Research Article

Preparation and Characterization of a Hydrophilic Polysulfone Membrane Using Graphene Oxide

Hoan Thi Vuong Nguyen ¹, Thu Hong Anh Ngo ², Khai Dinh Do,² Minh Ngoc Nguyen,¹
Nu Thi To Dang,¹ Tham Thi Hong Nguyen,³ Vo Vien ¹ and Tuan Anh Vu ⁴

¹Faculty of Chemistry, Quy Nhon University, Quy Nhon, Vietnam

²Faculty of Chemistry, VNU University of Science, Hanoi, Vietnam

³NTT Hi-Tech Institute, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

⁴Institute of Chemistry, Vietnam Academy of Science and Technology, Ha Noi, Vietnam

Correspondence should be addressed to Hoan Thi Vuong Nguyen; nguyenthivuonghoan@qnu.edu.vn and
Thu Hong Anh Ngo; anhthu@hus.edu.vn

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In general, the polysulfone (PSf) membranes are popular choices for water treatment because they have high thermal stability and good chemical resistance. On the other hand, the filtration capacity of the polysulfone membrane is limited because of its low water flux and poor antifouling ability, which are caused by the low surface hydrophilicity of the membranes. In this research, blending of graphene oxide (GO) or graphene oxide-titanium dioxide (GO-TiO₂) mixture into the polysulfone matrix had been carried out through the phase inversion method to enhance the hydrophilic and antifouling properties. Methods such as energy-dispersive X-ray spectroscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, and water contact angle measurement were used to examine the surface properties of the prepared membranes. Experimental results have led to a conclusion that graphene oxide can be stabilized into prepared membranes, and then, by reducing the water contact angle values, the surface of these membranes becomes hydrophilic, which increases the permeability and the water flux of methylene blue from the aqueous feed solution, improving the membrane's antifouling resistance.

1. Introduction

Today, membranes and membrane processes have been applied in cleaning technology and the environmental field [1, 2]. Efficiency and utility from membrane applications have led to the need for new membrane materials with properties suitable for their applications. Therefore, the type of material selected and the method of membrane preparation are the determining factors for the properties of the membrane.

Polysulfone (PSf) is the preferred choice in membrane fabrication, and its prominence is derived from chemical resistance, wide operating temperature and pH, and high mechanical strength [2–5]. However, at present, the operating costs of PSf membrane processes are still quite high

because of fouling, limitations on filtering capacity, and longevity, which are due to their high hydrophobic properties [2–4, 6, 7]. Recently, the increase in hydrophilicity and the minimization of fouling of PSf membranes have been tested through a variety of solutions including modifying the surface [8, 9], coating onto the membrane surface [10–14], and blending the hydrophilic materials into the membrane casting solution before fabricating the membrane [2, 5, 15–20]. Among the aforementioned methods, the method of blending PSf with some hydrophilic polymers or inorganic nanoparticles to increase the surface hydrophilic and antifouling properties has proven remarkably effective [2, 5, 20–23].

Zodrow et al. [21] blended nanosilver particles into the matrix of the PSf membrane to increase the membrane

hydrophilicity and reduce the biofouling and virus penetration. By using the phase inversion method, Kang et al. [2] prepared more hydrophilic PSf/SGO (sulfonated graphene oxide) membranes. After conducting the tests, the researchers found that mixing 1.5 w/w% SGO into the PSf matrix made this membrane reach a water flux higher than 125% compared to that of the PSf membrane. Prabhu et al. [5] blended the chitosan derivative 1H-pyrazole-4-carbaldehyde into the PSf matrix by the wet coagulation method. These observations indicate that hydrophilic groups (such as hydroxyl, amine, and imine) improved the hydrophilicity of the blended membrane as they cause a decrease in the contact angle (from $70 \pm 1^\circ$ of the PSf membrane down to $62 \pm 1^\circ$ of blended membranes) and the improvement in water flux (from 24 of the PSf membrane to $351 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ of the blended membrane at 0.8 MPa). Ravishankar et al. [20] blended graphene oxide (GO) nanoparticles into the PSf matrix to prepare PSf/GO membranes. The results showed that the PSf/GO membrane has a better hydrophobicity than the PSf membrane (the contact angle of water is 34.2° and the permeability is $52.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$).

Recently, graphene oxide (GO) has been one of the most common hydrophilic inorganic particles that are used for preparing blended membranes [3, 20]. It has been proven that the appearance of oxygen-containing groups including hydroxyl, epoxy, and carboxyl when fabricating a graphene oxide-blended membrane has shown that the membrane possess high effective flux and better antifouling capacity [20]. The strong hydrogen network with the water molecules is made up of oxygen functionalities, so it creates a strong hydrophilicity [22, 24]. The combination (blend) of GO into the membrane is prominent in increasing the permeability [25, 26] and antifouling [7] and antibacterial [23, 25–30] properties for membrane applications as have been recorded in many previous studies. All results show that GO-blended polymer membranes are more hydrophilic and antifouling than unblended membranes, and it means that GO membranes are hydrophilic [26–28].

To enhance the membrane-blending properties, titanium dioxide (TiO_2) or other hydrophilic nanoparticle materials are integrated into the polymer membrane by modifying these nanoparticles with GO by the surface hydrothermal method [29, 31]. Safarpour et al. [32] prepared the reverse osmosis membrane by incorporating the reduced graphene oxide (rGO)/ TiO_2 material onto its surface. The researchers found that the separation efficiency and the antifouling capacity of the membranes increased compared to unblended membranes (water flux improved from 34.3 to $51.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and antifouling resistance increased from 49% to 75% after 180 minutes filtering bovine serum albumin solution). In another article, Faria et al. [33] showed that the growth of bacteria and biofilm on membranes has been prevented by adding silver and graphene oxide to TFC-PA membranes. The reason for the decline in the flux is due to biofilm development, which has decreased by 30% after incorporating GOAg nanocomposites onto the TFC membrane.

Most polysulfone membranes are prepared by the phase inversion method as other polymer membranes. To begin the membrane forming process, the researchers dissolve the

polymer in the solvent or in an organic solvent mixture. Then, the coating solution is spread in the form of a thin layer onto the plate or on a rotating disc, and the next membrane is coagulated in a solvent-free medium to form a porous membrane [33, 34]. A spin coating method is a technique for making a highly homogeneous membrane [34].

In general, the coating of hydrophilic layers such as GO and TiO_2 onto the membrane matrix is an effective method for improving the membrane separation performance.

However, very little information on the preparation of the polysulfone membranes with GO and TiO_2 has been known.

In this study, graphene oxide nanoparticles and graphene oxide/titanium dioxide were blended into the polysulfone matrix to prepare polysulfone/GO (PSf/GO) and polysulfone/GO- TiO_2 (PSf/GO- TiO_2) membranes using the phase inversion method. Effects of GO and TiO_2 on the hydrophilic and antifouling properties of the blended membranes were also compared by determining permeability, retention, flux, and fouling resistance of methylene blue in aqueous solution.

2. Experimental Methods

2.1. Materials. Graphene oxide (GO) prepared from graphite powder (Merck) by Hummers' method [35] and TiO_2 prepared from tetrachloride TiCl_4 (Merck) titanium by the sol-gel method were used as additives in the coating solution. Polysulfone (molecular weight: $22,000 \text{ g}\cdot\text{mol}^{-1}$) was used as the original polymer supplied by Sigma-Aldrich in the casting solution. *N,N*-Dimethyl formamide (DMF) purchased from China Science Co., Ltd. was used as a solvent. Methylene blue (MB) (China) has been used to prepare feed solutions for membrane filtration experiments.

2.2. Preparation of PSf, PSf/GO, and PSf/GO- TiO_2 Membranes. The PSf, PSf/GO, and PSf/GO- TiO_2 membranes were prepared through phase inversion with DMF used as a solvent, GO and GO-modified TiO_2 as additives to prepare PSf/GO and PSf/GO- TiO_2 membranes, and deionized water as the nonsolvent in the coagulation bath.

Polysulfone and a different amount of GO (0.0, 1.0, and 2.0% by weight of PSf) were added to DMF and dissolved for 24 hours at 60°C by sonication to obtain a homogeneous mixture, and then to allow the mixture to release all the bubbles, it was left overnight.

To prepare PSf/GO- TiO_2 membranes, a different amount of TiO_2 (10, 15, and 20% by weight of GO) and GO were added to DMF and dissolved for 24 hours at 60°C by sonication to obtain a homogeneous mixture and then left overnight.

Using the spin coating method, the solutions are then dripped on clean glass supports (coating speed in the range of 1400 to 2400 rpm). Then, the solvent is evaporated in 30 seconds, and this solution is soaked in a freezer. After that, the membrane that was formed was peeled off and deionized water was used to wash it in order to remove any

remaining solvents. Before testing, the blended membranes must be kept carefully in deionized water.

2.3. Characteristics of Materials and Membranes. A D8 Advanced Bruker anode X-ray diffractometer with CuK α ($\lambda = 0.154$ nm) radiation using the scanning step of $0.02^\circ \cdot \text{s}^{-1}$ in the range of 2° to 80° was used to analyze X-ray diffraction (XRD). An electron microscope (SEM-EDX, Nova Nano SEM 450) and a transmission electron microscope (TEM, JEOL 2100F) were used to determine the morphology, size, and elemental mapping of the samples to be summed; the case is characterized by energy-dispersive X-ray spectroscopy. The results of the Fourier transform infrared (FTIR-ATR) spectroscopy method used for samples were recorded on a PerkinElmer spectrophotometer. Water contact angle measurement was used to calculate the moisture content of the unblended and blended membranes via CAM 101/KSV Instruments (Finland), which was used to capture ionized water drops located on the dry surface of the membrane at 25°C .

2.4. Assessment of Membrane Filtration Properties. Membrane separation tests are performed in a terminal filtration system, including 200 cm^3 stainless steel cylindrical cells and a paddle impeller; working pressure in all experiments is 0.87 bar. The filtrate was collected every 5 minutes, and the average throughput was calculated after 90 minutes of filtration. In all experiments, we carefully washed membrane cells with pure water (both before and after use).

Membrane filtration properties are determined through permeability J_w ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$) = $[V_w/(AtP)]$, where V_w is the volume of water through the membrane area of A during the pressure determination of P . Ratio of permeability normalization (J_w/J_{w0}), where J_w and J_{w0} are the permeabilities of the blended and unblended membranes, was used to examine the improved permeability of the membrane. The flux (J , $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) is evaluated by $J = [V/(At)]$, where V is the volume of the filtrate. The normalized flux ratio (J/J_0) has been used to determine the enhancement of flux of blended membranes, in which J and J_0 are the flux of the blended and unblended membranes, respectively. The retention (R) of methylene blue is calculated by $R = [(C_0 - C)/C_0] \cdot 100$ (%), where C_0 and C are methylene blue concentrations in feed and filtrate, respectively.

2.5. Assessment of Membrane Antifouling Property. The antifouling property was determined via the maintained flux ratios (FM, %) during filtration. The maintained flux ratio was evaluated by $\text{FM} = (J_t/J_{t0}) \cdot 100$ (%), where J_t and J_{t0} are the fluxes of membranes at t time and initial time ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$).

3. Results and Discussion

3.1. Characteristics of GO and GO-TiO₂ Nanoparticles. The successful synthesis of GO, TiO₂, and GO-TiO₂ materials has been confirmed through X-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM), energy-

dispersive X-ray spectroscopy-mapping (EDX-mapping), transmission electron microscopic (TEM) image, and Fourier transform infrared (FTIR) spectral analysis.

3.1.1. X-Ray Diffraction (XRD) Spectrum. Figure 1 shows the XRD spectrum of GO, TiO₂, and GO-TiO₂. The diffraction peak at a lower angle of about 11.4° GO implies the introduction of oxygen-containing functional groups of GO [36, 37]. However, two broad peaks at about 26° and 44° assigned to graphite can clearly see the complete non-oxidation of graphite. Also, Figures 1(a) and 1(b) shows the appearance of a titanium element in the TiO₂ and GO-TiO₂ nanoparticles, respectively. We can see that the TiO₂ materials appeared in the anatase phase (based on the standard library JCPDS 21-1272), with the occurrence of sharp peaks (101), (004), (105), (211), and (204) at 2θ 25.5° , 37.0° , 54.0° , 56.5° , and 62.5° . Besides, rutile phase also appeared (according to the standard library JCPDS 65-0190) along (110) and (111) at 2θ 27.5° and 41.2° . In Figure 1(b), the characteristic peaks of GO and TiO₂ appeared. Therefore, GO and GO-TiO₂ were synthesized successfully.

3.1.2. SEM, EDX Mapping, and TEM Images. Figures 2 and 3 display the SEM, EDX-mapping, and TEM images of GO and GO-TiO₂ nanoparticles. The results showed that GO had a wrinkled surface with some small pieces. This indicated the successful exfoliation of the GO sheet from graphite during graphite oxidation. As can be seen more clearly via the TEM image, there were many layers of GO onto the graphite surface. Thus, the GO material was synthesized successfully from graphite.

SEM images (Figure 3(a1) and 3(a2)) of synthesized GO-TiO₂ materials showed that the aggregated TiO₂ nanoparticles appeared with GO particles. TEM image of GO-TiO₂ materials showed that the average particle size of TiO₂ particles dispersed onto the GO sheet was 10 nm (Figure 3). Thus, the GO-TiO₂ material was synthesized successfully. EDX-mapping images were used to check the components in the synthesized material. Figures 3(b)–3(d) show that there is a homogeneous distribution of the C, O, and Ti elements in the materials.

3.1.3. FTIR Spectra. The FTIR-ATR spectra of GO, TiO₂, and GO-TiO₂ are shown in Figure 4. The peaks of GO (Figure 4(a)) were observed via the appearance of C-O stretching, C=O stretching, and O-H stretching, which include the bands at 1050 cm^{-1} , 1720 cm^{-1} , and 3350 cm^{-1} after oxidizing graphite into GO. These groups are hydrophilic. Thus, GO is also hydrophilic. Moreover, the spectrum of TiO₂ (Figure 4(b)) and GO-TiO₂ (Figure 4(c)) showed peaks at approximately $580\text{--}1000\text{ cm}^{-1}$ attributed to Ti-O-Ti stretching [38], showing the successful synthesis of TiO₂ particles into the GO-TiO₂ material.

3.2. Membrane Characteristics. After preparation of unblended and blended membranes with GO and GO-TiO₂, the hydrophilic ability of membranes was evaluated through

FIGURE 1: XRD spectrum of GO (inset), TiO_2 (a), and GO/ TiO_2 (b).

FIGURE 2: SEM and TEM images of GO.

scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy analysis, Fourier transform infrared (FTIR) spectroscopy analysis, and water contact angle (WCA) measurement.

3.2.1. SEM Images. SEM images of PSf, PSf/GO, and PSf/GO- TiO_2 membranes with various amounts of TiO_2 (10, 15, and 20 wt.% based on the weight of GO) are displayed in Figure 5.

Following the cross-sectional images, the PSf membrane has a porous structure with the dense skin layer and the membrane thickness was $64\ \mu\text{m}$. Adding GO to the membrane leads to a dramatic change in the PSf membrane structure. Figure 5 shows that GO is deposited onto the membrane surface, and the dispersed grain structure appeared smooth. GO particles make the membrane thickness higher ($79\ \mu\text{m}$). With the increased addition of TiO_2 to the polymer matrix, surface roughness and membrane thickness increase continuously (from 87.0 to $96.7\ \mu\text{m}$). It is clear that GO and TiO_2 nanoparticles are uniformly dispersed in the PSf matrix. In the higher content of TiO_2 , the holes have disappeared; the surface of the

blended membrane becomes thicker than that of the unblended membrane.

The formations of materials containing both hydrophilic GO and TiO_2 can lead to changes in chemical functionality and separation performance of the membrane.

3.2.2. FTIR-ATR Spectrum. Characteristics of the membrane surface were investigated by FTIR spectroscopy, and FTIR-ATR technique was used to demonstrate the successful incorporation of GO and TiO_2 into the polymer matrix of membranes.

Absorptions of the polysulfone layer are characterized by $\text{O}=\text{S}=\text{O}$ ($1000\text{--}1300\ \text{cm}^{-1}$) and $\text{C}=\text{C}$ ($1400\text{--}1600\ \text{cm}^{-1}$) for the polysulfone membrane (Figure 6(a)). The appearance of oxygen-containing groups of GO such as $\text{C}-\text{O}$ stretching ($1674\ \text{cm}^{-1}$) and $\text{C}=\text{O}$ stretching ($1101\ \text{cm}^{-1}$) was observed using spectroscopy (Figure 6(b)) for the blended PSf/GO membrane. With the existence of oxygen-containing groups of GO, the spectroscopy (Figure 6(c)) exhibits a new peak at $600\text{--}1000\ \text{cm}^{-1}$ for the blended PSf/GO- TiO_2 membrane, which attributes to the $\text{Ti}-\text{O}-\text{Ti}$ stretching [39, 40]; it shows the successful

FIGURE 3: SEM (a1, a2), TEM (a3), and EDX-mapping images of C K series (b), O K series (c), and Ti K series (d) elements of GO-TiO₂ materials.

FIGURE 4: FTIR spectra of GO (a), TiO₂ (b), and GO-TiO₂ (c) materials.

blending of TiO₂ and GO particles into the PSf membrane. Thus, the reason why the membrane becomes hydrophilic is the presence of GO and TiO₂.

3.2.3. EDX Analysis. To study the amount of elements of membranes, EDX had been conducted. Figure 7 shows the EDX spectra of unblended and blended membranes and the changes in the proportion of each element.

As can you see, compared to the PSf membrane (Figure 7(a)), the PSf/GO membrane (Figure 7(b)) increased

oxygen (from 9.76% to 19.26%) atomic ratio, but carbon and sulfur ratios were decreased (with a sharp decrease of C atoms from 87.85% to 79.34% and a sharp decrease of S atoms from 2.39% to 1.40%). For the PSf/GO-TiO₂ membrane (Figure 7(c)), the oxygen atomic ratio increased to 33.99% and carbon atomic ratio decreased to 64.79%; meanwhile, the Ti atomic ratio was 0.08%. These results proved that GO and TiO₂ nanoparticles exist on the PSf membrane.

3.2.4. Water Contact Angle Measurement. Changes in the water flux of membranes as a result of blending of hydrophilic materials (GO and TiO₂) were investigated via the water contact angle (WCA) measurements. Figure 8 shows the WCAs of the unblended and blended membranes. The results indicated that, by adding GO and TiO₂ into the PSf matrix, the blended membranes became more hydrophilic with a significant decrease of the WCA (Table 1), reducing from 83.4° for the unblended membrane to around 60.2° for the blended ones, which is because of the formation of the hydrophilic material on the blended membrane. Thus, the increase of the hydrophilic groups on the membrane reduced the water contact angle values. The obtained results imply that the presence of the GO and TiO₂ improves the hydrophilicity of the membrane.

3.3. Membrane Filtration Property. Indeed, with the appearance of the oxygen-containing groups of GO and TiO₂,

FIGURE 5: SEM images of the surface (a1, a2, a3, a4, a5; b2', b3', b4', b5') and the cross-sectional images (b1, b2, b3, b4, b5) of PSf, PSf/GO, and PSf/GO-TiO₂ membranes.

the blended membranes became more hydrophilic, and the obtained experimental results related to membrane separation performance are shown below.

3.3.1. Permeability. The permeability can be selected to characterize the changes in the hydrophilic property of the membrane surface. The permeability of the membrane will

FIGURE 6: FTIR-ATR spectra of PSf (a), PSf/GO (b), and PSf/GO-Ti15 (c) membranes.

FIGURE 7: EDX spectra of PSf (a), PSf/GO (b), and PSf/GO-Ti15 (c) membranes.

FIGURE 8: Water contact angle images of (a) PSf, (b) PSf/GO, and (c) PSf/GO-Ti15 membranes.

TABLE 1: Water contact angle values of PSf, PSf/GO, and PSf/GO-Ti15 membranes.

Membranes	PSf	PSf/GO	PSf/GO-Ti15
WCA (°)	83.4	76.2	60.2

be increased if the membrane becomes hydrophilic, which can be achieved by blending GO and TiO_2 into the membrane [22]. The normalized permeability between the unblended membrane and the blended membrane at different conditions of TiO_2 is shown in Figure 9. There is an increase

FIGURE 9: Normalized permeability of unblended and blended membranes.

(about 11 to 30%) in the permeability in membranes blended with GO and TiO_2 compared to unblended membranes. Thus, the presence of GO and TiO_2 functional groups that contain oxygen caused changes in water permeability. This also corresponds to the results of the WCA.

3.3.2. Separation Performance. Figure 10 shows the experimental results about the separation property of unblended and blended membranes at different conditions of TiO_2 .

These results show that the flux in the filtrate of the blended membranes could increase dramatically (from 20 to 40%) compared to that of the unblended ones. These results are similar to the result of Badrinezhad et al. [1]. By increasing the amount of titanium dioxide, the separation performance of blended membranes is also higher, approximately 20% higher than unblended ones. This improvement is due to a thin layer of hydration formed on the surface of the membrane caused by hydrogen bonding between water molecules under the influence of oxygen-containing groups. This layer makes the water flux higher. In addition, the retention improves from 38% to 59% for the blended membranes. The increase in the retention is due to a hydrophilic thin layer formed, making the membrane surfaces compact.

3.3.3. Antifouling Property. The hydrophilicity also helps mitigate adhesion of foulants and increase the membrane antifouling ability. Figure 11 shows the comparison of the maintained flux ratios of unblended and blended membranes. The results indicate that the flux degradation of the blended membrane is greatly reduced compared to that of the unblended membrane. However, the time required to keep the flow stable is shortened. After 90 min of filtration of the methylene blue feed solution, the flux maintaining ratio of the unblended membrane was about 41%; meanwhile, it was higher than 45% that of the blended one.

4. Conclusions

In this research, the PSf, PSf/GO, and PSf/GO- TiO_2 composite membranes with different ratios of TiO_2 are fabricated

FIGURE 10: Normalized flux and retention of unblended and blended membranes.

FIGURE 11: Maintained flux ratio of unblended and blended membranes.

and characterized. The presence of graphene oxide and titanium dioxide in the polysulfone polymer matrix is confirmed by SEM images, EDX spectra, FTIR-ATR spectroscopy, and WCA. The obtained results confirm the appearance of oxygen-containing groups of GO and TiO_2 . This makes the blended membrane more hydrophilic with the increase of permeability, retention, flux, and antifouling capacity.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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