INTRODUCTION

Among the water treatment technologies, membrane separation process has been largely interested and used as a strategic and effective process in water desalination, wastewater treatment of food, pharmaceutical and dye industries, and so on.\(^1\) Nanofiltration (NF) is a pressure-driven membrane process which has a lower operating pressure, higher flux, and lower cost compared to reverse osmosis (RO).\(^2\)

In this regard, NF has been rapidly developed in various industries such as water purification, dye, and pharmaceutical industries to separate molecules with molecular weight ranges from 200 to 1,000 g/mol.\(^3,4\) However, decrease in membrane water flux due to blocking of membrane pores is one of the obstacles of using membrane technologies which decreases the useful lifetime of the membrane.\(^5\) High hydrophobic nature of polymeric membrane induces pore fouling of this category of membranes through adsorption of non-polar solutes and hydrophobic particles or bacteria, thereby limiting long-term applications.\(^6\) For this reason, the modification of polymeric membranes is necessary to enhance its hydrophilicity.

Polyethersulfone (PES) has potential application for the fabrication of NF membranes due to their chemical, thermal,

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**Abstract**

In the present study, the polyethersulfone (PES) mixed matrix nanofiltration membranes with the embedding of the graphene oxide (GO) and sulfonated graphene oxide (s-GO) nanoparticles were fabricated via phase inversion method. The effect of GO and s-GO on the morphology and performance-fabricated PES membrane was evaluated in terms of pure water flux, dye retention, salt rejection, heavy metal removal, and antifouling properties. The fabricated membranes were characterized using FE-SEM, AFM, and water contact angle and porosity measurement. As a result, by adding GO and s-GO nanoparticles, the pure water flux (PWF) of mentioned membranes significantly improved due to the higher hydrophilicity. The increased hydrophilicity of the mentioned membranes was proved by the water contact angle data. The evaluation of nanofiltration performance was assessed by rejection measurement of cationic and anionic dyes. The rejection of heavy metals in the following order 97.5%, 87.8%, 76.3%, and 60.6% for Cr, Cd, Cu, and Ni, respectively, was obtained for the sample that contains 1 wt% s-GO. Moreover, other nanocomposite membranes showed relatively good results. The rejection results showed that GO and s-GO nanoparticles embedded membranes have higher dye retention ability than the bare PES. Fouling resistance of the membranes was evaluated by filtration of bovine serum albumin (BSA) solution. The results of antifouling properties showed that the membrane containing 0.5 wt% s-GO had the best fouling resistance.

**KEYWORDS**

antifouling, mixed matrix membrane, nanofiltration, polyethersulfone, sulfonated GO
and mechanical stability, high glass transition temperatures, and amorphous nature.\cite{17} To improve the antifouling property of PES membranes, different modification techniques have been proposed. The improvement of surface hydrophilicity of PES membranes has been categorized into two basic approaches, including bulk and surface modification. The most important bulk modification methods are the addition of various nanoparticles,\cite{8} sulfonation,\cite{9–12} carboxylation,\cite{9,10,13} and nitration of PES,\cite{14,15} and also grafting of different functional polymers onto PES backbone.\cite{9,10,16} In another approach, interfacial polymerization and different type of surface grafting polymerization, including ATRP, redox and ozone, thermal, plasma, and UV-induced grafting polymerization, have been investigated as the most effective surface modification methods to modify PES backbone.\cite{17}

So far, various nanoparticles such as TiO$_2$, Ag, ZnO, CNT, GO, and so on have been used in the preparation of nanocomposite membranes for separation applications.\cite{17,18}

Considering the unique features of GO, previously reported works on this nanofiller has been highlighted. In related studies, Mahalingam et al.\cite{19} prepared novel PES ultrafiltration membranes using a various amount of GO nanoparticles as filler. They observed higher flux and good rejection properties for the designed membranes. In another study, Gorgojo et al.\cite{20} studied GO-embedded ultrafiltration mixed matrix PES membranes. It was found that the prepared membranes not only have higher flux, but also demonstrate higher rejection and fouling resistance.

Moreover, Jones et al.\cite{21} modified the PES membrane surface in two steps, including amino functionalization of PES surface by UV radiation method and then its surface coating with GO nanoparticles in order to enhancing antifouling membrane properties. According to the obtained results, this approach can be employed as simple and effective methods to fabricate a GO-functionalized UF membrane with an enhanced antifouling property.

Also, Rezaee et al.\cite{22} prepared ultrathin PES membrane with a GO coating to remove arsenic. They showed that pure water flux decreased as the coated GO thickness increased. Furthermore, by increasing the coated GO, the rejection of arsenate ions increased significantly.

Furthermore, Homem et al.\cite{23} investigated the modification of polyethersulfone microfiltration membranes with GO to remove methylene blue dye in aqueous solution. In their filtration tests, the modified membrane presented much higher rejection rates (92.1%).

Considering that the use of bulk modification methods, especially in the case of nanoparticle usage, is more diverse and applicable. In this work, we also focus on utilizing this methodology. Therefore, in this research, we aim to enhance the pure water flux and also decrease membrane fouling properties of PES filled with GO nanoparticles and sulfonated GO nanoparticles (s-GO). In addition, the ability of the prepared nanocomposite nanofiltration membranes for the removal of cationic and anionic dyes, as well as some of the heavy metals, is investigated. Also, we study the effects of incorporating GO and s-GO nanoparticles on pure water flux, rejection efficiency, and antifouling properties of the PES nanofiltration membrane.

2 | EXPERIMENTAL

2.1 | Materials

Polyethersulfone (average $M_w = 150,000 \text{ g/mol}$) was purchased from Aldrich and used as substrate polymer matrix. N,N-dimethylformamide (DMF), polyvinylpyrrolidone (PVP) (average $M_w = 25,000 \text{ g/mol}$), potassium permanganate (KMnO$_4$), sulfuric acid ($\text{H}_2\text{SO}_4, 98\%$), graphite flakes (average particle size < 100 nm), acid blue 26 (or alphazurine B) $\text{C}_3\text{H}_9\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$ ($M_w = 729.13 \text{ g/mol}$), and bismark brown G (Y) (or basic brown) $\text{C}_{11}\text{H}_{20}\text{C}_{12}\text{N}_8$ ($M_w = 419.314 \text{ g/mol}$) with purity of 99% were purchased from Merck and used as received. MgSO$_4$ (%99), NaCl (%99.5), MgCl$_2$ (>98), Na$_2$SO$_4$ (%99), Ni ($\text{NO}_3$)$_2$ 6$\text{H}_2\text{O}$ (%97), Cd ($\text{NO}_3$)$_2$ 2$\text{H}_2\text{O}$ (%98), Cr ($\text{NO}_3$)$_3$ 9$\text{H}_2\text{O}$ (%99.99), and Cu ($\text{NO}_3$)$_2$ 2$\text{H}_2\text{O}$ (%99) were purchased from Merck and used as received. Bovine serum albumin (% 96 (electrophoresis), pH = 7, lyophilized powder) was purchased from Sigma-Aldrich and used as received.

2.2 | Synthesis of GO

Graphene oxide nanoparticles were prepared from graphite powder according to improved Hummers’ method.\cite{24} First, graphite powder (1.5 g) was added to a mixture of $\text{H}_2\text{SO}_4 / \text{H}_3\text{PO}_4$ (180:20 (V/V) %) and then stirred for 2 hr. Afterward, KMnO$_4$ (9.0 g) was added to the mixture and stirred at 50°C for 24 hr. The treatment of graphite was finished by adding ice-cold distilled water (200 ml) and $\text{H}_2\text{O}_2$ (3 ml, 30%w/w) at room temperature. The obtained product was rinsed with $\text{HCl}$ (100 ml, 30%w/w), ethanol (100 ml), and distilled water (100 ml), respectively. Then, the wet sediments were washed with distilled water several times to obtain the neutral pH. Finally, GO powder was dried in vacuum oven.

2.3 | Preparation of sulfonated graphene oxide nanoparticles (s-GO)

The desired amount of GO powder (10 mg) was added to fuming sulfuric acid (3 ml) and then stirred at room temperature under N$_2$ atmosphere for 3 days until to obtain a dark brown suspension. Afterward, this mixture was slowly added to anhydrous diethyl ether (40 ml) with vigorous stirring in an ice bath. Consequently, the dark brown powders were separated from the solution by centrifuging. Finally, the
sulfonated graphene oxide nanoparticles (s-GO) was purified by repeating the previous step and lastly dried in vacuum oven at 40°C overnight.\(^{[25]}\)

### 2.4 Preparation of PES/GO and PES/s-GO nanofiltration membranes

All nanocomposite membranes were prepared by phase inversion method. Casting solutions of all membranes were prepared according to Table 1 by dissolving the desired amount of components in DMF.

To obtain homogeneous casting solution, a desired amount of GO (or s-GO) nanoparticles was dispersed in DMF using an ultrasonic bath for 1 hr. Afterward, PES and PVP were added to the mixture and stirred for 24 hr. To remove air bubbles, the prepared mixture was placed in a sonication bath for 30 min. The prepared mixture was cast onto glass plate with a constant thickness of 250 ± 20 μm using casting knife and then immediately immersed into water as non-solvent bath. The prepared membranes were kept in fresh distilled water tanks to remove any soluble components and also to complete phase inversion process for 24 hr.

### 2.5 Characterization

The measurement of Fourier transform infrared spectrometer (FT-IR) was carried out using a Bruker TENSOR 27 spectrometer. The top surface and cross-sectional morphology and structure of the membranes were monitored by HITACHI S-4160 FE-SEM (field-emission scanning electron microscope). Cross-cut membranes were prepared by breaking the membranes in liquid nitrogen. The Raman spectra of GO samples were recorded by Takram P50COR10, Teksan Co. Atomic absorption (Varian Spectra AA-400) was used to detect elements in permeated solvent. The concentration of dye in permeated solvent was measured by an UV-Vis spectroscopy (Perkin Elmer, Lambda 850). The membrane surface topographies were observed by atomic force microscopy (AFM, ENTEGRA AFMNT-MDT (NT-MDT Co.)) using a scanning probe–optical microscope. The surface hydrophilicity of all membranes was evaluated by determination of the static water contact angle using a contact angle goniometer (OCA 15 plus, Data physics) at 25°C. This evaluation was done at least five random points on the surface of each membrane to determine the mean value of the contact angle, and the imaging of drops was taken by using a digital camera.

### 2.6 Porosity

The overall porosity (\(\varepsilon\)) is calculated according to the following Eq. (1):\(^{[7]}\)

\[
\varepsilon = \frac{(W_{\text{wet}} - W_{\text{dry}})}{A \times t \times d}
\]

where \(W_{\text{wet}}\) and \(W_{\text{dry}}\) are the weight of the wet membrane and the weight of the dry membrane, respectively. \(A\) is the membrane effective area (m\(^2\)), \(d\) is the water density (998 kg/m\(^3\)), and \(t\) is the membrane thickness (m).

### 2.7 Water uptake

To determine water uptake, the pieces of membrane were dipped in the distilled water for 24 hr. After this time period, the wet membrane was weighed. Then, the water uptake value of membrane samples was estimated by the following Eq. (2):\(^{[26]}\)

\[
\text{Water Uptake (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{wet}}} \times 100
\]

where \(W_{\text{wet}}\) and \(W_{\text{dry}}\) are the wet and dry membrane weight (g).

### 2.8 Mean pore radius

The membrane mean pore radius (\(r_m\)) was determined by the Guerout–Elford–Ferry equation (Eq. 3):\(^{[27]}\)

\[
r_m = \sqrt{\frac{8(2.9 - 1.75\varepsilon) \times \eta \times t \times Q}{A \times \varepsilon \times \Delta P}}
\]

where \(r_m\) is mean pore radius (nm), \(\eta\) is the water viscosity (8.9 × 10\(^{-3}\) Pa s), \(Q\) is the volume of the permeated pure water (m\(^3\)/s), and \(\Delta P\) is the operating pressure (5 bar).

### 2.9 Permeation and rejection experiments

The performance of the prepared membranes was investigated using a dead-end stirred cell filtration system coupled with a nitrogen gas line with the volume of 150 ml

<table>
<thead>
<tr>
<th>Membrane No.</th>
<th>PES (%)</th>
<th>s-GO (%)</th>
<th>GO (%)</th>
<th>PVP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M1</td>
<td>18</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>M2</td>
<td>18</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>M3</td>
<td>18</td>
<td>0</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>M4</td>
<td>18</td>
<td>1</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>M5</td>
<td>18</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>M6</td>
<td>18</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
at operating pressure of 5 bar and room temperature. The experiments were performed after the membranes were pretreated under the pressure of 5 bar with distilled water for 30 min in order to obtain a steady flux. The solution is stirred at the rate of 400 rpm to decrease concentration polarization during the experiments. The performance of fabricated nanofiltration membranes was investigated by determination of pure water flux, ability of dye removal, salt rejection (desalination), removal of heavy metals, and bovine serum albumin (BSA) fouling tests. The pure water flux \( J_{w,1} \) \( (\text{kg m}^{-2} \text{ hr}^{-1}) \) was calculated using the following Eq. (4):

\[
J_{w,1} = \frac{M}{A \times \Delta t}
\]

where \( M \), \( A \), and \( \Delta t \) are the total weight of the collected permeate pure water (kg), the membrane effective area (m\(^2\)), and the permeation time (hr), respectively. The experiments were repeated three times, and the average value was reported. The performance of all membranes was investigated by determination of the pure water flux, the rejection of several salts (such as NaCl, Na\(_2\)SO\(_4\), MgSO\(_4\), and MgCl\(_2\)) from aqueous solution and some of heavy metals (such as Cd, Cr, Cu, and Ni), dye removal (acid blue 26 and bismark brown G (Y), Figure 1), and fouling resistance of membrane via BSA solution.

Two aqueous feed dyes solution were prepared with the concentration of 30 ppm and 100 ppm. The UV-Vis spectrophotometric method was used to calculate the efficiency of dye removal in the appropriate wavelengths \( (\lambda_{\text{max}} = 535 \text{ and } 462 \text{ nm}) \) by calibration curve.\(^{29}\) Dye rejection was calculated by the following Eq. (5):\(^{28}\)

\[
R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

In this equation, \( C_p \) and \( C_f \) are the concentration of dye in permeate (ppm) and feed solution (ppm), respectively.

### 2.10 Antifouling experiments of the fabricated membranes

The antifouling features and flux recovery ratio (FRR) of the PES/GO and PES/s-GO nanocomposite membranes were measured according to the following procedure. After water flux tests, a BSA solution (500 ppm) as a good fouling agent was replaced in the equipped stirrer cell and the flux of BSA solution \( J_p \) was recorded as weight of permeated water at 5 bar for 90 min. After filtration of the BSA solution, this membrane was washed with distilled water for 30 min. Finally, the pure water flux of this washed and cleaned membrane was measured by distilled water \( J_{w,2} \).

The flux recovery ratio (FRR) as a parameter for comparing the antifouling features of the membranes is defined by the following Eq. (6):\(^{7}\)

\[
\text{FRR} = \left(\frac{J_{w,2}}{J_{w,1}}\right) \times 100
\]

Additionally, to analyze the study of membranes’ fouling resistance details, parameters such as total fouling ratio \( (R_t) \), reversible fouling ratio \( (R_r) \), and irreversible fouling ratio \( (R_{ir}) \) were estimated. Irreversible fouling ratio \( (R_{ir}) \) is caused by attachment of fouling agents onto membrane surface, and reversible fouling ratio \( (R_r) \) is occurred due to concentration polarization.\(^{30}\) These mentioned parameters were calculated by the following equations:\(^{28}\)

\[
R_t(\%) = \frac{J_{W,1} - J_p}{J_{W,1}} \times 100
\]

\[
R_r(\%) = \frac{J_{W,2} - J_p}{J_{W,1}} \times 100
\]

\[
R_{ir}(\%) = \frac{J_{W,1} - J_{W,2}}{J_{W,1}} \times 100
\]

**FIGURE 1** Structure of acid blue 26 (left) and bismark brown G (Y) (right) dyes
3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of GO and s-GO

Graphene oxide nanoparticles were prepared according to improved Hummer’s method.\textsuperscript{[24]} In addition, s-GO nanoparticles were prepared by sulfonation of the prepared GO using fuming sulfuric acid as sulfonic acid agent.\textsuperscript{[25]} In order to characterize the prepared GO and s-GO nanoparticles, FT-IR and Raman spectroscopy were employed. The FT-IR spectra of the prepared GO and s-GO nanoparticles and also graphite are shown in Figure 2.

As shown in Figure 2, for GO sample in comparison with graphite, the new peaks observed at 3,350, 1,715, 1,390, and 1,053 cm\textsuperscript{-1} are belonged to hydroxyl groups, carbonyl groups, and C–O vibration of epoxy groups, respectively. In addition, for s-GO sample, the new peaks at 1,325, 1,140, and 750–1,000 cm\textsuperscript{-1} can be assigned to S=O groups, -SO\textsubscript{3}H groups, and S–O bands, respectively. The appearance of these new peaks (1,325, 1,140, and 750–1,000 cm\textsuperscript{-1}) confirms the success of sulfonic acid functionalization of GO nanoparticles.\textsuperscript{[31–33]}

The Raman spectroscopy is one of the strongest techniques for studying of structural changes in graphite and its derivatives. The Raman spectra of the prepared GO and s-GO are shown in Figure 3. From the Raman spectra, the $I_D/I_G$ ratio of s-GO and GO are 0.93 and 0.84, respectively. The higher $I_D/I_G$ ratio for s-GO compared with GO sample is probably related to lower the sp\textsuperscript{2} domains in this sample and confirmed the presence of oxygen-containing groups onto the surface of s-GO nanoparticles. These results (FT-IR and Raman) are in good agreement with previously reported works by Stankovich\textsuperscript{[34]} and also Ren.\textsuperscript{[35]}

3.2 | Preparation and characterization of nanocomposite nanofiltration membranes

The PES-based nanocomposite nanofiltration membranes filled with GO and s-GO were prepared by phase inversion method. FE-SEM analysis was used to detect the existence of GO and s-GO into membrane matrix and also to observe structural changes in the prepared membranes in the presence of GO and s-GO nanoparticles as hydrophilic nanofillers. FE-SEM images of the top surface of the prepared nanocomposite membranes are shown in Figure 4.

The FE-SEM images clearly showed that GO and s-GO nanoparticles are immigrated to the surface of membranes. In addition, as can be seen from FE-SEM micrographs, GO and s-GO nanoparticles were well dispersed in the polymer matrix and also did not show significant agglomeration of GO nanoparticles to the membrane surface which is attributed to carbon-based structure of GO and s-GO nanoparticles. The cross-section FE-SEM images of the prepared nanocomposite membranes indicated that structural morphology of these membranes was greatly affected by the addition of GO and s-GO nanoparticles (Figure 5).

In general, all PES membranes with or without nanofillers displayed an asymmetric porous sub-layer structure with a dense top-layer and finger-like structure. As shown in Figure 5, size of the channels and voids in PES/GO and s-GO nanocomposite membranes is larger than neat PES membrane. In addition, the finger-like channels of PES/GO and also PES/s-GO are slightly broader than neat PES membrane. This finding suggests that the hydrophilic nature of GO and s-GO improves the mass exchange rate between solvent and non-solvent in the coagulation step, thereby making possible the formation of larger pore channels.\textsuperscript{[36,37]} Furthermore, the pore volume of all nanocomposite membranes in the sub-layer is bigger than neat PES membrane particularly upto...
0.5 wt% and after that it decreases. The reason of this occurrence can be attributed to the formation of agglomerated GO nanoparticles at high GO loading.

Increasing the viscosity of polymeric solution as a result of rising nanoparticle loading is an important property of nanofiller addition in polymeric solution. Although, the viscosity of polymeric solutions was not determined experimentally, however, the changing viscosity of polymeric casting solution by the addition of GO nanoparticles was clearly evident. According to many reports about this phenomenon, the higher viscosity caused to create lateral pores same as that pores observed in this research.\textsuperscript{[7,38,39]} Owing to the fact that surface roughness of membrane is a very effective parameter in its antifouling features, therefore, the surface roughnesses of the prepared nanocomposite membranes was investigated by AFM technique. The two- and three-dimensional AFM image of the nanocomposite membranes surface is shown in Figure 6.

As can be seen in AFM images, the surface roughness of nanocomposite membranes was increased by an increase in GO and s-GO content. This result is probably due to the hydrophilic nature of GO and s-GO which caused acceleration of phase exchange during phase inversion process, thereby providing migration of these nanoparticles to the membrane surface. According to AFM results, it could be concluded that GO nanoparticles were significantly grown up on the membrane surface. The surface roughness parameters of the prepared membrane are presented in Table 2. $S_a$ parameter represents the mean roughness of the scanning surface, and $S_q$ is the mean square root of the $z$ data, and finally, $S_z$ is the mean height difference between the points with highest and deep points. From Table 2, the surface roughness parameters of the PES/GO and PES/s-GO nanocomposite membranes are demonstrated roughness changing of PES membrane by incorporation of GO and s-GO nanoparticles.

Due to the fact that one of the most important surface properties affecting the antifouling performance of nanofiltration membranes is the hydrophilicity of the membrane surface; therefore, the evaluation of this property was carried out by...
FIGURE 4  Cross-section FE-SEM images of PES nanocomposite membranes: (a and b) bare PES, (c and d) GO 0.5 wt%, (e and f) s-GO 0.5 wt%, (g and h) GO 1 wt%, (i and j) s-GO 1 wt%, (k and l) GO 1 wt%, and (m and n) s-GO 1 wt%
FIGURE 6  2D and 3D AFM images of PES nanocomposite membranes: (a) bare PES, (b) GO 0.5 wt%, (c) s-GO 0.5 wt%, (d) GO 1 wt%, and (e) s-GO 1 wt%
membrane surface is more hydrophilic. The literature review showed that enhancing hydrophilicity nature of membrane surface can improve the pure water flux and fouling resistance features of membrane.\[^{40}\] The water contact angle value of the prepared nanocomposite membranes is shown in Figure 7.

According to these data, the water contact angle of nanocomposite membranes decreased significantly with the incorporation of GO and s-GO nanoparticles. The pristine PES has the greatest contact angle (86.8°) due to the hydrophobic nature of PES while M6 sample containing 1 wt% s-GO showed the lowest contact angle (58.4°). These results clearly approve the improvement of surface hydrophilicity of the corresponding nanocomposite membranes compared with the pristine PES membrane. The rising surface hydrophilicity and improving surface morphology of nanocomposite membranes due to the addition of hydrophilic nanoparticles are correspond to the reported results in the literatures.\[^{41}\] As previously mentioned, this improvement can be attributed to migration of the hydrophilic GO and s-GO nanoparticles to the membrane surface during the membrane formation processes.

The pure water flux value (PWF) of the prepared nanocomposite membranes is presented in Figure 8. As can be seen in Figure 8, by the addition of GO and s-GO nanoparticles, the PWF has substantially increased. The pure water flux was 25.6 for membrane M2 which is about 12 times higher than PWF of the pristine PES membrane.

Due to the fact that there is a direct relation between the PWF and hydrophilicity of membrane surface,\[^{42}\] these results are confirmed with the water contact angle results. In addition, the PWF was increased by adding GO and s-GO; however, there is a significant difference between the results of prepared nanocomposite membranes. This unusual behavior can probably be attributed to decreasing the radius of membrane pores or blockage of some membrane pores due to the accumulation of GO and s-GO them. Zhang et al.\[^{38}\] have already reported a similar observation in PVDF/GO nanocomposite membranes.

The measured porosity of the prepared membranes as well as their water content is shown in Figures 9 and 10, respectively.

**TABLE 2** Roughness parameters of some of the prepared membranes

<table>
<thead>
<tr>
<th>Membrane designation</th>
<th>Roughness parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_a$ (nm)</td>
</tr>
<tr>
<td>M0</td>
<td>40.8566</td>
</tr>
<tr>
<td>M1</td>
<td>9.94350</td>
</tr>
<tr>
<td>M2</td>
<td>5.10883</td>
</tr>
<tr>
<td>M5</td>
<td>38.1708</td>
</tr>
<tr>
<td>M6</td>
<td>39.6899</td>
</tr>
</tbody>
</table>

**FIGURE 7** The effect of GO and s-GO nanoparticle content on water contact angle of PES-based nanocomposite membranes

**FIGURE 8** The effect of GO and s-GO nanoparticle content on the pure water flux of PES membrane and its nanocomposite membranes

**FIGURE 9** The effect of GO and s-GO nanoparticle content on porosity of PES membrane and its nanocomposite membranes

It can be seen that both parameters have considerably increased for the prepared nanocomposite membranes in comparison with the pristine PES membranes. All nanocomposite membranes have porosity ranging from 61% to 81%,
which is very suitable for high-performance nanofiltration membranes. Owing to the fact that the pore size distribution plays an important role in the permeability and performance of nanofiltration membranes, the mean pore radius of nanocomposite membranes is measured and demonstrated in Figure 11. There is the overall correlation between the mean pore radius and PWF permeability of the prepared nanocomposite membranes. However, the M1 and M2 samples show higher flux, despite having less porosity, due to the larger radius of the pores. In this study, the performance of the prepared nanofiltration membranes was also investigated by evaluating the rejection of various components, including several salts, heavy metals, dyes, and also BSA. The results of salt rejection are shown in Figure 12.

All rejection measurements were carried out in a dead-end nanofiltration cell at pressure of 5 bar. The salt rejection value of all membranes has considerably improved compared to the pristine PES membrane. The following trend is observed for rejection of different salts: MgCl₂ > MgSO₄ > Na₂SO₄ < NaCl.

The rejection phenomena of membrane have been explained by several mechanisms such as molecular sieves, Donnan rejection effect, and differences in diffusion and solubility.[43] However, it has been reported that the predominant mechanism in membrane containing polar groups on its
Regarding the obtained results and also existence of GO and s-GO nanoparticles bearing polar groups, it can be deduced that the predominant mechanism in salt rejection of these nanocomposite membranes is Donnan effect.

The removal of heavy metals such as Cd, Ni, Cr, and so on from industrial wastewater is one of the most important challenges in the field of extraction and membrane technology. Thus, nowadays, the achievement of an effective way for the treatment of industrial wastewater is an important issue and requires more studying and practical research. Several approaches, including chemical precipitation with lime and soda, ion exchange process, and oxidation and reduction reactions, have been introduced to remove heavy metals from industrial wastewater; however, the membrane filtration methods such as reverse osmosis and nanofiltration have found a special place. To investigate the efficiency of the prepared nanocomposite membranes in the separation of heavy metals, removal of Cd, Cr, Cu, and Ni was carried out under nanofiltration conditions and at pressure of 5 bar. The results of this analysis are shown in Figure 13. From Figure 13, it is observed that M6 obtained the best results and showed 97.5%, 87.8%, 76.3%, and 60.6% rejection for Cr, Cd, Cu, and Ni, respectively. Moreover, other nanocomposite membranes showed relatively good results.

In general, it can be stated that the presence of GO and s-GO nanoparticles on the membrane surface and their proper distribution lead to the high rejection of heavy metal salts by changing the surface charge of membrane. In addition, the separation of organic dyes in industrial wastewater is important for preventing their entry into water resources. Therefore, the efficiency of the prepared nanocomposite membranes in the separation of organic dyes was also performed by filtration of blue 26 and Bismark Brown G(Y) as two common organic dyes. To measure the amount of dye passed through the membrane, the permeate solution was analyzed by UV technique. Dye retention performance of the prepared nanocomposite membranes is shown in Figure 14.

According to the obtained results, the dye rejection efficiency of all nanocomposite membranes against the PES membrane has been improved and the best results were shown
for M6. Also, in this case, the negative charge of membrane surface offered by GO and s-GO nanoparticles has led to an increase in rejection of organic dyes.

Membrane fouling as one of the major problems of membrane technology has various disadvantages such as reducing the flow, increasing the cost of operation, and maintenance and decreasing membrane performance. The reasons of membrane fouling are different, but it is mostly caused by hydrophobic character of membrane surface. In this study, to investigate the effect of GO and s-GO nanoparticles on the fouling resistance, the fouling phenomena of the pristine PES and prepared nanocomposite membranes were measured by determining the water flux recovery (FRR) via alternative filtration of pure water and BSA. Measuring the FRR of all membranes was carried out by the following filtration steps: determination of water flux for 120 min, 500 ppm BSA solution flux for 120 min, and then water flux for 120 min after 30 min washing with distilled water, respectively. As shown in Figure 15a, the BSA rejection of nanocomposite membranes is significantly higher than the pristine PES membrane. As can be seen after FRR test (Figure 15b), the permeability of the membranes is reduced which is due to membrane’s fouling.

Moreover, the greatest fouling was clearly observed for the pristine PES membranes, and interestingly, M6 membrane demonstrated the lower fouling. The FRR results of the prepared nanocomposite membranes are also provided in Figure 16.

It is known that the high FRR value represents better antifouling properties of membrane and means an easier washing of contaminating material from membrane surface. These findings indicate that the membranes containing GO and s-GO nanoparticles compared to the pristine PES membrane exhibit a significant FRR performance, and the best results were observed for the membrane containing 0.5% s-GO nanoparticle content. This result is more reasonable with regarding to the fact that surface hydrophilicity and surface roughness are the two main factors affecting the membrane antifouling property. In correlation with AFM and water contact angle data, these results indicate that these factors have significantly improved by the addition of GO or s-GO nanoparticles. Furthermore, the reversible and irreversible resistance results of the prepared membranes are demonstrated in Figure 17. As can be seen in Figure 17, the ratio values of total fouling ($R_T$) of the prepared membranes in comparison with the pristine PES membrane have been significantly improved. In addition, the irreversible resistance of nanocomposite membranes was drastically decreased by the addition of GO nanoparticles; this parameter was 5.5% and 45.3% for pristine PES and its nanocomposite.

4 | CONCLUSION

Graphene oxide and s-GO nanoparticles were synthesized and were used to fabricate PES nanocomposite membranes via phase inversion method. The FT-IR results revealed that with migration of the GO and s-GO nanoparticles to the top surface, the functional groups such as hydroxyl, carboxylic acid, and epoxy rings were available to a high degree. The nanofiltration performance of the prepared membranes was investigated with dye retention. The results obviously showed higher dye rejection for the membranes containing 0.5 wt% s-GO than the neat PES. Also, the results showed that PWF of the prepared membranes was higher than the neat PES membrane due to enhancement membrane hydrophilicity. The mixed matrix PES/s-GO filled with 0.5 wt% nanoparticle showed the minimum values for flux decreased ratio, which showed the higher antifouling ability. In addition, a high rejection of heavy metals (Cr, Cd, Cu, and Ni) for the sample that contains 1 wt% s-GO was obtained. The results from this study revealed that the GO and especially s-GO nanoparticles is an excellent additive as antifouling agent, which is promising for new applications.

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