

Article MoS₂-Cysteine Nanofiltration Membrane for Lead Removal

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Abstract: To overcome the limitations of polymers, such as the trade-off relationship between water permeance and solute rejection, as well as the difficulty of functionalization, research on nanomaterials is being actively conducted. One of the representative nanomaterials is graphene, which has a two-dimensional shape and chemical tunability. Graphene is usually used in the form of graphene oxide in the water treatment field because it has advantages such as high water permeance and functionality on its surface. However, there is a problem in that it lacks physical stability under water-contacted conditions due to the high hydrophilicity. To overcome this problem, MoS₂, which has a similar shape to graphene and hydrophobicity, can be a new option. In this study, bulk MoS₂ was dispersed in a mixed solvent of acetone/isopropyl alcohol, and MoS₂ nanosheet was obtained by applying sonic energy to exfoliate. In addition, Cysteine was functionalized in MoS₂ with a mild reaction. When the nanofiltration (NF) performance of the membrane was compared under various conditions, the composite membrane incorporated by Cysteine 10 wt % (vs. MoS₂) showed the best NF performances.

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Keywords: molybdenum disulfide; cysteine; lead; heavy metal; wastewater; nanofiltration

1. Introduction

The importance of technology to purify polluted water is growing because many water intake sources for obtaining clean water are being polluted due to the continuous population growth and industrial development in various countries [1,2]. Among pollutants, heavy metals such as lead, cadmium, mercury, and chromium can accumulate in the human body and cause serious problems such as Minamata disease, Itai-Itai disease, and cancer [3]. In addition, many industrial wastewaters containing heavy metals must be discharged into nature after removing those heavy metals. Most heavy metals harm the human body or organic life, but lead is especially damaging. Lead is emitted from various industries and causes a problem even if a small amount, as low as 0.01–0.5 ppm, is accumulated in the body [4,5]. According to US EPA (the United States Environmental Protection Agency) standards, the dissolved lead concentration in wastewater must not exceed 5.0 ppm [6]. To remove heavy metal ions contained in water, there are various methods, such as forward osmosis (FO), reverse osmosis (RO), nanofiltration (NF), chemical precipitation, ion exchange, and adsorption [7–9]. Among the various methods, precipitation, agglomeration, ion exchange, and adsorption have been widely used to remove ions [10-14]. However, the process that requires a chemical reaction has the disadvantages of having high costs and a long process time. Moreover, it needs the post-treatment process. Therefore, there is a need to more actively utilize inexpensive, efficient, and contaminant-free processes such as RO, NF, UF, MF, etc. Among them, the NF process can effectively reject inorganic ions by the size exclusion principle and the electrostatic interaction mechanism (Donnan exclusion) between the membrane and ions, and can improve the water flux by controlling the process conditions so that it consumes less energy than the RO process [15].



There are many studies that removed lead ions or other heavy metal ions that have been conducted using NF membranes. When a solution containing Pb²⁺ and Co²⁺ ions was passed through a commercial NF membrane, AFC30, the rejections were 84% and 64%, respectively, at pH 5 [16], and the rejections of AFC40 against $Co(NO_3)_2$ and $Pb(NO_3)_2$ were 76% and 60% at pH 6, respectively [17,18]. Another commercial membrane, NF 270, showed a rejection of 60–70% for Pb^{2+} and Co^{2+} at pH 5 [19]. On the other hand, NF90, an aromatic polyamide Thin-film composite membrane produced by Dow-FilmTec, showed a high rejection of 91–94% for Pb^{2+} at pH 5–6 because of the size exclusion effect which resulted from the small pore size [20]. The NF90 membrane is a tight NF membrane with a molecular weight cut-off (MWCO) of about 90 Da, and has a maximum operating pressure, flow rate, and temperature of 4137 kPa, 3.6 m³ h⁻¹, and 45 °C, respectively. It is also very robust with a usable pH range of 1 to 12 [20]. In addition, there are various tailormade membrane research cases. T.S. Chung et al. reported the hollow fiber membrane composed of polybenzimidazole/polyethersulfone dual-layer for the rejection of Pb^{2+} (93%, at pH 2.2) and Cd²⁺ (95%, pH 5) [21]. Moreover, they reported the NF membrane with a pentablock copolymer selective layer. It exhibited excellent rejection efficiency (>98%) for Pb²⁺ and Cd²⁺ at a pH range of 5.3–5.8 [22]. Moreover, PEI-based membranes showed better rejection for heavy metals than PIP-based membranes, but the PEI-based membranes had a lower permeate of 1 LMH bar⁻¹ than the PIP-based membranes (6–10 LMH bar⁻¹). The above cases have their own merits, but it is difficult to change membrane properties by engineering polymers without applying hetero material.

To overcome the trade-off relationship between water permeance and solute rejection, therefore, the focus of this study is the fabrication of 2D nanomaterial-based membrane using MoS_2 to maintain a certain level of water permeance while gaining a high level of lead ion rejection. The exfoliated MoS_2 nanosheet has several advantages when used in water treatment membranes: (1) MoS_2 nanosheets are not detached easily when applied to the water treatment process because it does not have a hydrophilic functional group, (2) free from the phenomenon of a decrease in permeance due to the attraction between hydrophilic functional groups and water molecules, (3) it receives less resistance from the movement of water molecules because the surface of the MoS_2 nanosheet is relatively smooth compared to graphene oxide (GO), and (4) the degree of deformation or compression under pressure is less than GO because the out-of-plane of the MoS_2 nanosheet is rigid [23–27]. Therefore, if these features are well utilized, NF membranes with high solute rejection with good water permeance can be manufactured. This performance is meaningful because it cannot be realized with conventional commercial membranes.

This study focused on improving the lead ion rejection of the membrane to obtain leadfree water after a single NF process. Instead of controlling the pore size of the membrane, a method of improving the rejection performance for lead ions via electrostatic interaction by controlling the surface characteristics is adopted. Considering the trade-off relationship between water permeance and solute rejection, the appropriate membrane thickness and operating pressure were selected. In addition, the composition of the membrane showing the optimal permeance and rejection values was studied.

2. Materials and Methods

2.1. Materials

Bulk MoS₂ powder (99%, metal basis), starting material, was purchased from Alfa Aesar (Ward Hill, MA, USA). Acetone (99.5%) and isopropyl alcohol (IPA) (99.5%) were obtained from DUKSAN (Danwon-gu, Ansan, Republic of Korea). L-Cysteine (97%) and *N*,*N*-Dimethylformamide (DMF, ACS reagent, \geq 99.8%) were acquired from Sigma-Aldrich. Polytetrafluoroethylene (PTFE, 0.1 microns, 47 mm, STERLITECH, Kent, WA, USA) was used as the filtering membrane for rinsing MoS₂ nanosheets. In the NF test, lead (II) nitrate (ACS reagent, \geq 99.0%, Sigma-Aldrich, Saint Louis, MO, USA) and polyethersulfone (PES, 1000 Da, 47 mm, NP010, Microdyn Nadir, Wiesbaden, Germany) were used as a feed solute and supporting membrane, respectively.

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2.2. Synthesis of Cysteine-Functionalized MoS₂ Nanosheets

Bulk MoS₂ is dispersed in a mixed solvent to exfoliate. Bulk MoS₂ powder (200 mg) was added to the prepared acetone-IPA (8:2) mixture solvent and sonicated in a bath for 10 h. After precipitating the powders that have not been exfoliated for 1 day, the supernatant is collected and centrifuged (3000 RPM, 30 min). After collecting the supernatant, carry out vacuum filtration through a PTFE membrane filter and then wash with ethanol and DI water. MoS₂ nanosheets were vacuum dried at 50 °C for 1 day and then collected. The MoS₂ nanosheet was redispersed in DMF to have a concentration of 100 ug mL⁻¹ (50 mL), and Cysteine was added to become 1, 2, 5, 10, 20, 40 wt % based on the MoS₂ mass. This MoS₂-Cysteine mixture was reacted by oil-bath at 70 °C for 30 min to obtain Cys-functionalized MoS₂ (MoS₂-Cys) nanosheets (Scheme 1). The synthesized composites were named MC0, MC1, MC2, MC5, MC10, MC20, and MC40 according to the Cysteine content 0–40 wt %.



Scheme 1. A procedure of the MoS₂ exfoliation and Cys-functionalized MoS₂ synthesis.

2.3. Fabrication of the NF Membrane

NF membranes for the test were fabricated by the facile vacuum filtration process (Figure S1). Pristine MoS_2 or MoS_2 -Cys dispersions were filtered on the PES flat sheet membrane (47 mm in diameter), and the membranes were dried at 50 °C in a vacuum state. The volume of dispersions was determined according to the target thickness of the final product. Based on the pristine MoS_2 dispersion, if 1 mL of the 100 µg mL⁻¹ solution is filtered, an active layer with a thickness of about 100 nm was obtained. If the volume of the solution is increased by 1 mL, the final thickness increases by about 100 nm. Thickness control was possible under the same conditions with pristine MoS_2 nanosheet even when Cysteine is functionalized, and the concentration of Cysteine has a little effect on the thickness change.

2.4. Characterizations

The MoS₂ nanosheet was analyzed by X-ray diffraction (XRD, D/Max–2500, Rigaku, Akishima-shi, Tokyo, Japan) and Raman spectroscopy (LabRAM HR, Horiba-Jobin-Yvon Co., Bensheim, Germany) with a LASER of 514 nm using the dried membrane form, and UV-Vis spectrometer (S-3100, SCINCO Co., Ltd., Gangnam-gu, Seoul, Korea) was carried out using the MoS₂ dispersion in acetone-IPA mixture solvent (>100 μ g mL⁻¹) to confirm the exfoliation state. Characterizations of the MoS₂-Cys nanosheet were carried out by

Fourier transform infrared spectroscopy (FTIR, Nicolet iS10 FTIR Spectrometer, Thermo Fisher Scientific, Waltham, MA, USA) with preparing pellet using MoS₂-Cys and KBr at a 1:100 wt % ratio, and X-ray photoelectron spectroscopy (XPS, Multilab 2000, Thermo Fisher Scientific, Waltham, MA, USA) was carried out using the dried membrane form. In addition, analysis of the membranes was performed by a Zeta potential instrument (ELSZ-2, Otsuka Electronics Co., Ltd., Hirakata-shi, Osaka, Japan), field-emission scanning electron microscopy (FESEM, JSM-7500F, JEOL, Akishima, Tokyo, Japan), and atomic force microscopy (AFM, XE-100, Park Systems, Gwanggyo-ro, Suwon, Korea) using the membrane that MoS₂-based material deposited onto the PES support.

2.5. NF Performances

An NF test was conducted using a lab-scale dead-end cell (HP4750, high pressure stirred cell, STERLITECH, Kent, WA, USA) under the pressure of 1–9 bar. The membranes were used after cutting to a circular shape to fit into the dead-end cell kit holder. The effective membrane area was 14.6 cm². Before all tests, pre-compaction was performed with DI water at 5 bar for 1 h. In the performance test, a Pb(NO₃)₂ aqueous solution of 1000 ppm was used as a feed solution after adjusting pH until 6 by adding 0.1 M NaOH aqueous solution. Water permeance (WP) and the rejection of Pb²⁺ ions were calculated using Equations (1) and (2) below, respectively:

$$WP = \frac{Q}{A\Delta P}$$
(1)

where *Q* is the flow rate (L h⁻¹) of permeate, *A* is the effective surface area (m²), Δp is the transmembrane pressure (bar).

$$\mathbf{R} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where C_p and C_f are the concentrations of lead in permeate and feed, respectively.

3. Results

3.1. Synthesis of MoS₂ Nanosheet

A physical property analysis was performed to check whether MoS₂ was well exfoliated or not. In the XRD pattern, it can be seen that the bulk MoS_2 pattern is in good agreement with the reference (JCPDS card 87-2416). After MoS₂ exfoliation, only the peak related to the (002) plane remained, and other peaks disappeared so that it was confirmed that the MoS_2 nanosheets were obtained (Figure 1a) and agree with the literatures [28,29]. Moreover, the same type of UV-Vis spectrum and absorption peaks as those previously reported in MoS₂ nanosheet-related literature were observed after exfoliation, while no absorption peak was observed in the spectrum of bulk MoS₂ (Figure 1b). Peaks 1 and 2 refer to the electron transition between the higher density of state regions, and Peaks 3 and 4 refer to direct transitions of electrons from the valence band to the conduction band [30,31]. In addition, in the Raman analysis results, E_{2g}^1 and A_{1g} peaks were blue-shifted ($\Delta p = 26.69 \text{ cm}^{-1}$) and red-shifted ($\Delta p = 24.90 \text{ cm}^{-1}$), respectively (Figure S2), after MoS₂ exfoliation. As the in-plane vibration between Mo and S atoms is strengthened, E_{2g}^1 is blue-shifted, and van der Waals interaction in the out-of-plane direction of S atoms is reduced, resulting in the redshift of A_{1g} [32]. When these results were considered together, it was confirmed that MoS₂ was well exfoliated in the form of nanosheets.



Figure 1. (a) XRD patterns and (b) UV-Vis spectra of the bulk MoS₂ and exfoliated MoS₂ nanosheet.

3.2. Physical/Chemical Analysis of Cysteine-Functionalized MoS₂

All the analysis results for the MoS₂-Cys membrane provided those for MC10 as representative. By checking the functional group of materials through ATR, the existence or bonding state was analyzed (Figure 2). MoS₂ nanosheet showed the general spectral shape of chemically exfoliated MoS₂ with bands of 3500–3200 cm⁻¹ and 1613 cm⁻¹ resulting from the –OH group, and the band of 1200–900 cm⁻¹ attributed to overlapping the stretching vibrations of Mo=O and S=O [33,34]. Through this result, the presence of MoS₂ nanosheets can be confirmed, and it can be seen that mild oxidation occurred in the process of exfoliating MoS₂ through a solution process. In the case of Cysteine, major bands were observed at 3436, 2950, 2515, 2020, and 1525–1315 cm⁻¹, and these corresponded to –OH, –NH₂, and S–H stretching vibrations; N–H stretching vibration; and the Mo=O and S=O stretch vibration bands at 1200–900 cm⁻¹ derived from MoS₂ were strengthened compared to that of the Cysteine. Considering that additional oxidation cannot occur in the process of functionalizing Cysteine on MoS₂, it can be analyzed that bonds between the oxygen functional groups of Cysteine and the components of MoS₂ are formed.



Figure 2. FTIR spectra of the MoS₂ nanosheet, Cysteine, and Cysteine-functionalized MoS₂.

The status of MoS₂-Cys was double-checked through XPS analysis. In Figure 3a,b, general peaks of the chemically exfoliated MoS₂ were observed from the Mo 3d corelevel spectra of MoS₂ and MoS₂-Cys [38,39]. Note that, even after the functionalization of Cysteine on MoS₂, it can be seen that additional oxidation did not occur because the intensity of the peak resulting from MoO₃ did not increase at all. On the other hand, the intensity of the S 2s spectrum next to the Mo 3d spectrum was enhanced after Cysteine was combined. In addition, in the S 2p spectra of MoS₂ and MoS₂-Cys (Figure 3c,d), it can be seen that there was no additional oxidation during the functionalization process because the S $2p_{1/2}$ and S $2p_{3/2}$ peaks do not change even after combining Cysteine to MoS₂. Cysteine-related peaks appeared at 164.5 eV and 163.6 eV (Figure 3d and Figure S3) [38,40].



Combining these results with the above FTIR results, it can be said that an interaction between MoS₂ and Cysteine has occurred.

Figure 3. Mo 3d XPS core-level spectra of the (**a**) MoS_2 nanosheet and (**b**) MoS_2 -Cys nanosheet. S 2p XPS core-level spectra of the (**c**) MoS_2 nanosheet and (**d**) MoS_2 -Cys nanosheet.

In addition, the morphology and nanosheet size were checked out (Figure S4). In the SEM images, it can be seen that the pristine MoS_2 membrane has a morphology in the form of stacked MoS_2 nanosheets, and the membrane composed of MoS_2 -Cys also had almost the same morphology (Figure S4a,b). Moreover, when individual MoS_2 and MoS_2 -Cys nanosheets were measured by AFM, the lateral sizes of nanosheets were 0.957 and 0.937 um, respectively (Figure S4c,d). The thickness of MoS_2 nanosheet was about 1.4 nm, and about 0.1 nm thicker for MoS_2 -Cys than MoS_2 , although there were slight variations. This slight difference may be due to the presence of Cys molecules.

3.3. Nanofiltration Performances

The NF performance of the MoS_2 -Cys membrane for the lead dissolved water was tested. First, we searched for the optimal active layer thickness and operating pressure using the pristine MoS_2 nanosheets. When the thickness of the MoS_2 nanosheet layer was controlled in the range of 100–500 nm under constant pressure (5 bar), the water permeance decreases as the thickness increases, and when the thickness increases from 100 to 200 nm, the Pb^{2+} rejection was greatly improved. However, the Pb^{2+} rejection was no longer significantly improved even though the thickness was increased to 300–500 nm so that the optimal thickness was determined to be 200 nm (Figure 4a). In addition, when observing the NF performances at various operating pressures from 1 to 9 bar with the thickness fixed at 200 nm, the water permeance increased and the rejection decreased as increasing operating pressure (Figure 4b). However, since it was confirmed that the decrease in rejection becomes magnified when the pressure is higher than 5 bar, the operating pressure was set to 5 bar.



Figure 4. Water permeance and Pb^{2+} ion rejection of the MoS₂ nanosheet membrane according to (**a**) MoS₂ layer thickness and (**b**) applied pressure (the error bars were calculated based on the repeated experiments).

Based on the previous test results, the thickness of the active layer was 200 nm and the operating pressure was fixed at 5 bar, and the NF performances of the MoS₂-based membranes were evaluated according to the Cysteine content using the Pb(NO₃)₂ aqueous solution-adjusted pH 6 (Figure 5). The water permeance of the MoS_2 nanosheet membrane was 22.3 LMH bar⁻¹, and as the Cysteine content increased from 1 wt % to 10 wt %, the water permeance also gradually improved, obtaining the maximum permeance of 56.7 LMH bar $^{-1}$ in MC10. This phenomenon resulted from increasing the content of hydrophilic Cysteine functional groups on the MoS₂ (MoS₂-Cys itself was still hydrophobic) (Figure S5a). When the concentration of Cysteine was increased to 20 and 40 wt %, it seems that the excessive Cysteine present in the membrane hinders the mobility of water molecules regardless of whether it is hydrophilic or not. In addition, the rejection of Pb²⁺ ions continued to increase as the Cysteine content increased, but MC20 and MC40 showed a very small increase in rejection so that the optimal condition can be determined as MC10 with considering water permeance. The rejection of Pb²⁺ ions was improved after combining the Cysteine to MoS_2 via the Donnan exclusion effect because there is no reason for the dramatic change in the overall pore size or structure of the MoS_2 membrane by the introduction of Cysteine. In fact, when checking the Zeta potential of MoS₂ nanosheet and MC10 membranes under various pH conditions, MC10 showed positive Zeta at pH 6 where the NF test was performed (Figure S5b). Therefore, it was possible to effectively improve the rejection of Pb²⁺ ions by controlling the electrochemical state of the material surface without changing the physical structure of the membrane or the state of the water channel. In addition, the residual Pb metal was confirmed from the MoS₂-Cys membrane surface after nanofiltration (Figure S6).



Figure 5. NF performance MoS₂-based membrane according to Cysteine concentrations.

4. Conclusions

Bulk MoS_2 was exfoliated in a nanosheet state based on a simple and industrially applicable solution process, and Cysteine was incorporated therein. When an appropriate amount of Cysteine was applied to MoS_2 , both the water permeance and Pb^{2+} rejection were improved, overcoming the trade-off relationship between solvent permeance and solute rejection in the NF system. In particular, since the NF performance was improved by controlling the electrochemical properties of the surface without changing the physical structure or state of the membrane, it is quite valuable in that it can enhance the efficiency of the fabrication process. However, in order to improve the completeness of this research in the future, it is necessary to study how the NF performance changes under various pH conditions or how good the long-term operation stability is. In addition, it would be worthy of checking the rejection performance of not only the Pb^{2+} ions but also the other heavy metal ions that are frequently released from the industry.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/chemengineering5030041/s1, Figure S1: A fabrication process of MoS₂-Cys NF membranes, Figure S2: Raman spectra of the bulk MoS₂ and exfoliated MoS₂ nanosheet, Figure S3: S 2p XPS core-level spectra of the Cysteine, Figure S4: SEM images of (a) pristine MoS₂ and (b) MoS₂-Cys membranes. AFM results of (c) pristine MoS₂ and (d) MoS₂-Cys membranes. Figure S5: (a) Water contact angle according to Cysteine concentration and (b) Zeta potential of the MoS₂ nanosheet and MC10 in various pH.

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