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Employing lignin in formation of the selective layer of thin-film composite membranes for pervaporation desalination

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This work reports a study on employing lignin in formation of the selective layer of thin-film composite (TFC) membranes for pervaporation desalination. The TFC membranes with lignin-based separation layers are fabricated with a solution-casting method. With a reduction of the separation layer thickness to about 0.47 μm, a water permeation flux of 18.5 kg h⁻¹ m⁻² and a salt rejection of above 99.95% have been recorded on the lignin based TFC membrane with a feeding solution of 3.5 wt% NaCl(aq) at 45 °C. The membrane also exhibits high stability in long-term operation tests and ability for operations on high salinity water (up to 15 wt% NaCl(aq)). While being applied to seawater desalination, the membrane exhibits a water permeation flux of about 20.4 kg h⁻¹ m⁻² and a salt rejection of above 99.95% at 45 °C. A membrane separation process, which uses sustainable materials for salty wastewater treatments and water resource generation, has been demonstrated.

Introduction

Pervaporation desalination, compared to other membrane-based desalination processes, shows some attractive features including high salt rejection ability and sustainability for high-salinity solutions. Based on the solution-diffusion model for mass (water) transfer through the membranes in pervaporation separation, a selective layer with high hydrophilicity is favorable for water permeation. Consequently, poly(vinyl alcohol) (PVA) based membranes have been widely reported for pervaporation dehydration. Stabilization of the PVA based membranes through chemical crosslinking and formation of mixed matrix membranes have also been examined. For example, PVA/graphene oxides (GO) mixed matrix membranes were reported to demonstrate high water permeation fluxes and high salt rejection ability, as GO forming hydrophilic channels in the membranes to provide water permeation pathways through the membranes. Moreover, GO itself has been directly employed in formation of the separative layer of thin-film composite (TFC) membrane for pervaporation desalination. Another 2D nanomaterial, MXene, has also shown great potential in membrane application on pervaporation desalination. With a target on searching potential materials for membrane-based pervaporation desalination, this work reports the first study on employing lignin as the raw material for separation membranes on pervaporation desalination basing on its hydrophilic and environmentally benign features.

As a biomass, lignin has been used as feedstocks and raw materials for production of chemicals and agents and as reactive additives for polymeric materials. Utilization of lignin in membrane modification have also been reported. Ding and coworkers used lignin-cellulose nanofibrils (LCN) to modify polyethersulfone ultrafiltration membranes showing enhanced membrane hydrophilicity and mechanical strengths. Zhang et al. modified reverse osmosis membranes with deposition of alkaline lignin on the surface of separative polyamide layers to gain enhanced salt rejection ability and antifouling properties. Bahi et al. prepared electrospun lignin-zeolite composite nanofibers. Nevertheless, the membranes did not show significant attractions compared to other polymer-based fibrous membranes. In our previous work, lignin was used to modify crosslinked polybenzoxazine membranes. Introduction of hydrophilic lignin to the membranes successfully increased the permeation fluxes without sacrifice of the membrane selectivity in pervaporation separation on tetrahydrofuran-water mixtures. In another work, we used lignin as a thickener for increasing the viscosity of polybenzoxazine solutions in fabrication of interconnected porous membranes of crosslinked polybenzoxazine for oil-water separation.

Based on the above discussion, this work reports the first study, to our best knowledge, on preparation of lignin-based dense membranes for pervaporation desalination. With a 10 wt% of PVA as a binder, the lignin-based TFC membrane (thickness of the selective layer: 0.47 μm) shows a water permeation flux of about 18.5 kg h⁻¹ m⁻² and a salt rejection ratio of about 99.95% on a feeding solution of 3.5 wt% NaCl(aq) at 45 °C. Details in the pervaporation desalination results under various conditions have been examined and discussed in this work.
Experimental

Materials

Dealkalined lignin is a commercial product from TCI chemical company and was used as received. PVA with a deacetylation degree of about 99% was received from Chang Chun Petrochemical Company (Taiwan). Maleic anhydride (99%) was purchased from Sigma-Aldrich chemical company. Polyacrylonitrile (PAN, molecular weight: 150,000 Da) was from Tong-Hwa Synthetic Fiber Co. Ltd. (Taiwan). PAN-based porous layer was applied to a polyester nonwoven fabric with a phase-inversion process. The PAN-nonwoven porous membranes were utilized as the substrates for fabrication of the lignin-based TFC membranes. Reagent grade salts have been used for preparation of the salted water as feeding solutions for pervaporation tests.

Instrumental characterization

Surface hydrophilicity of the prepared membranes was evaluated with measurements of their water contact angles (WCAs) with a surface analyzer from the First Ten Angstroms Co. (FTA, Model: FTA 1000 B). Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum II FTIR equipped with an attenuated total reflectance accessory part. A field-emission scanning electron microscopy (SEM) from Hitachi Instrumental Co. (SU 8010) was employed in observation of membrane morphology.

Preparation of lignin-based TFC membranes

PVA (1.0 g) was dissolved in 190 mL water at about 90 °C. After being added with lignin (9.0 g), the solution was heated at 70 °C for 12 h. Maleic anhydride (0.5 g) and 0.5 mL of acetic acid aqueous solution (10 wt%) were added to the solution result in the casting solution of lignin/PVA-90 (90 means the weight fraction of lignin over lignin and PVA). Casting solutions with various lignin fractions from 70 wt% to 90 wt% were prepared in this work.

The porous PAN-nonwoven substrate (200 μm) was treated with a 1.0 M NaOH (aq) (60 °C, 0.5 h) for oxidation of the PAN layer surface,36 washed with water, and dried at 50 °C under vacuum overnight. The sample was then observed to measure the surface hydrophilicity of the alkali-treated PAN layer of the substrate, the substrate was stored in water prior to use. The substrate was fixed on a glass plate. The casting solution of lignin was applied to the substrate surface with a casting knife in various gaps between 230-300 μm. After the casting solution thickness of about 30-100 μm applied to the substrate, the samples were dried at 45 °C under a reduced pressure of 60 mmHg, and then thermally treated at 120 °C for 2 h for crosslinking the lignin/PVA layers. The prepared membrane was coded as L-TFC-X, where X denoting to the weight fraction of lignin/(lignin+PVA) in the casting solution.

Pervaporation desalination tests

A laboratory-assembled facility has been employed for pervaporation desalination tests.34 The cell for fixing the membrane gives an effective membrane area (A) of about 15.9 cm². In the pervaporation desalination operation, the downstream pressure is kept at around 400.667 Pa. When a stable condition was reached, the permeated liquid in a period of collection time (t, about 20 min) was collected with a liquid nitrogen bath and weighted (W). The data is applied to determination of the permeation flux (P) of the tested membrane according to the equation of 

\[ P = \frac{W}{At} \]  

(1)

where \( C_p \) and \( C_f \) is the salt concentration of the permeated liquid and the feeding solution, respectively. Since salt could not be vaporized, all the salt collected at the backside of the membrane has been taken into the calculation of the value of \( C_f \).

Results and discussion

Preparation of lignin-based TFC membranes

Although filtration-deposition processes have been taken for preparation of 2-D nanomaterials (such as graphene and graphene oxide) based TFC membranes,37 this process is not suitable for lignin due to the relatively small size of lignin molecules. In this work, lignin is considered as a polymeric material to be processed under the conventional solution-casting method for preparation of lignin-based TFC membranes. Nevertheless, for the TFC membrane made with the neat lignin, the lignin layer has a poor adhesion to the porous substrate. To solve this problem, PVA and maleic anhydride are utilized as a binder and a crosslinking agent for lignin, respectively (Figure 1).38 On the other hand, to enhance the interfacial adhesion between the separation layer and the substrate, the PAN-nonwoven substrates have been treated with a 1.0 M NaOH (aq) at 60 °C in various periods for oxidation of the -CN groups of the PAN layer to -COOH moieties.36,39 The oxidation reaction has been traced with FTIR analysis and surface WCAs measurements. In FTIR analysis, the absorption intensity of -CN group at about 2240 cm⁻¹ decreases and the absorption of -COOH at 3372 cm⁻¹ increases with increasing the treatment time, supporting to the occurrence of the oxidation reaction at the -CN groups of PAN layer. The oxidation reaction also results in an increase in the surface hydrophilicity of the substrate surface. With a 0.5 h treatment, the WCA value recorded on the substrate surface drops from 62° to 11°. Nevertheless, a prolonged treatment time does not result in further decreases in the WCA values, as the membrane within an 1 h and 1.5 h treatment gives a WCA value of about 28° and 52°, respectively. A longer reaction time might allow the reagent penetrating into the PAN layer, resulting in the oxidation reaction taking place in the inner part of the PAN layer. Consequently, the chain mobility of PAN was enhanced and the relatively hydrophobic PAN segments moving toward to the membrane surface.
Lignin-based TFC membranes with different lignin fractions

Toward preparation of lignin-based TFC membranes, L-TFC-90 membrane (the selective layer possessing 90 wt% lignin and 10 wt% PVA binder) has been fabricated with the 0.5 h-treated substrate. The membranes with lignin contents above 90 wt% are not successfully obtained due to delamination between the separation layer and the substrate either in membrane fabrication process or pervaporation desalination tests. For comparison, L-TFC-70 and L-TFC-80 membranes are also prepared.

The L-TFC-X membranes have been applied to pervaporation desalination tests on a 3.5 wt% NaCl(aq) solution at 25 °C (Table 1). Although all the membranes show high salt rejection of above 99.6%, the salt rejection of 99.96% recorded on the L-TFC-90 membrane is noteworthy. Meanwhile, the L-TFC-90 membrane still exhibits the highest thickness-normalized permeation flux (permeability, 3.0 kg·m·h⁻¹·m⁻²) among the membranes. The L-TFC-90 membrane is of potential for pervaporation desalination application. More test results on the L-TFC-90 membrane are discussed below.

| Membrane | Separation layer thickness (μm) | Permeation Flux (kg·h⁻¹·m⁻²) | Permeability (kg·m·h⁻¹·m⁻²) | Salt Rejection (%) |
|----------|---------------------------------|-----------------------------|----------------------------|--------------------|
| L-TFC-70 | 0.67                            | 3.9±0.20                    | 2.6±0.13                   | 99.74              |
| L-TFC-80 | 0.55                            | 5.0±0.38                    | 2.7±0.21                   | 99.79              |
| L-TFC-90 | 0.64                            | 4.7±0.16                    | 3.0±0.10                   | >99.95             |

Pervaporation desalination within the L-TFC-90 membrane

For TFC membranes, the relatively small thickness of the separative layer is attractive for low permeation resistance to water and increased water permeation fluxes. Preparation of
the L-TFC-90 membranes with various thicknesses (from 0.47 μm to 1.75 μm) of the separative layer has been achieved with adjusting the concentrations of the lignin/PVA casting solutions (2 wt% - 5 wt%) and gap thicknesses of the casting knife. As shown in Figure 4, all the L-TFC-90 membranes show satisfied salt rejection of 99.93% to 99.97%. The high salt rejection of the L-TFC-90 membranes support its pinhole-free structure. Reduction of the separation layer thickness does not scarify the salt rejection performance of the membranes and significantly increases the water permeation fluxes to 6.1 kg h⁻¹ m⁻². It is noteworthy that the water permeation fluxes of the membrane are linearly proportional to the reciprocal of the separation layer thickness, indicating the water permeation through the membrane could follow the Fickian behavior in the solution-diffusion model. The water permeation flux of the L-TFC-90 membrane could be further increased with raising the operation temperatures. While increasing the operation temperature from 25 °C to 45 °C, the water permeation flux increases from 6.1 kg h⁻¹ m⁻² to 18.5 kg h⁻¹ m⁻² without any sacrifice of the salt rejection. Although operation of the desalination process at temperatures above room temperature requires extra consumption of energy, the L-TFC-90 membrane might be applicable to systems with external waste heat/energy since it demonstrates a high flux at 45 °C. Moreover, the lignin-based membrane did not exhibit satisfied stabilization for operation at high temperatures, as the recorded permeation fluxes having relatively high errors. This fact could be attributed to the small amount of PVA binder, which is not enough to provide satisfied stabilization on the lignin component. Further studies on the optimization between membrane stability and permeation fluxes are interested in. The desalination performance of the L-TFC-90 membrane could be comparable to the data reported in the literature (Table 2). The activation energy for the water permeation through the membrane is calculated to be about 44.0 kJ mol⁻¹. Compared to the values of 16 to 51 kJ mol⁻¹ reported in the literature, the activation energy is in the relatively high region to suggest a high energy barrier for water permeation through the membrane, which could be an overall effect of temperature on the factors affecting the water permeation including water solubility and diffusivity within the membrane and the driving force of the permeation. The stability of the L-TFC-90 membrane with a separation layer thickness of 0.47 μm has been employed with the tests discussed below. First, the stability of the membrane in a 20 h pervaporation desalination operation has been examined (Figure 5). The membrane keeps its high salt rejection above 99.95% in the duration of tests. The water permeation fluxes stably vary at about 6.0 kg h⁻¹ m⁻², warranting the membrane stability for continuous operation. In another test, the membrane is soaked in the feeding solution (3.5 wt% NaCl(aq)) and picked out for pervaporation desalination measurements at certain periods. In a 22 days test, the membrane still maintains its stability with high salt rejections of above 99.95% and stable water permeation fluxes.

![Figure 4](image_url)

**Figure 4.** Pervaporation desalination performance of (a) L-TFC-90 membranes with different thickness of separation layers and (b) L-TFC-90 membrane with a 0.47 μm separation layer at different temperatures. Feeding solution: 3.5 wt% NaCl(aq) solution (2 wt% - 5 wt%) and gap thicknesses of the casting knife. As shown in Figure 4, all the L-TFC-90 membranes show satisfied salt rejection of 99.93% to 99.97%. The high salt rejection of the L-TFC-90 membranes support its pinhole-free structure. Reduction of the separation layer thickness does not scarify the salt rejection performance of the membranes and significantly increases the water permeation fluxes to 6.1 kg h⁻¹ m⁻². It is noteworthy that the water permeation fluxes of the membrane are linearly proportional to the reciprocal of the separation layer thickness, indicating the water permeation through the membrane could follow the Fickian behavior in the solution-diffusion model. The water permeation flux of the L-TFC-90 membrane could be further increased with raising the operation temperatures. While increasing the operation temperature from 25 °C to 45 °C, the water permeation flux increases from 6.1 kg h⁻¹ m⁻² to 18.5 kg h⁻¹ m⁻² without any sacrifice of the salt rejection. Although operation of the desalination process at temperatures above room temperature requires extra consumption of energy, the L-TFC-90 membrane might be applicable to systems with external waste heat/energy since it demonstrates a high flux at 45 °C. Moreover, the lignin-based membrane did not exhibit satisfied stabilization for operation at high temperatures, as the recorded permeation fluxes having relatively high errors. This fact could be attributed to the small amount of PVA binder, which is not enough to provide satisfied stabilization on the lignin component. Further studies on the optimization between membrane stability and permeation fluxes are interested in. The desalination performance of the L-TFC-90 membrane could be comparable to the data reported in the literature (Table 2). The activation energy for the water permeation through the membrane is calculated to be about 44.0 kJ mol⁻¹. Compared to the values of 16 to 51 kJ mol⁻¹ reported in the literature, the activation energy is in the relatively high region to suggest a high energy barrier for water permeation through the membrane, which could be an overall effect of temperature on the factors affecting the water permeation including water solubility and diffusivity within the membrane and the driving force of the permeation. The stability of the L-TFC-90 membrane with a separation layer thickness of 0.47 μm has been employed with the tests discussed below. First, the stability of the membrane in a 20 h pervaporation desalination operation has been examined (Figure 5). The membrane keeps its high salt rejection above 99.95% in the duration of tests. The water permeation fluxes stably vary at about 6.0 kg h⁻¹ m⁻², warranting the membrane stability for continuous operation. In another test, the membrane is soaked in the feeding solution (3.5 wt% NaCl(aq)) and picked out for pervaporation desalination measurements at certain periods. In a 22 days test, the membrane still maintains its stability with high salt rejections of above 99.95% and stable water permeation fluxes.

| Materials for separation layer | Membrane substrate | Temp. (°C) | Separation layer thickness (μm) | Flux (kg h⁻¹ m⁻²) | Permeability (kg m⁻¹ h⁻¹ m⁻²) | Salt Rejection (%) | Reference |
|-------------------------------|--------------------|-----------|-------------------------------|------------------|-------------------------------|-------------------|-----------|
| PVA                           | PSf hollow fiber   | 70        | 0.1                           | 7.4              | 0.74                          | 99.9              | [6]       |
| PVA-silica                    | PSf hollow fiber   | 60        | 0.22                          | 10.4             | 2.29                          | 99.9              | [7]       |
| PVA                           | PAN UF             | 70        | 4.9                           | 27.9             | 137                           | 99.8              | [8]       |
| PVA                           | PSf UF             | 70        | 1.12                          | 60.8             | 68.1                          | 99.8              | [44]      |
| PVA                           | PAN electrospun mat| 75        | 0.73                          | 234.9            | 171                           | 99.7              | [4]       |
| GO                            | PAN UF             | 90        | 0.1                           | 65.1             | 6.15                          | 99.8              | [45]      |
| GO-PVA                        | PAN electrospun mat| 30        | 0.12                          | 18.3             | 2.20                          >99.8             | [3]       |
| Silica                        | Alumina            | 22        | 0.47                          | ≈ 6.8            | 3.20                          | 90.0              | [46]      |
| Cellulose triacetate/Al₂O₃   |                    | 70        | 13                            | 6.7              | 87.1                          | 99.8              | [47]      |
| PVA                           | PTFE               | 75        | 2.6                           | 120              | 312                           | -                 | [48]      |
| MXene                         | PAN UF             | 30        | 0.06                          | 48.2             | 2.90                          | 99.5              | [18]      |
| Lignin                        | PAN UF             | 45        | 0.47                          | 18.5             | 8.70                          >99.95            | This study |

a. PSf: polysulfone; GO: graphene oxide.
Salt effects on the pervaporation desalination performance of the L-TFC-90 membrane

The ability of the pervaporation desalination membrane facing to feeding solutions containing various salt concentrations and various types of salts is examined. While NaCl being employed as the salt, the feeding solutions in various concentrations from 3.5 wt% to 15 wt% have been applied for the tests. The membrane still exhibits high salt rejection in the tests (Figure 6). The water permeation fluxes could keep at a high level for the feeding solutions of concentrations below 7.0 wt%. The membrane is still workable for concentrated NaCl(aq) up to 15 wt% although with a significant drop of permeation fluxes. The results demonstrate that the lignin-based TFC membrane has high potentials for applications in high salinity water treatment. The effect of types of salts on the pervaporation desalination performance of the L-TFC-90 membrane has been examined.18 The membrane shows similar pervaporation desalination results for NaCl, KCl, and LiCl. While the anion changes from Cl⁻ (NaCl) to Br⁻ (NaBr), the water permeation flux drops from 5.9 g h⁻¹ m⁻² to 4.2 kg h⁻¹ m⁻² due to the relatively large size of Br⁻. Compared to Cl⁻ ions, diffusion of Br⁻ ions into the lignin layer is relatively difficult. A small swelling effect happens to the membrane, consequently, to result in a small water permeation flux. Similar results have been observed with the divalent cation salts (CaCl₂, MgCl₂, and MgSO₄). The high permeation flux recorded on NaNO₃ salt could be attributed to the high affinity between lignin and nitrate ions,51 which shows high tendency of diffusion into the lignin membrane. Furthermore, the test employing an artificial seawater as the feeding solution has been done (Table 3). The pervaporation desalination performance (water permeation flux: 20.4 kg h⁻¹ m⁻²; salt rejection: >99.95 % at 45 °C) which is superior over the data reported to polymeric membranes (Table 3). Although the membranes based on MXene and GO showed relatively high permeation fluxes, the high cost of the utilized materials and complicated fabrication processes of the membranes might limit their practical applications. On the other hand, the lignin-based membranes utilize renewable and low-cost raw materials and employ simple fabrication processes. The features warrant the application potential of the L-TFC-90 membrane for production of drinkable water from seawater.43
Table 3. Pervaporation desalination on artificial seawater with different membranes reported in literature and this work.

| Materials for separation layer* | Temp. (°C) | Permeation Flux (kg h\(^{-1}\) m\(^{-2}\)) | Salt Rejection (%) | Reference |
|--------------------------------|------------|-----------------------------------------|--------------------|-----------|
| S-SEBS 35.0%                   | 60         | N.A.                                    | >99.5              | [43]      |
| PVDF/PVP                       | 60         | 1.6                                     | 99.9               | [49]      |
| MXene                          | 65         | 52.94                                   | >99.5              | [16]      |
| GO                             | 75         | 31.3                                    | >99.7              | [50]      |
| Lignin                         | 45         | 20.4                                    | >99.95             | This work |

* S-SEBS: sulfonated styrene/ethylene-butylene/styrene (S-SEBS) triblock polymer; PVDF/PVP: poly(vinylidene difluoride)/poly(vinyl pyridine) mixture; GO: graphene

Conclusions

Lignin, a polymeric material from biomass, has been demonstrated to be an effective raw material for fabrication of separation membranes. The results first explore that the lignin-based TFC membranes could be obtained with conventional solution-casting processes. Based on the hydrophilicity of lignin, the lignin-based TFC membranes show satisfied performance on pervaporation desalination on high salinity water treatments and production of drinkable water from seawater. This work has successfully demonstrated a process using sustainable materials for wastewater treatments and water resource generation. Continuing studies on adjusting the membrane structures might further enhance the desalination performance. Moreover, lignin is potential for studies on other membrane applications like ultrafiltration and nanofiltration.

Conflicts of interest

There are no conflicts to declare.

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