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Comparing Graphene Oxide and Reduced Graphene Oxide as Blending Materials for Polysulfone and Polyvinylidene Difluoride Membranes

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Abstract: Graphene is a single atomic plane of graphite, and it exhibits unique electronic, thermal, and mechanical properties. Exfoliated graphene oxide (GO) contains various hydrophilic functional groups, such as hydroxyl, epoxide, and carboxyl groups, that can modify the hydrophobic characteristics of a membrane surface. Though reduced graphene oxide (rGO) has fewer functional groups than GO, its associated sp^2 structures and physical properties can be recovered. A considerable amount of research has focused on the use of GO to obtain a pristine graphene material via reduction processes. In this study, polysulfone (PSf) and polyvinylidene fluoride (PVDF) membranes that were blended with GO and rGO, respectively, were fabricated by using the immersion phase inversion method and an *N*-methylpyrrolidone (NMP) solvent. Results showed that the graphene nanomaterials, GO and rGO, can change the pore morphology (size and structure) of both PSf and PVDF membranes. The optimum content of both was then investigated, and the highest flux enhancement was observed with the 0.10 wt% GO-blended PSf membrane. The presence of functional groups in GO within prepared PSf and PVDF membranes alters the membrane characteristics to hydrophilic. An antifouling test and rejection efficiency evaluation also showed that the 0.10 wt% membrane provided the best performance.

Keywords: graphene oxide; reduced graphene oxide; membrane; polysulfone; polyvinylidene fluoride; water treatment

1. Introduction

Membrane filtration processes are used extensively in water treatment and in food processing and pharmaceutical industries because they provide advantages such as being energy efficient and easy to operate at room temperature [1]. Membrane properties play an important role in the filtration process, and problems such as membrane fouling and low water flux have limited the application of this technology [2]. Several characteristic membrane parameters (such as hydrophilicity, surface roughness, pore size, and surface charge) have an influence on membrane antifouling properties [3]. Many efforts have been made to improve the hydrophilicity and antifouling properties of membranes, including the use of physical blending, plasma treatment, polymer grafting, and chemical reactions, and it is known that the most effective modification methods involve blending membranes with inorganic nanoparticles, such as Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 [4–7].

Recently, carbon nanomaterials (such as carbon nanotubes (CNTs)) and graphene-based nanomaterials have been used to prepare membranes and improve their properties, and high permeability, excellent ion rejection, and antifouling effects have been determined [8–10]. Graphene is a single atomic plane of graphite that exhibits unique electronic, thermal, and mechanical properties [11]. Furthermore, exfoliated graphene oxide (GO) contains various hydrophilic functional groups, such as hydroxyl, epoxide, and carboxyl groups, and it could thus be used to modify membrane surfaces and alter characteristics from hydrophobic to hydrophilic [12]. Reduced graphene oxide (rGO) has fewer functional groups than GO, but its sp^2 structures and physical properties can still be recovered. rGO is a material closer to the graphene properties obtained through reduction; it is purer than GO, and its application has been continuously researched [13–16]. Therefore, its ability to enhance the mechanical strength of water treatment membranes requires investigation, even though it may be difficult to expect the hydrophilic effects of rGO.

Polysulfone (PSf) based membranes are predominantly used in membrane filtration processes because they provide excellent heat resistance, chemical compatibility, and mechanical resistance over a wide pH range [9,17]. However, polyvinylidene fluoride (PVDF) has also received tremendous attention with respect to its industrial application and, particularly, for its use in wastewater treatment, as it has a high mechanical strength, is thermally stable, is chemically resistant, and is of high purity [4]. However, the inherent hydrophobic characteristic of polymers (such as PSf and PVDF) often result in severe membrane fouling and a decline in permeability, and this has been a barrier for their further development and application in treating water. There have been several research papers reporting the membrane mixed with GO, but no papers have compared GO and rGO and at the same time compare PSf and PVDF membranes. In this study, therefore, PSf and PVDF membranes blended with GO and rGO were fabricated to comparatively investigate any increases in surface hydrophilicity and antifouling properties.

2. Materials and Methods

2.1. Materials and Chemicals

PSf (Solvay Korea, Seoul, Korea) and PVDF (Solvay Korea, Seoul, Korea) were used as the basis polymer materials of the membrane, and *N*-methyl-2-pyrrolidinone (NMP) (Duksan Chemical, Yongin, Korea) was employed as the solvent for preparing the cast solutions. Graphenes, GO and rGO, were used as the blending materials with PSf and PVDF. For the graphenes, natural graphite powder (50 μm) was obtained from Bay Carbon, and potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%), and hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%) were purchased from Sigma Aldrich (St. Louis, MO, USA). To conduct the membrane fouling and separation performance test, kaolin (powder), sodium alginate, the sodium hypochlorite solution (NaOCl), and sodium hydroxide (NaOH , anhydrous, 97%) were purchased from Sigma Aldrich. Distilled-deionized (DDI) water was used in all experiments.

2.2. Fabrication of GO and rGO

GO was synthesized from natural graphite by using a modified Hummers method [18]. Graphite powder was added to 98% H_2SO_4 , and KMnO_4 was then added slowly while stirring at a temperature below 10 $^\circ\text{C}$. Stirring was continued for 2 h at 10 $^\circ\text{C}$, and the mixture was then stirred for five days at room temperature until a brown paste was obtained. Subsequently, a 5% H_2SO_4 aqueous solution was added, and the mixture was stirred for 2 h. A 30% H_2O_2 aqueous solution was then added and the mixture was stirred for a further 2 h, and a bright yellow mixture was obtained. To remove residual metal ions, the mixture was centrifuged and washed several times with 3% by weight (wt%) H_2SO_4 and a 0.5 wt% H_2O_2 aqueous solution. The resulting mixture was centrifuged with pure water until the pH value of the supernatant was neutral (pH 7) through the removal of the remaining sulfuric acid. The rinsed mixture was dried at room temperature for 24 h in a vacuum chamber, and graphite

oxide powder was obtained. Finally, GO was obtained through the ultrasonic treatment of the graphite oxide powder dispersed in pure water, and to obtain a GO sheet, the supernatant of the centrifuged GO solution was filtered by using a vacuum filter. Finally, rGO was synthesized from the GO solution (1 mg GO/1 mg DDI water ratio) via a reduction process that used $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ while stirring for 2 h at 90 °C [19].

2.3. Preparation of Membranes and Permeation Test

To prepare the graphene-based membranes, concentrations of GO and rGO at 0.01, 0.05, 0.10, and 0.15 wt% were added to the NMP solution and exfoliated by sonication. A polymer concentration of 15 wt% (PSf and PVDF) was then dispersed in the NMP solution and stirred for 12 h at 50 °C. After sonication for 1 h, the solution was maintained at room temperature overnight without stirring until the solution contained no bubbles. The membranes were produced by using the immersion phase inversion method with a micrometric film applicator. To conduct full liquid–liquid de-mixing, the embryonic membranes were submerged in a water bath for 24 h. The average thickness of the final membrane was 120 μm .

Membrane permeation tests were conducted by using a dead-end stirred cell system (Millipore™, Burlington, MA, USA) with a capacity of 800 mL (Figure 1). The membrane effective area was 15 cm^2 , and the permeation test was conducted at 20 °C and 0.1 MPa. Prior to the permeation testing, each membrane was first compacted at 0.15 MPa with distilled water for 20 min to obtain a steady flux. The pure water fluxes of the membranes were calculated with Equation (1):

$$J_W = \frac{V}{S \times t} \quad (1)$$

where J_W is the pure water flux (LMH), V is the permeate volume (L), S is the membrane area (m^2), and t is time (h). All permeation data, including those from fouling and rejection tests, were obtained three times and represented as the average value.

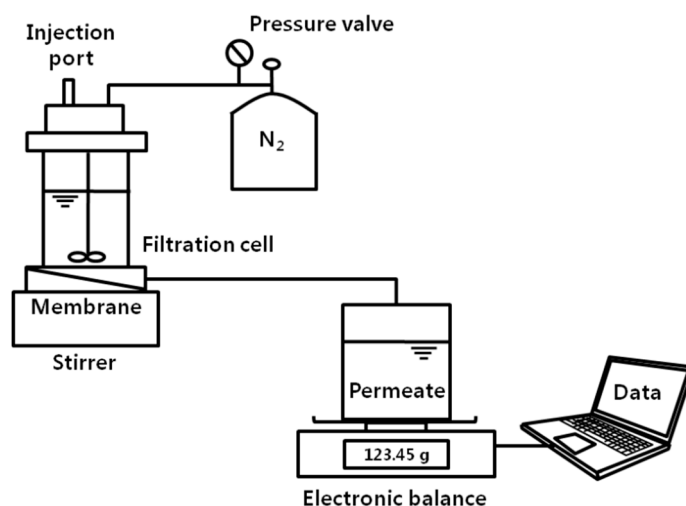


Figure 1. Schematic diagram of membrane cell system.

2.4. Characterization Techniques

Graphene characterization were conducted by using X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA2000, JEOL, Tokyo, Japan). XPS spectra indicate the chemical states of elements, especially those of carbon of GO and rGO in this study. Membrane characterizations were conducted by using a field emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL, Tokyo, Japan) and water contact angle measurement (K100SF, KRUSS, Hamburg, Germany). The cross-section morphologies of membranes were observed by the FE-SEM. After cooling in liquid nitrogen, the

membrane was fractured to obtain a cross-sectional sample. The cross-sections of the samples were gold sputtered for 3 min for observation. To investigate the hydrophilicity of the GO-blended membrane, the dynamic contact angle was measured by using deionized water as the probe liquid.

2.5. Analytical Methods in Rejection Test

The water characteristics of synthetic feed water and the permeate after rejection test were analyzed by using a turbidity meter (TN 100, EUTECH Instruments, Toronto, ON, Canada), a total dissolved solid (TDS) meter (Orion Star A212, Thermo Scientific, Waltham, MA, USA), a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Berlin, Germany), and an ultraviolet (UV) spectrometer (Cary 50, VARIAN, Palo Alto, CA, USA).

3. Results and Discussion

3.1. Characterization of Graphenes and Membranes

Graphene (GO and rGO) and membrane characterization was conducted by using XPS and FE-SEM. The XPS C1 spectra of GO and rGO are shown in Figure 2, which also shows the carbon element peaks within them. A non-oxidized carbon peak (C–C, 284.5 eV) was observed in GO and rGO at approximately 22% and 52%, respectively. However, considerably more oxygen-containing functional groups, such as the C–O bond (representing hydroxyl and epoxide groups, 286.7 eV) and the C=O bond (carbonyl, 288.5 eV), were detected in GO compared to rGO [20]. It is considered that GO and rGO have different effects on the hydrophilicity of the membrane. As hydrophilic functional groups (such as hydroxyl, epoxide, and carbonyl groups) are abundant in GO, the presence of GO on the membrane could increase the hydrophilicity of the membrane (compared to one without GO or with rGO).

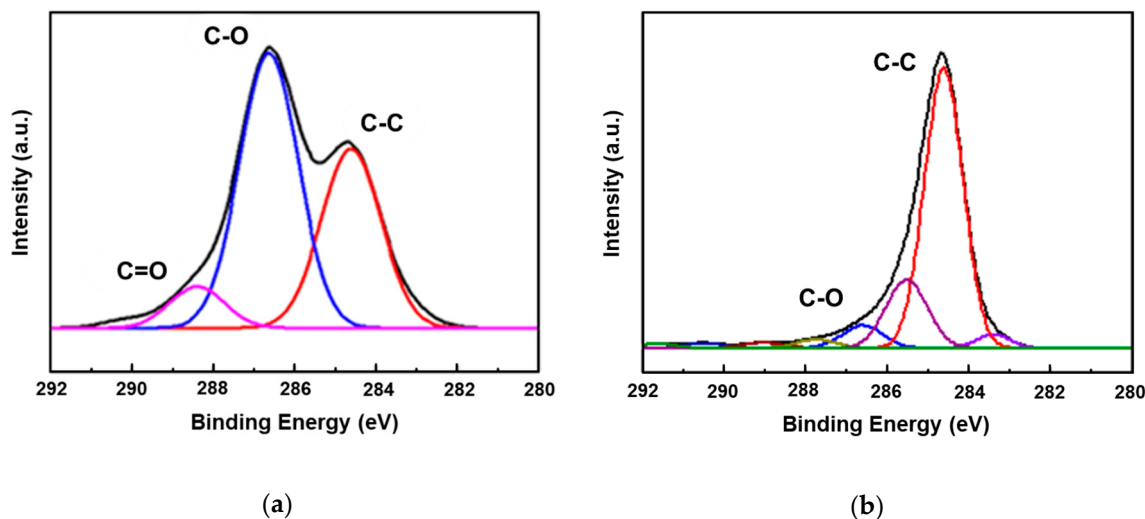


Figure 2. XPS spectra of (a) graphene oxide (GO) and (b) reduced graphene oxide (rGO): C1s spectra.

FE-SEM images of the GO-blended membrane cross-sectional structure are shown in Figure 3, where it is evident that the addition of GO contributed to the expansion of membrane pores. In particular, the membrane contained a greater number of large and straight pores with a GO content of 0.10 wt%. However, a dense subsurface layer was evident in both the PSf/GO (Figure 3a) and PVDF/GO (Figure 3b) membranes with a GO content of 0.15 wt%, and this phenomenon reduced the membrane flux. These results showed that to improve the morphology, it is necessary to incorporate an appropriate amount of GO nanomaterial into the membrane.

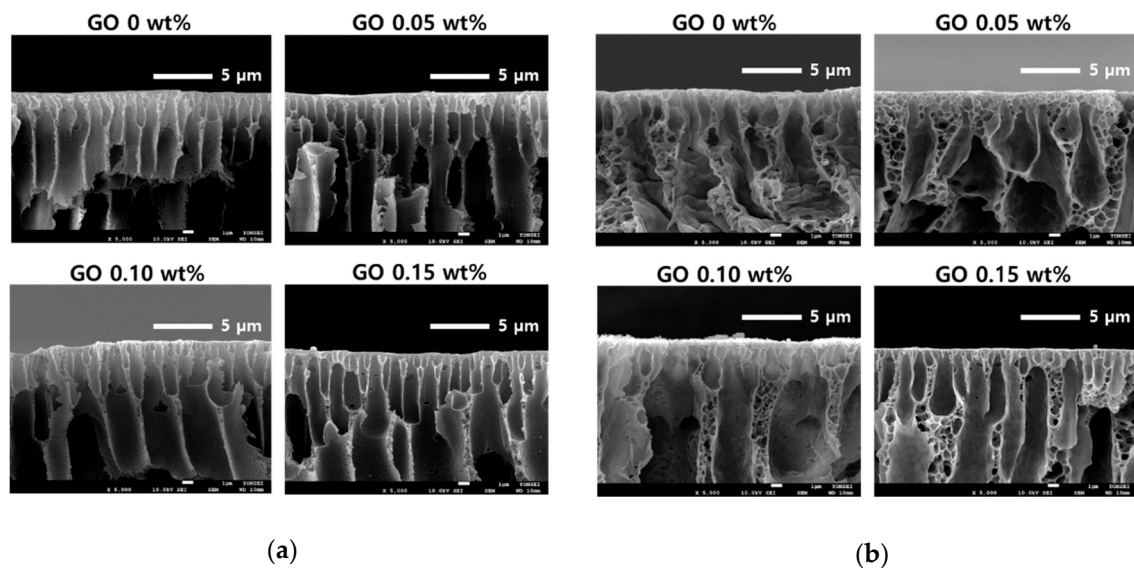


Figure 3. FE-SEM images of cross-section morphologies for (a) GO-blended polysulfone (PSf) membrane and (b) GO-blended polyvinylidene fluoride (PVDF) membrane. Scale bars, 5 μm .

3.2. Effect of GO and rGO on Membrane Flux Increase

The results showed that graphene nanomaterials (GO and rGO) increased the pure water flux with both PSf and PVDF membranes with only specific graphenes contents (Figure 4) via their hydrophilicity and pore expansion effects. The highest flux enhancement was observed with the PSf/GO membrane due to its superior hydrophilicity; however, flux enhancement was very low with rGO, as it is less hydrophilic and has fewer surface functional groups.

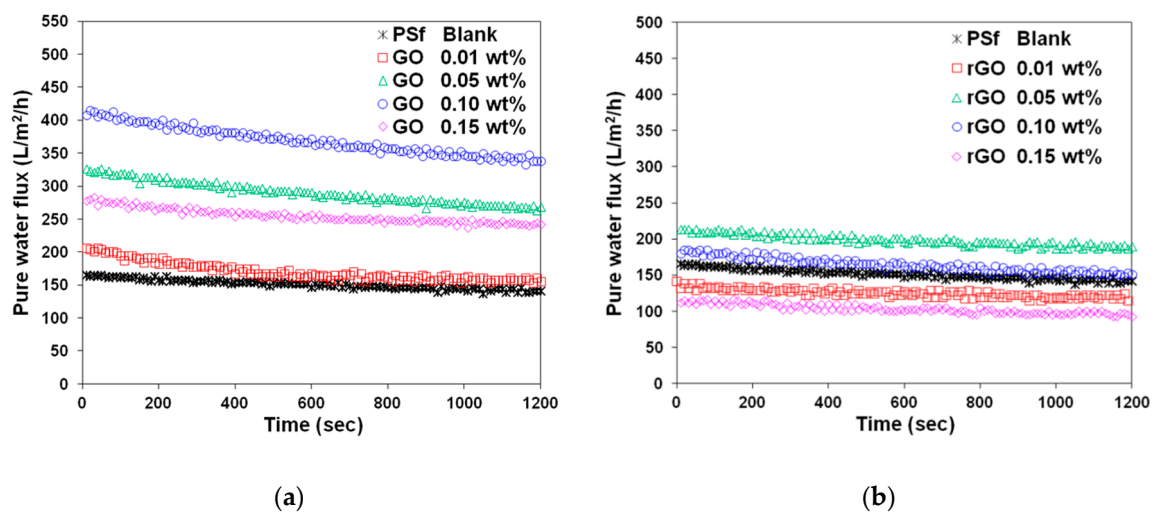


Figure 4. Cont.

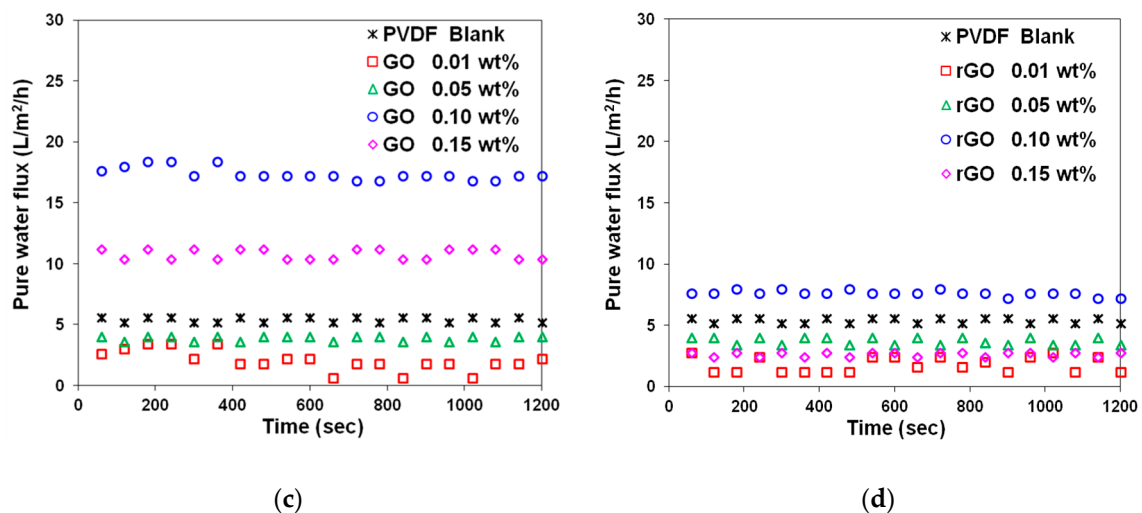


Figure 4. Pure water fluxes of PSf and PVDF membranes with differing graphene contents: (a) GO-blended PSf membrane; (b) rGO-blended PSf membrane; (c) GO-blended PVDF membrane; and (d) rGO-blended PVDF membrane. (All experiments were performed at 20 °C and pH 6.5 ~ 6.8).

To better understand the effect of the graphene content on the water flux, the flux change trend was analyzed for the type of polymer and graphene used, and the results are shown in Figure 5. For the PSf/GO membrane, the water flux increased with an increase in the GO content up to 0.10 wt% but then decreased at a GO content of 0.15 wt% (Figure 5a). This trend was influenced by the GO content and was related to the water contact angle; the angle continued to decrease with increases in the GO content (PSf blank: 88.5°, 0.01 wt%: 87.1°, 0.05 wt%: 82.7°, 0.10 wt%: 79.3°, 0.15 wt%: 78.2°), which indicated that the membrane had considerable hydrophilicity. However, excess amounts of GO increased the viscosity of the polymer solution and consequently delayed de-mixing, which allowed for creep relaxation to relieve stress and smaller pores to form [12]. This fact suggests that the optimum GO fraction value for pure water flux is 0.10 wt% GO.

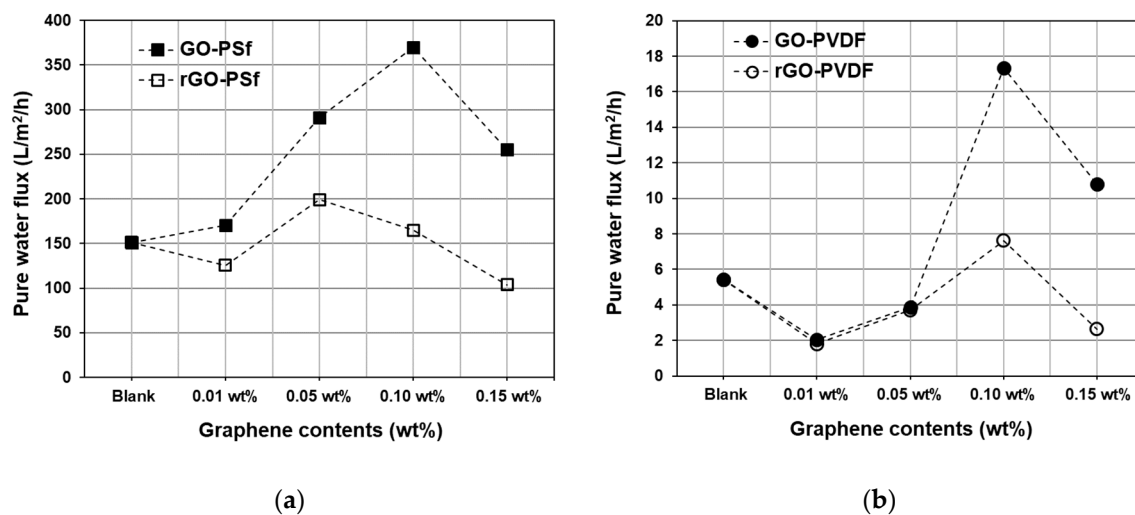


Figure 5. Flux change trends in graphene-based membranes: (a) GO-blended PSf membrane and rGO-blended PSf membrane and (b) GO-blended PVDF membrane and rGO-blended PVDF membrane.

3.3. Fouling and Rejection Test

As the PSf/GO membrane was found to be the most efficient with respect to flux testing and characterization, its antifouling effect and rejection efficiency were evaluated. The fouling test was conducted in four steps to compare PSf/GO and PSf/rGO using a synthetic raw water containing kaolin

(250 NTU as turbidity) and alginate (10.8 mg/L as total organic carbon) (Figure 6). Step 1 involved physical backwashing at the point when the flux was reduced by 50%. Step 2 used a starting flux of 166 L/m²/h, and 69.4% of the flux was recovered when the GO content was 0.10 wt%. Step 3 was also followed by physical cleaning, and a slight decrease in the flux recovery occurred. Finally, in Step 4, flux changes were observed after chemical cleaning when using NaOCl (2000 mg/L) and an NaOH solution (5000 mg/L). For the 0.10 wt% PSf/GO membrane, 72.7% of the flux was recovered in the final step, and the antifouling effect was higher than that of the PSf blank membrane. However, the rGO-blended membrane showed no antifouling effect at all compared to the PSf blank membrane. Therefore, these results showed that in addition to its other attributes, the 0.10 wt% PSf/GO membrane also provided the highest antifouling performance.

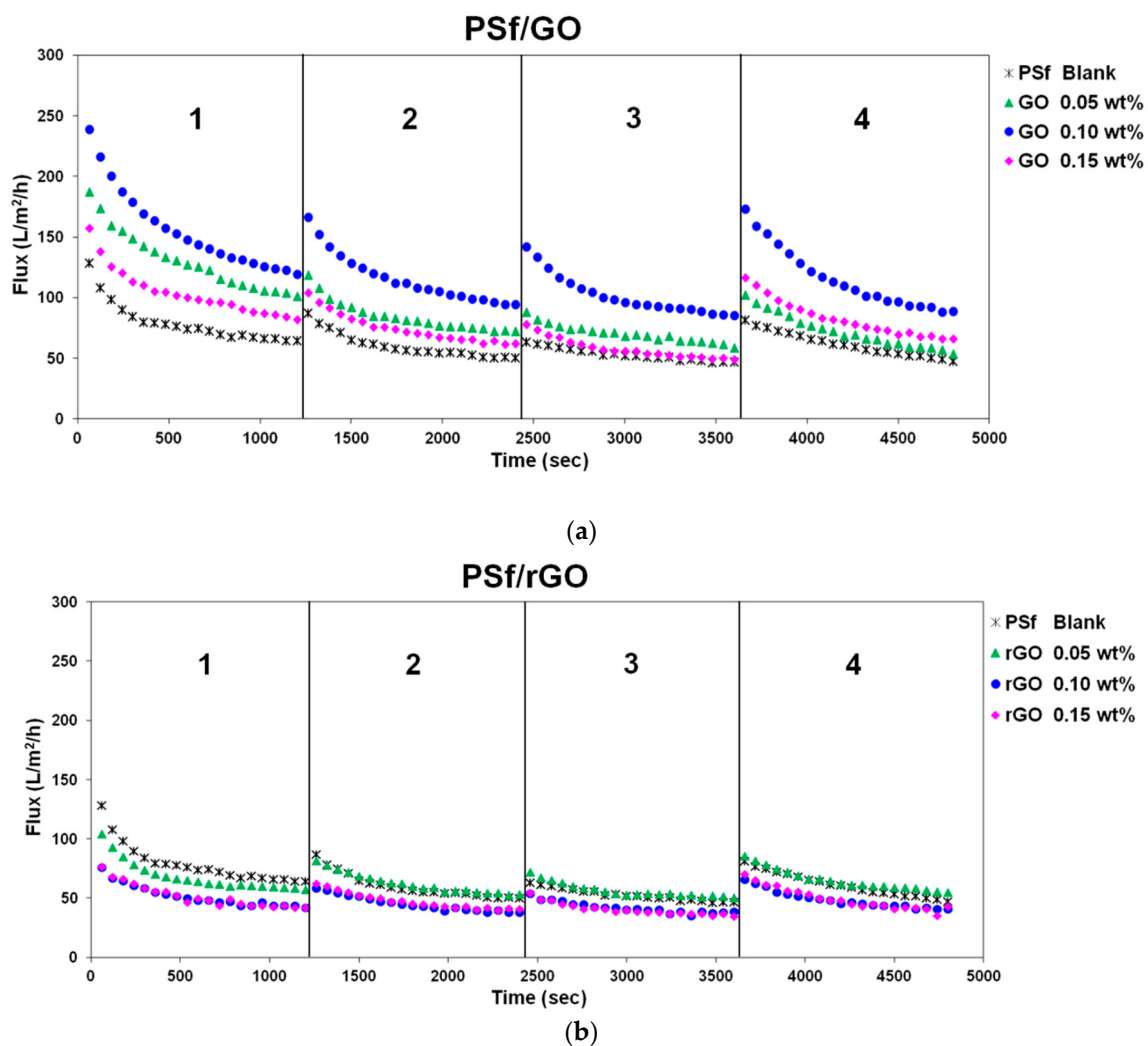


Figure 6. Membrane fouling and backwashing test conducted on (a) PSf/GO and (b) PSf/rGO membranes (Step 1: initial flux. Steps 2 and 3: after physical cleaning. Step 4: after chemical cleaning by using 2000 mg/L of NaOCl and 5000 mg/L of an NaOH solution. All experiments were performed at 20 °C and pH 6.7 ~ 7.0).

The fouling phenomenon that caused the flux decline could be quantified by using the membrane resistance model. The synthetic raw water that was used as the model foulant in this study was employed in the resistance-in-series model to determine the fouling mechanism of the PSf/GO

membrane [21]. Flux decline can be determined by using Darcy's law as a theoretical basis and is as follows:

$$J = \frac{\Delta P}{\mu \times R_t} \quad (2)$$

where J is the permeate flux, ΔP the change in transmembrane pressure (TMP), μ the water viscosity, and R_t the total fouling resistance. The total resistance, R_t , can be obtained by the sum of all the individual resistances:

$$R_t = R_m + R_c + R_f \quad (3)$$

where R_m is the inherent membrane resistance, R_c is the membrane resistance due to the cake layer formed on the membrane surface, and R_f is the fouling resistance caused by pore plugging and the irreversible adsorption of foulants on the membrane pore wall or surface. As shown in Figure 7, overall, fouling resistance contributed the most to total resistance, and it is notable that although no significant changes in cake resistance occurred, the resistance of the membrane itself was lowest in case of a GO content of 0.10 wt%. In particular, fouling resistance was the lowest with the 0.10 wt% PSf/GO membrane. The results of the model calculation indicated that fouling was mainly caused by the adsorption of foulants in the membrane pores or onto the membrane surface. Therefore, R_f contributed the most to total resistance. In addition, resistance, R_f , is an irreversible resistance that cannot be recovered by physical cleaning, and it can only be recovered by using a desorption strategy, such as chemical cleaning [22].

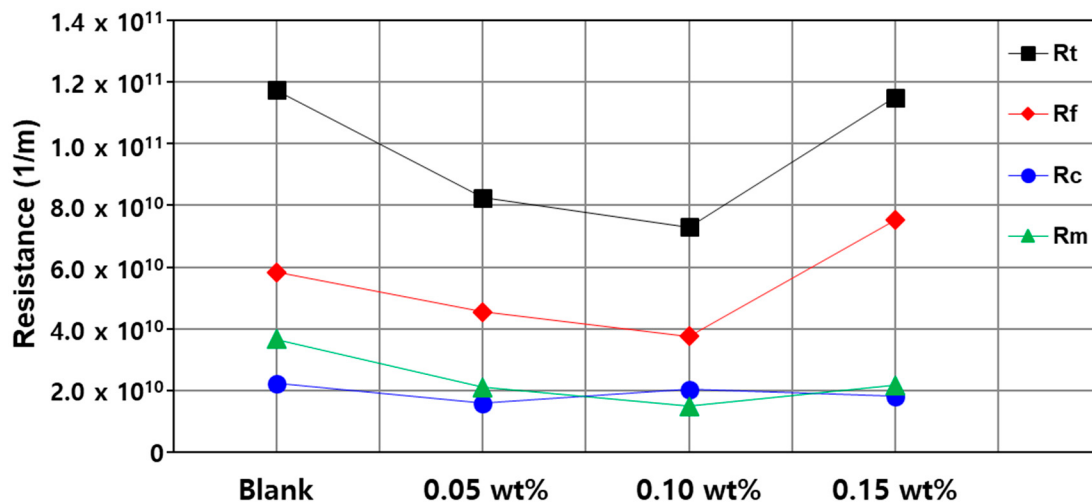


Figure 7. Membrane resistance of the PSf/GO membrane.

The separation performances of GO- and rGO-blended membranes were then investigated by using the synthetic raw water containing kaolin and alginate (Table 1). The feed water had a turbidity of 250 NTU, it contained TDS and TOC of 16 and 10.8 mg/L, respectively, and UVA_{254} (UV absorbance at 254 nm wavelength) was 1.057. All experiments were performed at 20 °C and pH 6.7 ~ 7.0. Compared with the blank PSf membrane, the removal efficiency was increased when using the membrane that contained the optimum amount and type of graphene-based nanomaterials: the GO-blended PSf membrane with a GO content of 0.10 wt% showed the best performance with respect to its flux increase, antifouling effect, and rejection efficiency. For rGO, the removal rate was the best at 0.10 wt% rGO, but its efficiency was lower than that of the GO membrane. These results provide further evidence that the use of GO-blending membranes would facilitate the application of graphene-based materials in water treatment processes.

Table 1. Rejection efficiency of PSf/GO and PSf/rGO membranes.

Parameters	Turbidity (NTU)	TDS (mg/L)	UVA ₂₅₄ (UV Absorbance at 254 nm)	TOC (mg/L)
Feed water	250	16	1.057	10.8
PSf Blank	1.1	6.0	0.0100	1.1
PSf/GO 0.05 wt%	0.8	5.0	0.0047	0.9
PSf/GO 0.10 wt%	0.5	4.0	0.0043	0.8
PSf/GO 0.15 wt%	2.2	4.0	0.0290	1.2
PSf/rGO 0.05 wt%	1.7	5.0	0.0111	1.3
PSf/rGO 0.10 wt%	0.88	5.0	0.0065	0.97
PSf/rGO 0.15 wt%	2.54	5.0	0.0208	1.6

4. Conclusions

Graphene-based flake nanomaterials, GO and rGO, were applied to fabricate an enhanced water treatment membrane, and the GO- and rGO-blended membranes were comparatively evaluated to identify which type of membrane maintained its rejection rate while increasing flux efficiency and exhibiting an antifouling effect. The effect of the graphene nanomaterial contents on the hydrophilic and antifouling properties of the membrane was investigated. Results showed that the GO-blended membrane provided the best performance, as it had hydrophilicity due to its surface functional group, while the PSf membrane had larger pores and a higher permeability than the PVDF membrane. For both PSf and PVDF membranes, the highest permeability was found with the GO-blended membrane when GO was mixed at a rate of 0.10 wt%. Scanning electron microscopy showed a widening of the membrane pores when the graphene materials were blended. However, the pores narrowed and were blocked when the amount of GO exceeded 0.10 wt%. A mixed solution of kaolin and alginate was employed to evaluate the membrane fouling and rejection efficiencies, and the PSf membrane with GO at 0.10 wt% was found to provide the best membrane fouling reduction, pollutant removal rate, and best permeability.

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