface modification via coating, grafting, and plasma techniques; (ii) making a thin film composite via interfacial polymerization using various aromatic/aliphatic amines and trimesoyl chloride (TMC); and (iii) bulk modification either by blending PES polymer with an additive such as hydrophilic polymers or nanomaterials or by copolymerization.<sup>[6–17]</sup> Compared with the other approaches used for hydrophilic modification, blending PES with nanomaterials is an effective, simple, and one-step method to produce a membrane with increased hydrophilicity and antifouling properties.<sup>[18–21]</sup>

Nanomaterials of a large variety of inorganic and organic materials have been reported in the literature for the development of polymers matrix nanocomposite membrane.<sup>[22,23]</sup> The most widely reported nanoparticles include TiO<sub>2</sub>, ZnO, SiO<sub>2</sub>, graphene oxide (GO), carbon nanotubes (CNTs), and polyaniline (PANI).<sup>[24-34]</sup> Of these nanomaterials, GO has shown great potential in developing a PES nanocomposite membrane with improved hydrophilicity at relatively low GO content. This is due to its excellent solution processability resulting from the polar functional groups' availability.<sup>[35,36]</sup> Less than 1 wt% is reported to be sufficient for preparing a hydrophilic membrane, which is much less compared to other nanomaterials. In addition, recent studies have demonstrated that the incorporation of GO into PES polymer not only tunes the physicochemical properties (including hydrophilicity, porosity, charge density, chemical stability, thermal stability, and mechanical stability) of the membranes but also introduces unique functionalities such as antibacterial and photocatalytic characteristics into the resulting membranes.<sup>[37–40]</sup> Although an extensive series of studies have been carried out in recent years on GO as a nanoadditive to improve the properties of commercial membrane materials, most studies focused on flat sheet nanocomposite membranes. However, to the best of our knowledge, there have been far fewer studies of the fabrication of hollow fiber nanocomposite membranes based on GO. In this study, a series of nanocomposite hollow fiber membranes (i.e., so-called PES/GO hollow fiber nanocomposite membranes) were prepared by a wet spinning process. The focus of the research is to investigate the effect of varying the GO content on the performance of the membrane in terms of water permeability, molecular weight cut-off (MWCO), porosity, and long-term protein fouling resistance. As a result, a membrane prepared with a 0.5 wt% GO loading recovered more than approximately 96% of its initial pure water flux after washing, demonstrating excellent protein resistance. The increased resistance to protein fouling is due to an enhanced surface hydrophilicity, an increased negative charge on surface, along with the membrane's asymmetric morphology and surface topography with a narrow spacing between adjacent ridges and valleys.

# 2 | EXPERIMENTAL

### 2.1 | Materials

Polyethersulfone (PES) was kindly supplied by Solvay Advanced Polymers, USA. Polyethylene glycol (PEG,  $M_w$  600 Da, 1, 3, 4, 6 10, 20, 30, 35 kDa), sodium hydroxide, potassium chloride, sodium azide, and glycerol were obtained from Merck. GO, sodium dodecyl sulfate (SDS), and the proteins bovine serum albumin (BSA, 66 kDa), pepsin (35 kDa), trypsin (23 kDa), and lysozyme (14.7 kDa) were obtained from Sigma Aldrich. All chemicals were used as received. Anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were obtained from *SD* Fine-Chem Limited, India and were used to prepare the phosphate buffer solutions for protein analysis. Millipore MQ purified water was used for the ultrafiltration experiments and to prepare the gelation bath.

# 2.2 | Methods

# **2.2.1** | Preparation of PES/GO nanocomposite dope solutions

A series of dope solutions was prepared by in situ blending of PES as the matrix, PEG 600 Da as the pore-forming agent, 1-methyl-2-pyrrolidone (NMP) as the solvent, and GO as the hydrophilic nanoadditive. In the preparation of the dope solution, the NMP/PES/PEG ratio was kept constant (7/2.5/0.5), while the concentration of GO was varied (0.2,0.5, 1.0 wt%). In the first step, GO was added to the NMP. This mixture was then sonicated with a probe for 30 min at room temperature to minimize the aggregation of GO. After that, PES and PEG were added to the NMP/GO mixture and stirred gently using a mechanical paddle type stirrer at 70 rpm and a temperature of  $70 \pm 2^{\circ}$ C until a homogeneous solution was formed. Finally, the homogenized PES/GO nanocomposite solution, also called the dope solution, was then left for 3 hr to remove the bubbles entrained during blending and stirring.

# 2.2.2 | Fiber spinning

Hollow fibers of PES/GO nanocomposite were spun using the dry–wet spinning process, which is described elsewhere in the literature.<sup>[41]</sup> In the spinning process, the dope solution and the bore fluid, or inner coagulant, composed of deionized water were fed from separate stainless steel tanks to the spinneret by precision gear pumps to spin or extrude hollow fibers. The extruded fibers were immersed in air for a certain period to evaporate the solvent from the fibers, followed immediately by immersion in the coagulant bath, in which phase inversion occurred and the morphology of the membrane was formed. Finally, the as-spun fibers were collected by a take-up stick and kept in a flat stainless steel tray filled with deionized water for approximately 2 days, with daily change in the water to remove residual solvent and pore forming agent. After that, the fibers were thoroughly washed three times with deionized water and then post-treated with a 20 wt% glycerol aqueous solution as a nonsolvent exchange for 1 day to minimize fiber shrinkage and pore collapse. The detailed spinning parameters are listed in Table 1.

# 2.2.3 | Module preparation

The procedure of hollow fiber module preparation consisted of two main steps: bundle preparation and sealing of the ends of the fiber bundle using epoxy resin. For bundle preparation, 100 lengths of fibers were first selected and inspected to make sure that the fibers were free from defects (such as uneven thickness, rigidified polymer surface, pinholes, creases, collapses, and membrane surface wrinkles). The fibers were then placed side by side, parallel to each other, and formed into a bundle. Next, parafilm was wrapped on both ends of the bundle, which helped to make the fiber bundle denser. After that, the bundle was housed in the plastic module and sealed with epoxy. To ensure that the passageway between the fibers was blocked, the epoxy resin was slowly filled until it could be seen at the lower outlet of the module. Then, the epoxy resin cured for 24 hr. Finally, the solidified, wrapped end was cut with a sharp blade to yield a smooth cross-section and then connected to the feed and retentate manifolds of the permeation apparatus. The image of the hollow fiber test

module is given in Figure 1.

# 2.3 | Characterizations

# 2.3.1 | Atomic force microscopy

Atomic force microscopy was used to characterize surface features, that is, texture and roughness. Surface imaging was taken in a tapping mode at ambient temperature at a scan

**TABLE 1** Spinning conditions for the hollow fiber membrane preparation

Polymer composition	25 wt%
External coagulant	Double-distilled water
Bore fluid composition (wt %)	Water/NMP (95/5)
Dope flow rate (ml/min)	8
Bore fluid flow rate (ml/min)	2
Air gap (cm)	10
Temperature of the dope solution	$50 \pm 1^{\circ}C$
Spinneret temperature	$50 \pm 1^{\circ}C$
Coagulation bath temperature	Room temperature
Humidity of spinning chamber	44%

frequency of 0.999 Hz using a silicon (Si) tip. The measurements for the surface roughness and structure of a sample were accomplished under a scan range of  $5 \times 5 \,\mu\text{m}$  and  $500 \times 500 \,\text{nm}$ , using the Veeco NanoScope V MultiMode software.

# 2.3.2 | Scanning electron microscopy

Membrane morphology characteristics were investigated by scanning electron microscopy (SEM), JEOL, Japan. For the SEM study, the membrane samples, which were approximately  $0.5 \text{ cm}^2$ , were mounted onto a stub with carbon-based double-sided tape and then sputter coated with approximately 10 nm of platinum. For imaging the cross-section, the samples were oriented perpendicular to the incoming electron beam. SEM images were taken using an operating voltage of 5 kV and a working distance of 6 mm over different magnifications.

# 2.3.3 | Mechanical and thermal analysis

A Lloyd-LR5KPlus (USA) was used to examine the mechanical properties of the hollow fiber membrane samples. Tensile testing was performed at room temperature using a crosshead speed of 10 mm/min. The tensile test data were acquired with NEXYGEN Plus software. In addition, a thermogravimetric analyzer (TGA), (Mettler, Austria) was used to analyze the thermal characteristics of the as-prepared hollow fiber membranes. Thermal tests of 10 mg sample were carried out in a temperature range of 100–750°C under a N<sub>2</sub> atmosphere using a heating rate 10°C/min.



**FIGURE 1** Scheme of hollow fiber membrane module preparation

# 2.3.4 | Contact angle measurement

The contact angle,  $\theta$ , which quantifies the surface hydrophilicity of a membrane was measured by a tensiometer (Atension; MAC 200, the Netherlands) using the sessile drop method, which is the method used most frequently in literature reports.<sup>[42]</sup> In this method, a water droplet is placed on different locations of the membrane surface with a microliter syringe to measure the contact angle on both sides of the droplet. A volume of 3 µl of deionized water was used for each droplet. The profile of the water droplet on the surface was captured by an optical subsystem with a digital camera. The reported contact angle values were the average of 3–5 measurements.

#### 2.3.5 | Zeta potential measurement

A SurPASS Electrokinetic analyzer (Anton Paar, GmbH, Austria) was used to measure the zeta potential and the isoelectric point of the prepared hollow fiber membrane via the tangential streaming potential (TSP) method. A 5 mm length of membrane was inserted in a 1.4 mm diameter cylindrical sample holder containing 1 mM KCl electrolyte solution to measure the zeta potential of the fiber surface as a function pH. The built-in titration unit of the SurPASS was used to measure the streaming potential at different pH, including pH 5.6–2.5 and pH 5.6–9.0. The pH of the electrolyte solution was adjusted with 0.05 M HCl and 0.05 M NaOH via the titration unit. Finally, the zeta potential measurements using the Fairbrother and Mastin (F–M) relationship reported in the literature.<sup>[43,44]</sup>

# 2.3.6 | Molecular weight cut-off and porosity experiments

The MWCO was determined for a series of hollow fiber membranes using polyethylene glycol (PEG) with molecular weights ranging from 600 Da to 35 kDa. Prior to an MWCO measurement, each cross-flow membrane module with an effective membrane area of 0.14 m<sup>2</sup> was pressurized at the test pressure for a minimum of 1 hr to reach steady state conditions. The filtration test solution was prepared by dissolving the PEG in deionized water at a concentration of 1 g/L. PEG filtration was carried out under cross-flow at 1 bar pressure and room temperature (23–25°C). Feed and permeate compositions were analyzed with a total organic carbon (TOC) analyzer (Sievers 5310 C, GE Analytical Instruments). PEG rejection (*R*) was calculated using the following Equation (1)<sup>[45]</sup>:

$$R(\%) = \left[ \left( 1 - \frac{C_{\rm p}}{C_{\rm f}} \right) \times 100 \right] \tag{1}$$

where  $C_p$  and  $C_f$  correspond to the PEG concentrations in the permeate and feed, respectively.

In addition, porosity was measured by soaking the hollow fiber membranes in kerosene for 1 day. Residual kerosene on the surface of the hollow fibers was removed by blotting with tissue paper. The weights before and after immersing membrane in kerosene were measured using a digital microbalance. The membrane porosity ( $\epsilon$ ) is calculated with Equation (2)<sup>[46]</sup>:

$$\varepsilon$$
 (%) =  $\frac{W_{\rm W} - W_{\rm D}}{(W_{\rm W} - W_{\rm D})(\rho_{\rm w} - \rho_{\rm p})} \times 100$  (2)

where  $W_{\rm W}$  = weight of the wet membrane,  $W_{\rm D}$  = weight of the dried membrane,  $\rho_{\rm w}$  = kerosene density (0.82 g/cm<sup>3</sup>) and  $\rho_{\rm p}$  = polymer density.

## 2.3.7 | Membrane filtration studies

#### Water permeability test

Hollow fiber membrane permeability to pure water was measured in a cross-flow ultrafiltration cell (Dalton, 8400, Italy.) connected to an air-pressurized 2-L solution reservoir. For permeability measurement, the hollow fiber membrane module was first conditioned/compacted with deionized water at  $25 \pm 0.5^{\circ}$ C by gradually increasing the pressure until a constant flux was achieved. After compaction, the water flux was collected at different transmembrane pressures (TMP, ranging from 0.5 to 2 bar), and at least three readings were taken to obtain an average value. The permeability to pure water was measured using Equation (3)<sup>[47]</sup>:

$$J_{\rm pw} = \frac{Q}{A \times \Delta t} \tag{3}$$

where  $J_{pw}$  (Lm<sup>-2</sup> hr<sup>-1</sup>) is the pure water flux, Q is the volume of the permeate water,  $\Delta t$  (hr) is the permeation time, and A (m<sup>2</sup>) is the effective membrane area.

From the slope of the linear relationship between the water flux and transmembrane pressure, the hydraulic permeability was calculated using Equation (4):

$$H_{\rm p} = \frac{J_{\rm pw}}{\Delta P} \tag{4}$$

where  $H_p = hydraulic$  permeability  $(Lm^{-2} hr^{-1} bar^{-1})$ , and  $\Delta P = transmembrane pressure driving force (bar).$ 

### 2.3.8 | Antifouling properties

After pure water flux  $(J_{pw})$  testing, the deionized water was replaced by a 1 g/L BSA solution prepared in a phosphate buffer solution (PB 0.1 M, pH 7.0 ± 0.2) and a permeate flux labeled  $J_v$ BSA was measured at 1 bar for 90 min. A fouled membrane was then cleaned with deionized water. Then, the permeate flux for pure water through the cleaned membrane  $(J_{pw1})$  was remeasured at the same operating conditions. Similarly, after BSA solution testing, this ultrafiltration process was repeated with the other proteins solutions used in this study, that is, trypsin, pepsin, and lysozyme. Finally, to evaluate the fouling resistance ability of hollow fiber membrane, a flux recovery ratio which  $(J_v RR)$  was calculated using Equation (5)<sup>[32]</sup>:

$$J_{\rm v} {\rm RR} \ (\%) = \frac{J_{\rm pw1}}{J_{\rm pw}} \times 100$$
 (5)

where  $J_{pw}$  and  $J_{pw1}$  are the pure water permeation fluxes for the fresh and cleaned membranes, respectively.

In addition, the flux decline ratio  $(J_v DR)$  was calculated using Equation (6):

$$J_{\rm v} {\rm DR} \ (\%) = \frac{J_{\rm pw} - J_{\rm pwl}}{J_{\rm pw}} \times 100 \tag{6}$$

# **3** | **RESULTS AND DISCUSSION**

### 3.1 | Membrane morphology

Figure 2 shows the SEM images of the cross-section of hollow fiber membranes made from PES and PES/GO with three different concentrations of GOs (0.1, 0.5, and 1.0 wt%). The results demonstrated the remarkable changes in the morphology of the membrane after the addition of GO to the dope. It can be clearly seen in Figure 2b–d that the crosssectional structures for the PES/GO nanocomposite membrane are asymmetric, consisting of a thin top layer and a porous sublayer with larger and uniform finger-like pores and macrovoids. In addition, the top layer of the PES/GO nanocomposite membranes consists of closely packed nodules with micron-size void spaces as shown in Figure 2c,d, in marked contrast to the neat PES membrane. The formation of such asymmetric structures is attributed to the stronger interaction/affinity of the dope with the nonsolvent which



**FIGURE 2** Scanning electron microscopy cross-section images of membranes. (a) Pure PES. (b) PES/GO-0.2. (c) PES/GO-0.5. (d) PES/GO-1.0. PES, polyethersulfone; GO, graphene oxide

results in a faster coagulation when the dope contacts the nonsolvent, ultimately creating more nodular structures and forming large, finger-like structures.<sup>[48–50]</sup> However, when the dope was composed of only PES, the membrane structure was different in many ways. For example, the outer layer of the hollow fiber becomes porous with a sponge-like substructure spanning approximately half of the cross-section of the membrane as shown in Figure 2a, and the cross-section of the inner side appears to be much less structurally asymmetrical. However, as shown in the figures, the finger-like macrovoids of the PES/GO nanocomposite membranes were larger and longer with a uniform shape from top to bottom while the macrovoids were smaller for the membrane spun from the neat PES dope. Moreover, teardrop-shaped structures exist in the sublayer of the neat PES membrane. This is attributed

to a slow exchange rate of solvent and nonsolvent during the coagulation process. However, no morphological differences between samples were observed when the GO concentration was increased.

The surface topography of all the prepared hollow fiber membrane samples observed by AFM is illustrated in Figure 3a– e. As can be clearly seen from the AFM images, the surface texture of the pure PES and PES/GO nanocomposite hollow fiber membranes are different. The hollow fiber spun from PES only showed a large-scale surface roughness with a ridges-andvalleys structure. In addition, the ridges and valleys on the surface appeared to be nonuniformly spaced. However, the surface roughness of the PES/GO nanocomposites hollow fibers was relatively lower than the roughness of the neat PES membrane. In addition, the ridge and valley structure of the nanocomposite



**FIGURE 3** Atomic force microscopy 3D images of the membranes surface. (a) Pure PES. (b) PES/GO-0.2. (c) PES/GO-0.5. (d) PES/GO-1.0. (e) PES/GO-0.5 with 500 × 500 nm scale. PES, polyethersulfone; GO, graphene oxide

membranes was spaced more closely together. On the other hand, surface irregularities were observed on the membrane surface, as illustrated by Figure 3a,b, when the GO concentration increased to 1.0 wt%. This was due to GO agglomeration in the dope and GO intruding on the membrane surface. The surface roughness parameters obtained from AFM analysis are shown in 3D images.

# **3.2** | Mechanical and thermal properties

Figure 4a shows the effect of GO addition on the mechanical properties of the membranes. The results revealed that the

PES/GO nanocomposite hollow fiber membranes showed better mechanical properties compared to the pure PES hollow fiber membrane. The tensile strength of the membrane with an optimum amount of GO (0.5 wt%) reached 1.937 MPa, while the elongation at break of the membrane was found to be decreased when GO concentrations were added. The increase in strength of the membrane with 0.5 wt% GO can be explained by the uniform dispersion of GO in membrane. The uniform dispersion of a nanomaterial in a nanocomposite results in good stress transfer from the matrix to the nanomaterial, leading to a uniform stress distribution and minimizing the presence of stress concentration



**FIGURE 4** (a) Mechanical properties and (b) Thermal properties of pure PES, PES/GO-0.2, PES/GO-0.5, and PES/GO-1.0 membranes. PES, polyethersulfone; GO, graphene oxide

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centers.<sup>[51,52]</sup> However, increasing the GO content to 1.0 wt% decreased the elongation further due to the rigidity of the nanocomposite resulting from the increase in GO interactions with the membrane matrix reducing the movement of the polymer chains. Figure 4b shows the TGA results, where the PES/GO nanocomposite hollow fiber membrane specimens exhibited more thermal stability and lower weight loss compared to the pure PES hollow fiber membrane over the 100-750°C temperature range. The effect of increasing the wt% of GO is clearly seen in TGA curve, that is, as the wt% of GO increased from 0.2 to 1.0, the thermal stability increased. The improved thermal stability can be related to the strong interfacial interaction between the GO and the PES matrix. Hence, the addition of GO in the PES matrix improved the mechanical and thermal properties of the hollow fiber membrane.

## **3.3** | Surface properties

Surface properties, including hydrophilicity and charge, are the predominant factors affecting membrane fouling. These properties were investigated using contact angle and zeta potential, and results are given in Figures 5 and 6. Figure 5 shows that the contact angle of the membrane gradually decreased with increasing GO content in the PES matrix due to the hydrophilic nature of GO stemming from the available hydroxyl groups on its surface. However, the membrane hydrophilicity decreased when the GO content exceeded 0.5 wt%. This can be explained by the effects of agglomeration and irregular positioning of the GO for the membrane with 1.0 wt% GO, which decreased the available hydroxyl groups on the surface of the membrane. Overall, GO addition increased the hydrophilicity of the PES/GO nanocomposite hollow fiber membranes. Figure 6 shows the zeta potential of the membranes measured at pH between 2.5 and 9, as a function of the GO concentrations. Adding GO produced a higher negative charge on the PES/GO nanocomposite hollow fiber membranes. While the zeta potential of the neat PES hollow fiber membrane was  $-13 \pm 0.5$  mV at ambient pH, it decreased to  $-17 \pm 0.3$ ,  $-34 \pm 0.6$ , and  $-22 \pm 0.2$  mV for the membrane prepared with GO 0.2, 0.5, and 1.0 wt%, respectively, due to the highly negatively charged nature of the GO. In addition, the isoelectric point (IEP), that is the pH value where virtually no charge is present at the membrane surface, was shifted to lower pH values with the addition of GO. Overall, a negative potential of  $-34 \pm 0.6$  mV at neutral pH suggests that the 0.5 wt% GO/PES nanocomposite membrane is strongly negatively charged, and thus, the membrane showed higher resistant to fouling due to a charge repulsion mechanism at the membrane surface.<sup>[53]</sup>



**FIGURE 5** Water contact angle and porosity of pure PES, PES/GO-0.2, PES/GO-0.5, and PES/GO-1.0 membranes. PES, polyethersulfone; GO, graphene oxide



**FIGURE 6** The surface zeta potential as a function of pH for pure PES, PES/GO-0.2, PES/GO-0.5, and PES/GO-1.0 membranes. PES, polyethersulfone; GO, graphene oxide

# **3.4** | Membrane performance

# 3.4.1 | Hydraulic permeability

Figure 7a,b shows the results of the hydraulic permeability to pure water ( $H_p$ ) and MWCO of the prepared hollow fiber membranes. From a permeability result, the  $H_p$  values of the PES/GO nanocomposite hollow fiber membranes were higher than that of the neat PES hollow fiber membrane. The PES hollow fiber membrane had a water permeability of  $19 \pm 2 \text{ Lm}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$ . It increased to  $21 \pm 1.7 \text{ Lm}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$  for the 0.2 wt% GO membrane and  $30 \pm 1.5 \text{ Lm}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$  for the 0.5 wt% GO membrane, an increase of over approximately 36% compared to the PES hollow fiber membrane. However, at a content of 1.0 wt% GO in the membrane, the  $H_p$  decreased to  $27 \pm 2 \text{ Lm}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$ , which is almost equal to that of the neat PES hollow fiber membrane. When comparing the  $H_p$  values of the nanocomposite hollow fiber membranes with different GO content, the 0.5 wt% GO membrane exhibited a superior water permeability due to its higher hydrophilicity resulting from the uniform dispersion of GO in the membrane.<sup>[37,54]</sup> Additionally, as shown in the SEM image in Figure 2c, the nanocomposite membrane prepared from 0.5 wt% GO membrane showed the typical asymmetric structure with more porous and larger

finger-like macrovoids and open-ends compared to the neat PES membrane, which enhanced membrane permeability. In addition to these features, the rough surface with evenly spaced tiny ridges and valleys increases the interfacial area of water-membrane contact, promoting the flux of pure water and thus improving the membrane permeability. However, increasing the GO content from 0.5 to 1.0 wt% decreased the water permeability from  $30 \pm 1.5$  to  $27 \pm 2$  Lm<sup>-2</sup> hr<sup>-1</sup> bar<sup>-1</sup>. The higher GO content (more than 0.5 wt%) in the membrane led to a decrease in the water permeability because of pore blockage caused by excessive GO and pore collapse in the membrane cross-section resulted from GO aggregation and the large size GO cluster formation. Although the membrane



**FIGURE 7** (a) Molecular weight cut-off (MWCO) and (b) Water permeability of pure PES, PES/GO-0.2, PES/GO-0.5, and PES/GO-1.0 membranes. PES, polyethersulfone; GO, graphene oxide

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Membrane antifouling performance of pure PES, PES/GO-0.2, PES/GO-0.5, and PES/GO-1.0 using long-term filtration tests for FIGURE 8 different proteins: (a) bovine serum albumin (BSA), (b) pepsin, (c) trypsin, and (d) lysozyme. PES, polyethersulfone; GO, graphene oxide

hydrophilicity has been enhanced and it is expected to rise the membrane water flux, pores plugging of membrane neutralizes the effect of hydrophilicity thus the flux of membrane prepared by more than 0.5 wt% GO is almost similar to the pure PES membrane. Hence, we demonstrated that the  $H_{\rm p}$  depends on the GO content added to the nanocomposite membrane. To evaluate the membrane separation performance, the molecular weight cut-off (MWCO) was investigated, and the results are shown in Figure 7a. The results demonstrated that the MWCO of the membranes was significantly increased by the addition of the GO nanoadditive to the dope solution. The increased value of MWCO for the hollow fiber membrane with 0.5 wt% GO nanoadditive is attributed to the increase in porosity of the membrane (as shown in Figure 5).

#### 3.5 **Antifouling properties**

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For characterizing membrane fouling, the flux recovery ratio,  $J_{y}$ RR (%) and the flux decline rate,  $J_{y}$ DR (%), were measured, the results of which are depicted in Figure 8a-d.

The results showed that hollow fiber membrane spun from the PES/GO nanocomposite dope had recovery rates of approximately 96% and 93% for pepsin and BSA, respectively. This explained their low fouling behavior compared to the neat PES hollow fiber membrane. In addition, the decline in membrane flux during the ultrafiltration of both pepsin and BSA was not as severe compared to the declines experienced with trypsin or lysozyme in the feed solution due to the solution pH being above the isoelectric point of pepsin and BSA (reported IEP for pepsin and BSA is 1.0 and 4.7, respectively<sup>[55]</sup>). When comparing antifouling properties of the prepared hollow fiber nanocomposite membranes, the highest  $J_{v}$ RR value of approximately 96% and the lowest flux decline rate of approximately 3.6% were observed for the hollow fiber membrane prepared with 0.5 wt% GO. This is mainly attributed to the relatively higher hydrophilicity of that membrane due to the presence of the large number of uniformly dispersed hydrophilic GO nanoparticles in the membrane structure. The literature also reports that higher hydrophilicity results in the formation of a water molecule

layer on the membrane surface and in the pores, which retards deposition of hydrophobic proteins, and consequently decreases the rate of flux decline (as shown in Figure 8a-d). Another factor that increases the antifouling properties of the same membrane is its more negatively charged surface (as shown in the results of zeta potential, Figure 6), which leads to a minimal deposit of the proteins due to the electrostatic repulsion force caused by the similarity in charge of the membrane surface and proteins. Consequently, membranes were less fouled, leading to a lower flux decline. There are several reports available in the literature on this phenomenon, in which a negatively charged membrane repels negatively charged proteins, particularly pepsin and BSA, due to the effect of electrostatic repulsion.<sup>[8,24,32,56]</sup> Apart from these reasons, many references report that surface texture is also a significant factor that affects membrane fouling in addition to the hydrophilicity and surface charge. As shown in the AFM images, Figure 3c, ridges and valleys on the surface of the membrane prepared with 0.5 wt% GO appeared to be uniform and closely together spaced. The spacing between adjacent ridges and valleys was too small, and therefore, protein molecules did not accumulate on the membrane surface. Thus, the performance of the membrane remained stable over time.

# 4 | CONCLUSION

In this study, hollow fiber membranes made from nanocomposites of PES and varying content (0.2, 0.5, and 1.0 wt %) of GO were prepared by the dry-wet spinning process. The incorporation of GO into the dope increased the permeate flux of water by nearly a factor of two, due to the combined effects of improved hydrophilicity, favorable surface roughness, and a membrane morphology with a typical asymmetric structure. In addition, the results demonstrated that membranes containing GO had a negatively charged surface, thereby reducing fouling of the membrane by protein molecules. When comparing the performances of all the prepared hollow fiber membranes, the PES/GO membrane with 0.5 wt% GO loading exhibited a superior fouling resistance  $(J_{\nu}RR \text{ of approxi-}$ mately 96% compared to approximately  $J_{\nu}R$  62% for the PES membrane) with only an approximately 3.6% flux decline. Moreover, the same membrane showed an enhancement in tensile strength and better thermal stability compared to a pure PES hollow fiber membrane.

#### ACKNOWLEDGMENT

The authors are thankful for the financial support of the King Abdullah Institute for Nanotechnology, Deanship of Scientific Research, King Saud University, Riyadh, Saudi Arabia.

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**How to cite this article:** Alam J, Shukla AK, Alhoshan M, et al. Graphene oxide, an effective nanoadditive for a development of hollow fiber nanocomposite membrane with antifouling properties. *Adv Polym Technol.* 2018;00:1–12. https://doi.org/10.1002/adv.21935