PVdF/GO 나노섬유 복합 분리막의 제조 및 중금속 제거 특성

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Preparation of PVdF/GO Nanofiber Composite Membranes and its Heavy Metal Removal Characteristics

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초록: 본 연구에서는 전기방사법을 이용하여 PVdF/GO 나노섬유 복합분리막을 제조하고, 중금속(납, 카드뮴)이온에 대한 제거특성평가를 진행하였다. 합성된 GO 및 복합분리막은 SEM, FTIR, Raman 분석 및 tensometer를 이용하여 특성평가를 진행하였으며, 위 결과로부터 다양한 기능기를 가진 GO의 합성 및 PVdF 나노섬유 내에 복합화되어 있는 것을 확인하였다. 또한 합성된 GO의 Langmuir 및 Freundlich 흡착 등온선 연구를 실시하였다. PVdF/GO 나노섬유 복합분리막은 친수특성을 보여주고 있으며, PVdF 나노섬유 분리막 대비 최대 3배 이상의 높은 수투과도를 나타내었다. PVdF/GO20의 중금속 제거율은 시간에 따라 점차 증가하였으며, 2시간 이후 95.2% (Pb), 98.3% (Cd)에 각각 도달하는 것을 확인하였다. 위 결과로부터 제조된 PVdF/GO 나노섬유 복합분리막은 하폐수처리 시스템에 충분히 활용할 수 있을 것으로 판단된다.

Abstract: This paper describes the preparation of PVdF/graphene oxide (GO) nanofiber composite membranes via electrospining and their removal characteristics of heavy metal ions (e.g., lead and cadmium). The synthesized GO and composite membranes were characterized by SEM, FTIR, Raman analysis, and tensometry. These results demonstrated the successful synthesis of GO with various functional groups and their incorporation into the PVdF nanofibers. In addition, the adsorption isotherm studies of the synthesized GO using both the Langmuir and Freundlich models were carried out. The PVdF/GO nanofiber composite membranes showed hydrophilic characteristics and higher pure water flux (up to 3 times) than that of a neat PVdF nanofiber membranes. The heavy removal rate of PVdF/GO20 increased gradually as a function of time which reached at 95.2% (Pb) and 98.3% (Cd) after 2 h, respectively. From these results, prepared PVdF/GO nanofiber composite membranes have shown a great potential to be utilized for the wastewater system.

Keywords: graphene oxide (GO), lead, cadmium, electrospinning, nanofiber membranes.

Introduction

Heavy metal ion containing wastewater is directly or indirectly discharged into the environment with the rapid development of manufacturing and agricultural industries including metal plating, mining, fertilizer, battery, paper, and pesticide.[1] Among many heavy metal ions, lead and cadmium are known to be highly toxic and are main pollutants found on surface and subsurface water.[2] Acute and chronic exposure of cadmium often results in renal damage, emphysema, hypertension, testicular atrophy, and skeletal malformation in fetus.[3,4] Lead can cause a central nervous system damage. In addition, lead can easily damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The common toxic symptoms are associated with anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages.[3,5] As a result, it is very important to effectively eliminate toxic heavy metal ions from various wastewater sources before releasing them into the environment. In particular, lowering the acceptable level of lead (0.01 mg/L, 10 ppb) and cadmium (0.005 mg/L, 5 ppb) concentrations could potentially allow for their recycling as drinking water.

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Numerous methods including chemical precipitation,[6] ion exchange,[7] adsorption,[8] membrane filtration,[9] and electro-chemical technique[10] have been proposed for the efficient removal of heavy metal ions particularly from wastewater. Among these processes, the adsorption approach has been widely used due to the easy operation, high efficiency, and low maintenance cost.[1,3,10] Recently, incorporating nano-scale metal oxide particles,[11] carbon nanotubes,[12] and graphene deriva-tives[3,4,13] into the adsorption technique has shown highly attrac-tive features for the removal of heavy metal ions. Among these adsorbents, graphene oxide (GO)-based materials have shown many advantages in terms of surface area (2630 m^2/g), chem-ical stability, and recyclability. In addition, as GO derivatives can offer hydrophilicity and possess high adsorption/selective sites due to their many negative functionalities including hydroxyl, carboxyl, and carbonyl groups, these GO-type mate-rials can serve as great adsorbents for heavy metal ions from polluted and other natural water resources.[14,15] Although GO-based materials exhibit these features, limited studies have been reported for their possible use as heavy metal ion removal applications (e.g., water purification membranes).[16]

Several studies on GO-based materials for water purification have received an immense interest from the membrane com-munity.[17] The composite membranes consisting of GO-embed-ded polymer matrix (e.g., PVdF or polysulfone) exhibited enhanced water permeability, anti-fouling, and anti-bacterial properties.[18,19] Our previous work demonstrated the reliable preparation of PVdF/GO composite membranes via an elec-trospinning method for the water purification application which exhibited 3 times higher water permeability and out-standing flux declining against Kaolin solution.[20] Although an electrospinning technique is a relatively new approach to design microfiltration (MF) or ultrafiltration (UF) membranes, the resulting materials often exhibit poor mechanical stability for practical use.[21-24] As such, we have further improved our electrospinning method to introduce reinforced nanofibrous membranes by systematically increasing nanofiber layers and thermal treatment within the glass temperature range, which exhibits about 10 times higher tensile strength comparing to a neat nanofibrous mat.[25,26] These electrospun nanofibrous mem-branes can potentially provide many advantages including a high surface area-to-volume ratio, outstanding selectivity of polymer materials, and easy incorporation of various func-tional groups. With these findings, here we demonstrate the successful preparation of PVdF/GO composite nanofiber membranes and their reinforced properties as well as heavy

metal ion adsorption abilities using Pb and Cd ions, which will eventually allow for the development of selective and stable filtration systems for wastewater treatment.

Experimental

Materials. Materials used to synthesize GO were graphite flake (Bay city, Michigan 48706), sulfuric acid (≥98%, Duksan Pure Chemical Co. Ltd. in South Korea), potassium per-manganate (≥99.9%, Sigma Aldrich), hydrogen peroxide (35%, Samchen Co. Ltd. in South Korea), and hydrochloric acid (1 N, Duksan Pure Chemical Co. Ltd. in South Korea).

Materials used to prepare nanofiber composite membranes were PVdF (Arkema, Kynar 761), *N,N*-dimethyl formamide (≥99.0%, Duksan Pure Chemical Co. Ltd. in South Korea), acetone (≥99.0%, Duksan Pure Chemical Co. Ltd.).

Materials used to analyze heavy metal ion removal char-acteristics were Pb and Cd standard solutions (1000±2 ppm, Sigma Aldrich). Hydrochloric acid and sodium hydroxide (1 N, Duksan Pure Chemical Co. Ltd. in South Korea) were used to control the pH of stock solutions.

The deionized water was purified through a Millipore sys-tem (~18 MΩ·cm). All of chemicals and reagents were used as received without further purification.

Synthesis of Graphene Oxide and Fabrication of PVdF and PVdF/GO Nanofiber Composite Membranes. The detailed procedure for the synthesis of GO nanosheets and preparation of PVdF, PVdF/GO nanofiber composite mem-branes were reported previously.[20] Specifically, GO was syn-thesized by the oxidation of natural graphite flake using the modified Hummer's method. 3 g of graphite flake was initially mixed with sulfuric acid (75 mL) under stirring at room tem-perature, and then 9 g of KMnO$_4$ was slowly added into the mixture. After stirring for 30 min, the resulting mixture was placed in an oil-bath and stirred for 1 h at 100 °C. The tem-perature of mixture was decreased to 50 °C, followed by the addition of DI water. The mixture was then fully dispersed by sonication for 3 h after the addition of 15 mL of H$_2$O$_2$. The oxidize graphite powder was obtained by vacuum filtration, washed several times with DI water, and adjusted the pH of the top solution to become neutral using 1 *N*-hydrochloric acid. The oxidized graphite was centrifuged (Hanil Science Indus-trial Co., Ltd., FLETA 5) at 4000 rpm for 10 min. The pre-cipitate, these oxidized graphite, was vacuum dried for 1 day. Exfoliation of graphite oxide to GO was achieved using a tip sonicator (Sonic VCX-750, Sonics & Materials, Inc.) with

Table 1. Compositions of Electrospinning Solutions

Sample code	PVdF (wt%)	GO (wt%)	DMF (wt%)	Acetone (wt%)
Neat PVdF	17	0.0	66.4	16.6
PVdF/GO05	17	0.5	66.4	16.6
PVdF/GO10	17	1.0	66.4	16.6
PVdF/GO20	17	2.0	66.4	16.6

1 mg/mL of graphite oxide solution for 1 h. Then, the final GO sheets were obtained by filtering the GO solution with a vacuum filtration system with 0.45 μm PVdF filter (Millipore Co., Ltd.).

The PVdF and PVdF/GO nanofiber composites were prepared by an electrospinning method. A PVdF electrospinning solution was prepared by mixing PVdF powder (17 wt%) with a various content of GO (0.5 to 2.0 wt%) in a mixture of DMF (66.4 wt%) and acetone (16.6 wt%) solvents. The GO was initially dispersed in the solution by ultrasonication for 2 h, followed by the addition of PVdF powder into the GO solution. The mixture was then stirred for 24 h at room temperature to completely dissolve the polymer. The overall composition ratios of a series of solution are listed in Table 1. The prepared solutions were filled into a 5 mL syringe equipped with a 23 gauge needle for electrospinning. The electrospun fibers from the mixture was collected on an aluminum foil using the following; flow rate 0.6 mL/h (KDS100, KD Scientific Inc.), applied voltage 15 kV (CPS 60K02VIT, Chungpa EMT Co., Ltd.), TCD (tip to collector distance) 15 cm, duration 6 h. To improve physical property and control pore diameter, the prepared nanofiber sheets were thermally treated in a dry-oven at 120 °C for 24 h after stacking it's layers between glass plates. After peeling off the layered nanofiber composites from the glass plates, the composite materials were copiously rinsed with methanol and distilled water to remove any residue. Upon drying, the final PVdF/GO composite materials were tested as water purification membranes for heavy metal ions.

Characterizations of Synthesized GO and Prepared Nanofiber Membranes. Morphology and Structure of Synthesized GO and Prepared Nanofiber Membranes: FTIR (Thermo Scientific, Is50) was used to examine the presence of various functional groups within the synthesized GO and prepared nanofiber composite membranes.

The SEM (Hitach, S-4800) analysis was also performed to examine the overall surface morphology of the GO and the nanofiber composite membranes. The SEM samples were completely dried in a vacuum oven at room temperature for 1 h and were coated with osmium (Os) for 5 s using a vacuum sputter prior to analysis. Raman spectrometer (Thermo, Almega X) was used to determine the presence of GO in the nanofiber membranes. The Raman samples (2.0 cm^2) were mounted on a glass substrate, and the spectra were collected on multiple spots using a 532 nm laser (30 s scans and 15 mW laser intensity).

Pore Size and Porosity Analysis of Prepared Nanofiber Membranes. To analyze the pore-diameters of the composite membranes, circular samples (1.85 cm in diameter) was prepared and placed in a Capillary Flow Porometer (porolux 1000, IB-FT GmbH, Porous Materials Inc.) after applying a Porewick solution as a doping solution (16.0 dynes/cm surface tension).

To analyze the porosity of the prepared composite membranes (4 cm×4 cm) were soaked in n-butanol (Junsei Chemical Co. Ltd.) at room temperature for 2 h. The membranes were then taken out from the solvent and wiped with Kimwipes to remove excess n-butanol. The mass of these wet membranes (W_{wet}) was compared to the dry membranes. To determine the mass of dry membranes (W_{dry}) and volume (V_{dry}), the wet membranes were dried in the oven at 100 °C for 24 h. The average water uptake values were determined based on five measurements. The porosity was then determined by the following eq. (1).

$$Porosity\ (\%) = \left(\frac{W_{wet} - W_{dry}}{\rho_b \times V_{dry}} \right) \times 100 \tag{1}$$

Where ρ_b is the density of n-butanol.

Mechanical Properties of Prepared Nanofiber Membranes. The tensile strength of nanofiber membranes was measured by a Kyung-Sung testing machine with an 1 KN capacity load cell. The mechanical test was performed according to ASTM D882, and all samples were compared with a neat PVdF membrane to evaluate the effect of GO content. The samples were cut in a rectangular shape with dimension of 100 mm×20 mm. The test was performed using pneumatic grips with 90 psi and 25 mm×25 mm rubber jawfaces at a crosshead speed of 500 mm/min.

Contact Angle and Pure Water Flux Analysis of Synthesized GO and Prepared Nanofiber Membranes. The contact angle (Phoenix 300, SEO) of the synthesized GO and nanofiber composite membranes were carried out with a water droplet to examine the hydrophilicity of the surface upon the modification of nanofiber as a function of GO content. The

angles were obtained from the average of minimum five measurements to minimize experimental random errors.

The pure water flux experiments of the nanofiber composite membranes were carried out using a dead-end-cell device with a filtration area of 38.5 cm^2. The schematic diagram of the filtration system can be found our previous publication.[20]

The DI water was prepared in a bomb filter and mixed well using a magnetic stirrer to eliminate bubbles in the membranes. The filtration pressure was adjusted by a compressed N$_2$. The filtrate was collected in a receiver on a balance. The mass of the filtrate was recorded throughout the filtration and was plotted against time. Water flux was then determined according to the following eq. (2).

$$Water\ flux\ (\text{kg/m}^2 \cdot \text{h}) = m_x / \Delta t \cdot A_x \tag{2}$$

Where, m_x is the weight of the filtrate (kg), t is filtration time (h), and A_x is effective area of membrane (m^2).

Adsorption Experiments of Pb and Cd Ions with the GO and Various Nanofiber Composites Membranes. Adsorption for a wide range of adsorbate concentrations is often described by the Langmuir and Freundlich isotherms. The general Langmuir model was explained by eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{q_m \times b} \tag{3}$$

Where, C_e (mg/L) is the equilibrium concentration of the adsorbent, q_e (mg/g) is the mass of adsorbate adsorbed per mass of adsorbent, q_m (mg/g) is the maximum adsorption capacity of adsorbent, and b (L/mg) is the Langmuir's constant related to the absorption rate. The value of q_m (slope) and b (intercept value) are calculated by plotting C_e/q_e *versus* C_e, respectively. The Freundlich isotherm can be linearized by the following eq. (4).

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \tag{4}$$

Where, C_e (mg/L) is the equilibrium concentration of the adsorbent, q_e (mg/g) is the mass of adsorbate adsorbed per mass of adsorbent, and K_F and n are adsorption capacity and affinity, respectively.

The adsorption experiments of the nanofiber composite membranes (8×8 cm) were performed using 100 mL of stock solution (100 ppb) at 6.8~7.1 pH (adjusted with 1 N NaOH or HCl). The membranes were placed in an incubator containing the solution and shaken for 24 h at room temperature to completely react with metal ions. After collecting the supernatant,

the sorption effect was investigated by an inductively coupled plasma spectrometer (ICP, Optima 7300DV, Perkin-Elmer). The removal rate of prepared nanofiber membranes was calculated using eq. (5).

$$R\ (\%) = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \tag{5}$$

Where, the R is removal rate (%), C_i and C_f are before and after concentration of metal ion solutions, respectively.

Results and Discussion

Morphology and Structure of Synthesized GO and Prepared Nanofiber Membranes. The exfoliated GO is readily dispersed in organic solvent (DMF) with a mild ultrasonic treatment and the resulting stable solution was used for electrospinning (Figure 1). The PVdF/GO mixture solution was gradually changed from white to dark brown colour with the increase of GO amount. The STEM analysis was carried out to show the surface morphology of the GO and prepared nanofiber membranes (Figure 2(a)-(d)). The flat feature of the GO was clearly observed from the SEM image (Figure 2(e)). Upon dispersion of the GO in DMF, single layer and/or multi-layered GO can be embedded within the nanofibers during electrospinning. All prepared membranes exhibited network-like layers of nano-sized fibers with pores. The average diameter of nanofiber was measured to be 600~700 nm (ranging from 400 to 1500 nm in diameter). The two dimensional flat feature (white circles in Figure 2) was repeatedly observed in the nanofiber composite membranes presumably due to the presence of the embedded GO sheets, while neat PVdF membranes only show the multi-layers of round nanofibers.
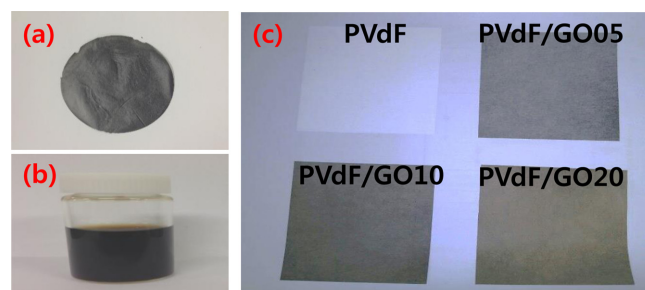
The functional groups of the GO and prepared nanofiber

Figure 1. Optical images: (a) synthesized GO; (b) GO solution dispersed in DMF; (c) neat PVdF and PVdF/GO nanofiber composite membranes as a function of GO content (0.5 wt%, 1.0 wt%, and 2.0 wt%).
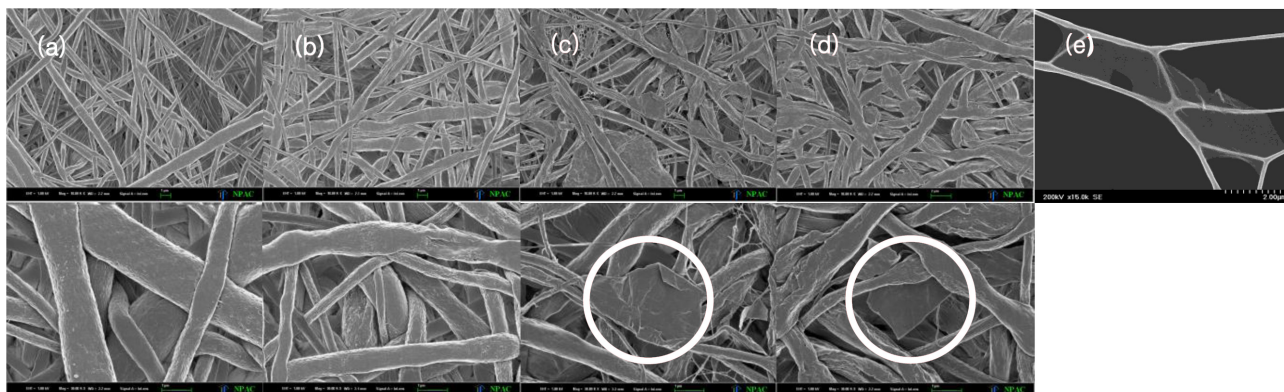
Figure 2. STEM images: (a) neat PVdF; (b) PVdF/GO05; (c) PVdF/GO10; (d) PVdF/GO20 (upon; low magnitude (10000×), bottom; high magnitude (30000×)); (e) GO layers (TEM images, 200000×).

Figure 3. FTIR spectra: (a) synthesized GO; (b) neat PVdF; (c) PVdF/GO05; (d) PVdF/GO10; (e) PVdF/GO20.
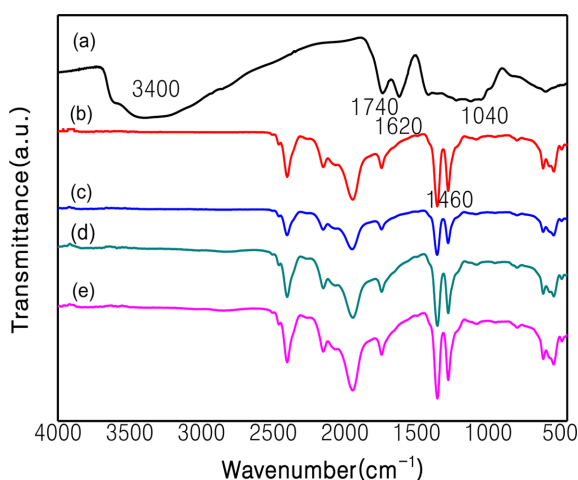

Figure 4. Raman spectra: (a) synthesized GO; (b) PVdF/GO 20; (c) PVdF/GO10; (d) PVdF/GO05; (e) neat PVdF.

membranes were characterized by FTIR (Figure 3). The spectrum (Figure 3(a)) of the GO clearly shows the representative functional groups (O-C-O group at $1040 \, cm^{-1}$, C=O group at $1740 \, cm^{-1}$ and C=C group at $1620 \, cm^{-1}$, and -OH group at around $3400 \, cm^{-1}$), implying the successful formation of GO. However, these functional groups were not clearly observed from the neat PVdF nanofiber and PVdF/GO nanofiber composite membranes (Figure 3(b)-(e)), probably due the small amount of GO content (e.g., ≤2% maximum) and the limited sensitivity of FTIR. In order to examine the presence of GO in the nanofiber membranes, Raman spectroscopy analysis was carried out because this technique has been known as an efficient and quick method for determining the structure of graphene derivatives.

The Raman spectra of GO typically display two main features; the G band arising from the first order scattering of the
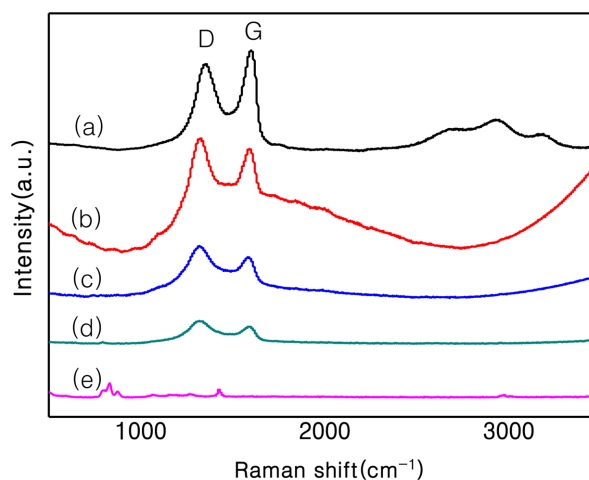
E2g mode of sp^2 C atoms (at ~$1575 \, cm^{-1}$) and the D band arising from a breathing mode of κ-point photons of A1g symmetry (at ~$1350 \, cm^{-1}$) associated with structural defects, amorphous carbon, or edges.[15] Figure 4 showed the presence of the clear D- and G- band peaks in PVdF/GO nanofiber composite membranes. Unlike FTIR, these Raman spectroscopy results clearly demonstrate that the GO was successfully incorporated within the PVdF nanofiber membranes.

Pore Size and Porosity Analysis of Nanofiber Membranes. The common transport mechanism of filter systems depends on sieving and solution-diffusion. In particular, the transport mechanism of microfiltration (MF)-based filtration having a range of $10^{-5} \sim 10^{-7}$ m pore diameter highly follows the sieving mechanism, whose permeation across the membrane is typically transported by convective flow through micro-pores under a gradient pressure as a driving force.[27] As the elec-

Table 2. Pore-properties of Prepared Nanofiber Membranes

Sample code	Biggest pore diameter (μm)	Avg. pore diameter (μm)	Smallest pore diameter (μm)	Porosity (%)	Thickness (μm)
Neat PVdF	0.378±0.060	0.277±0.062	0.260±0.016	40±1.1	50-55
PVdF/GO05	0.377±0.024	0.271±0.021	0.178±0.016	42±0.9	55-61
PVdF/GO10	0.362±0.003	0.253±0.034	0.163±0.009	45±1.5	60-67
PVdF/GO20	0.339±0.007	0.252±0.027	0.156±0.015	41±2.2	59-65

trospun nanofiber is usually composed of micro-pores greater than 0.1 μm, which can be considered as MF-based filtration systems. Our neat PVdF nanofiber membranes had a bubble point of 0.37 μm and mean pore diameter of 0.28 μm. With increasing the content of GO in PVdF nanofiber, the pore diameter of PVdF/GO nanofiber composite membranes gradually decreased to 0.25 μm. The pore properties of a series of prepared nanofiber membranes are summarized in Table 2. Although the membrane pore sizes somewhat decreased as a function of GO content, overall porosities of the membranes were measured about 40%, then the thickness was a range of 55~65 μm.

Mechanical Properties of Prepared Nanofiber Membranes. Figure 5 shows the mechanical properties of various nanofiber membranes as a function of GO content. The previous study showed that the tensile strength gradually increased when the increase of GO contents was less than 0.1 wt%[20] because of the increased hydrogen bonding interaction between the GO and PVdF nanofiber. However, the tensile strength gradually decreased with the increase of the amount of GO in nanofiber under our synthetic conditions. As our composite materials contain more than 0.5 wt% GO, we speculate that the excess GO could undergo aggregations within polymer matrix and be responsible for the decrease in tensile strength with the increase of GO content (i.e., the composite nanofiber showed brittle feature).[19] In addition, it was speculated that physical cohesion properties of polymer matrix itself during thermal treatments were reduced due to the increase of glass transition temperature (T_g) caused by excessive GO contents.[28]

Contact Angle Analysis of Synthesized GO and Prepared Nanofiber Membranes. The contact angle experiments were carried out with a water droplet to examine the overall hydrophilicity of nanofiber membranes as a function of GO content (Figure 6). The angle of bare GO sheets was initial ~25° (i.e., hydrophilic) and bare PVdF membrane was ~85° (i.e., hydrophobic), respectively. As the gradual increase of GO contents in the PVdF nanofiber membranes, the contact angle gradually decreased from 85° to 59°. Based on these results, the hydrophobic PVdF gradually exhibit hydrophilic properties upon incorporation of small amount of GO for their possible use as water purification membranes.

Pure water flux analysis of prepared nanofiber membranes. Figure 7 shows the pure water flux of the nanofiber composite membranes as a function of GO content under low pressures (e.g., 0.1 to 0.3 bar). Based on the contact angle measurements (Figure 6), the water flux values of the composite membranes
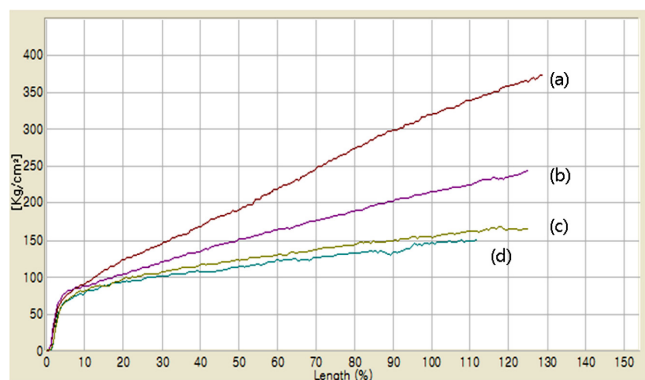

Figure 5. Strain-stress curve of prepared nanofiber membranes: (a) neat PVdF; (b) PVdF/GO05; (c) PVdF/GO10; (d) PVdF/GO20.
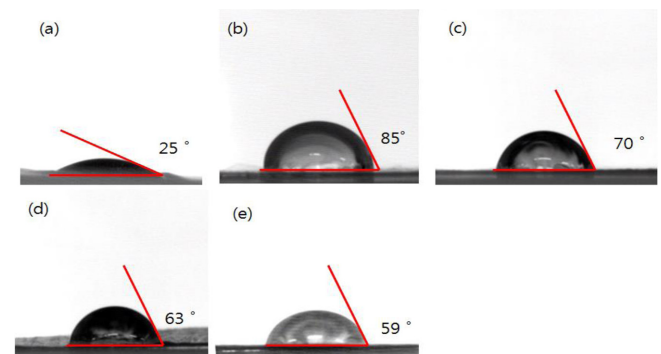

Figure 6. Contact angles of water droplet on GO sheets and prepared membranes: (a) GO nanosheets; (b) neat PVdF; (c) PVdF/GO05; (d) PVdF/GO10; (e) PVdF/GO20.
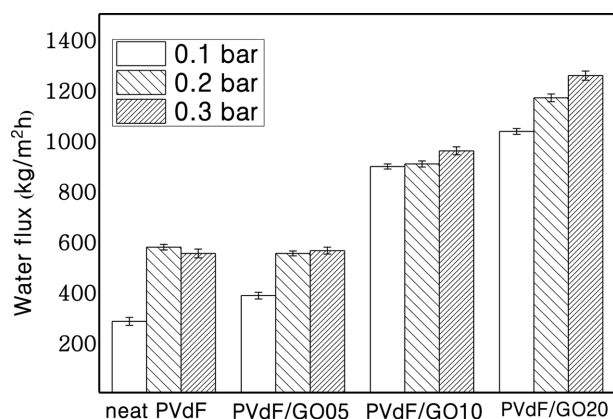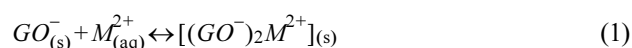
Figure 7. Pure water flux results of prepared nanofiber membranes at low pressures (0.1 to 0.3 bar) and room temperature.

increased against those of the neat PVdF nanofiber membranes due to their hydrophilic nature. At 0.1 bar pressure, the water flux values of nanofiber composite membranes gradually increased with the increase of GO content. In particular, the PVdF/GO20 sample showed 3 times higher values of water flux than those of the neat PVdF due to its hydrophilic property. However, the PVdF/GO05 sample showed negligible changes of the water flux values compared to those of the neat PVdF membrane both at 0.2 and 0.3 bar pressures, presumably due to the low hydrophilic property. As a whole, the overall

water flux of the PVdF-based nanofiber composite membranes can be systematically enhanced with the increased of GO amount.

Adsorption experiments of synthesized GO. The synthesized GO by oxidation and exfoliation process have many oxygen-containing functional groups including hydroxyl, carboxyl, epoxy, and carbonyl group as well as increased hydrophilicity. These properties of GO-based materials could provide high water flux and additional adsorption sites for the removal of heavy metal ions from pollutant and other natural water resources. As further deprotonated surface of GO sheets can easily interact with metal (II) ions, the sorption of Pb(II) and Cd(II) on GO sheets was evaluated using the following reactions:

$$GO^-_{(s)} + M^{2+}_{(aq)} \leftrightarrow [(GO^-)_2 M^{2+}]_{(s)} \qquad (1)$$

Where M is metal ion.

Figure 8 shows the Langmuir and Freundlich sorption isotherms for a series of Pb and Cd concentrations (from 0.1 to 1.0 mg/L) treated with 0.1g GO embedded nanosheets, and Table 3 lists the relative parameters calculated from the Langmuir and Freundlich models. The adsorption of Pb on the GO sheets is well fitted to the Freundlich isotherm model with high R^2 (0.9959), while the adsorption of Cd on the GO sheets is
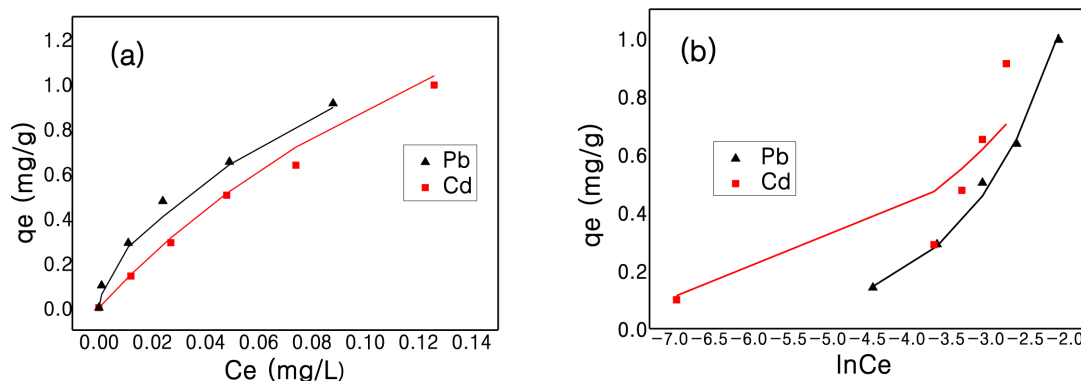

Figure 8. Langmuir (a); Freundlich (b) adsorption isotherm as a function of Pb and Cd concentration (0.1 to 1.0 mg/L) with 0.1 g GO sheets at pH 7 and room temperature.

Table 3. Parameters for Langmuir and Freundlich Models of Pb and Cd adsorption on GO sheets

Heavy-metal ion	Langmuir				Freundlich		
	Adsorbent [g]	q_m [mg/g]	B [L/mg]	R^2	K_F	n	R^2
Lead	0.1	2.65	4.61	0.9409	5.68	1.21	0.9959
Cadmium	0.1	1.11	4.49	0.9217	37.49	0.75	0.9056

fitted to the Langmuir isotherm model with high R^2 (0.9217). These results agree well with the precedent and acceptable experimental results.[3,13] Based on these models, the maximum amount of metal ions adsorbed per unit weight of GO (q_m) was calculated to be at 2.65 mg/g (Pb) and 1.11 mg/g (Cd), respectively.

Pb and Cd Removal Analysis of Prepared Nanofiber Membranes. The synthesized GO has shown outstanding removal characteristics for Pb and Cd heavy metal ions through the isotherm studies. The GO-embedded PVdF (i.e., PVdF/GO composite) nanofiber membranes with increased stability could also show the heavy metal ion removal characteristics, which were confirmed by a batch test using 100 mL stock solution (100 ppb, Pb and Cd ions in pure water) (Figure 9). The neat PVdF nanofi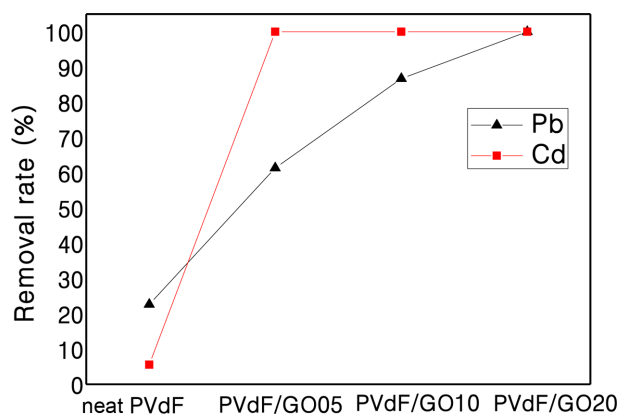ber membrane did not show a notable removal efficiency for both Cd and Pb ions (less than ~22%). However, the PVdF/GO nanofiber composite membranes have shown high absorption rates with the increase of the GO content. Although the overall Pb removal was gradually increased from 65.4 to 100% as a function of GO content in the PVdF membranes, the removal of Cd was achieved almost 100% even with the composite membranes having the lowest GO content (i.e., ~0.5 wt%). In addition, the heavy metal removal rates of the composite membrane were investigated as a function of time using fixed dead-end cell test tools with 100 ppb of Pb, Cd stock solutions (Figure 10). The removal rates of PVdF/GO20 nanofiber composite membranes for both Pb and Cd ions rapidly increased within 15 min, followed by gradually increase with time, and were finally reached to 95.2% (Pb) and 98.3% (Cd) after 2 h, respectively.

Figure 9. Adsorption rate of prepared nanofiber membranes with 100 mL stock solution (100 ppb Pb and Cd ions) at pH 7 and room temperature.
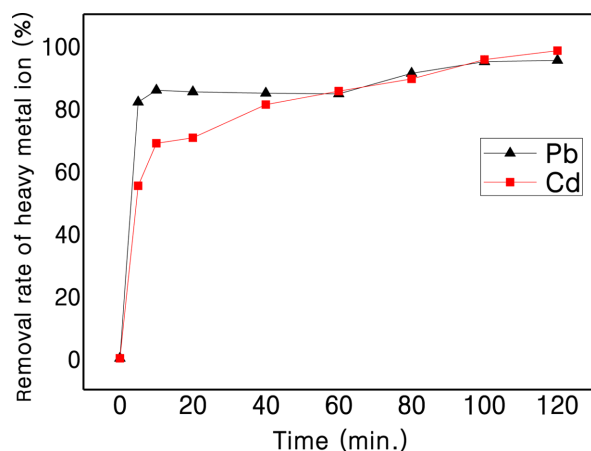

Figure 10. Removal rate of PVdF/GO20 nanofiber composite membrane for 100 ppb Pb and Cd ions feed solution as a function of time consumption at 0.1 bar pressure and room temperature.

Conclusions

We have demonstrated the successful preparation of porous PVdF/GO nanofiber composite membranes and their heavy metal ion removal characteristics from water. The formation of nanofiber composite membranes was completed via electrospinning using a solution containing a mixture of PVdF powder and exfoliated GO in DMF and acetone. Subsequently, the mechanical property and pore-diameter of the resulting nanofiber sheets were improved by the thermal treatment and/or controlling the number of their layers. The prepared nanofiber membranes and synthesized GO were characterized by SEM, FTIR, Raman analysis, and tensometer. These results demonstrate the successful synthesis of GO with many adsorption sites (-OH, -COOH, -C=O, and -CH(O)CH-) and their incorporation into the multi-layered PVdF nanofiber sheets to serve as membranes. These prepared PVdF/GO nanofiber composite membranes exhibited a uniform distribution of pore sizes and hydrophilic characteristics as well as a high water flux property. Lastly, based on the adsorption isotherms of the synthesized GO using both the Langmuir and Freundlich models, the maximum amount of heavy metal ions adsorbed per unit weight of the GO was calculated to be 2.65 mg/g (Pb) and 1.11 mg/g (Cd), respectively. The PVdF/GO nanofiber composite membranes have shown the high removal rates of both Pb and Cd ions compared to those with a neat PVdF membrane. Regardless of the GO contents, the adsorption of the composite membranes for Cd ions was nearly 100%. In case of Pb ions, the adsorption was gradually increased from 65.4 to 100% with the increase of GO content. Based on the filtration test,

the removal rate of PVdF/GO20 composite nanofiber membrane for both Pb and Cd ions increased gradually as a function of time which reached at 95.2% (Pb) and 98.3% (Cd) after 2 h, respectively. From these results, prepared PVdF/GO nanofiber composite membranes have shown a great potential to be utilized for wastewater treatment applications.

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