Lignin modified PVDF membrane with antifouling properties for oil filtration

# Lignin modified PVDF membrane with antifouling properties for oily water filtration

**N.A. Zakaria[1], M. Hazwan Hussin[2], A.L. Ahmad[1], C.P. Leo[1,*], Phaik Eong Poh[3], Kourosh Behzadian[4], Isaac I. Akinwumi[5], Alireza Moghayedi[6], Joaquin Diazsolano[7]**

*[1]School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia*

*[2]Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia*

*[3]Chemical Engineering Discipline, School of Engineering, Monash University Malaysia, Jalan Lagoon, 47500 Bandar Sunway, Selangor, Malaysia*

*[4]School of Engineering and Computing, University of West London, St. Mary's Rd, London, W55RF, UK*

*[5]Department of Civil Engineering, College of Engineering, Covenant University, Ota, Ogun State, Nigeria*

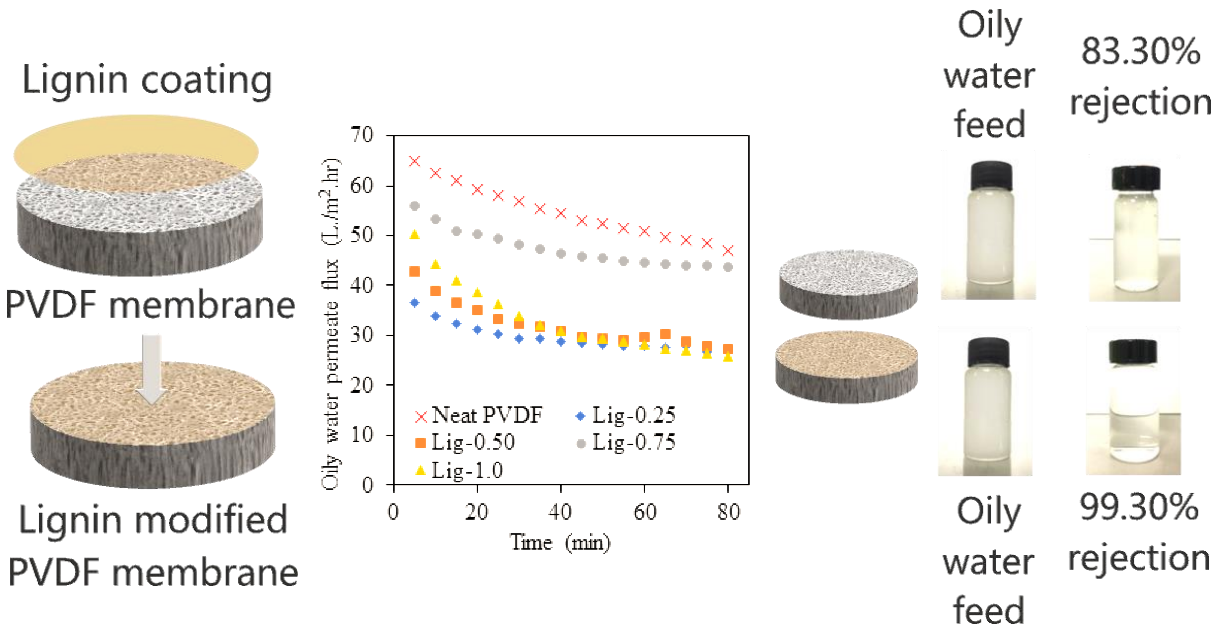
*[6]Faculty of Engineering and Built Environment, University of Cape Town, 7700, Cape Town, South Africa*

*[7]Tekmann, SA de CV, Cda de Profr Miguel F. Trommer lote 5, 42950, Tlaxcoapan, Hidalgo, México*

## HIGHLIGHTS

- Lignin dissolved in NaOH solution was coated on PVDF membrane.
- The alkaline concentration should be restricted to avoid membrane degradation.
- The increasing lignin concentration enhanced water permeability, although pore size was reduced.
- The lignin coated membrane reject 99.30% of oil and attained a stable flux.

**Graphical Abstract**



# Lignin modified PVDF membrane with antifouling properties for oil filtration

**N.A. Zakaria[1], M. Hazwan Hussin[2], A.L. Ahmad[1], C.P. Leo[1,*] Phaik Eong Poh[3], Kourosh Behzadian[4], Isaac I. Akinwumi[5], Alireza Moghayedi[6], Joaquin Diazsolano[7]**

[1]*School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia*

[2]*Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia*

[3]*Chemical Engineering Discipline, School of Engineering, Monash University Malaysia, Jalan Lagoon, 47500 Bandar Sunway, Selangor, Malaysia*

[4]*School of Engineering and Computing, University of West London, St. Mary's Rd, London, W55RF, UK*

[5]*Department of Civil Engineering, College of Engineering, Covenant University, Ota, Ogun State, Nigeria*

[6]*Faculty of Enginering and Built Environment, University of Cape Tow, 7700, Cape Town, South Africa*

[7]*Tekmann, SA de CV, Cda de Profr Miguel F. Trommer lote 5, 42950, Tlaxcoapan, Hidalgo, México*

## ABSTRACT

Lignin is a sustainable chemical that can be extracted from a wide range of lignocellulosic biowaste. It was blended into polymeric membranes to improve membrane morphology for filtration. Lignin dissolved in NaOH solution can be coated on different substrates to improve the surface hydrophilicity. In this work, the polyvinylidene fluoride (PVDF) membrane was coated with lignin to improve the filtration of oily water. Lignin was dissolved in NaOH solution with varied alkaline

concentration (0.25-1.50 wt.%) and lignin concentration (0.25-1.00 wt.%). The PVDF membrane degraded in the highly alkaline solution, but the increasing lignin content reduced the membrane pore size for the effective rejection of oil emulsion. The PVDF membrane modified with 0.75 wt% of lignin in 0.5 wt% of NaOH solution attained a permeate flux about 70 $L \cdot m^{-2} \cdot hr^{-1}$, but a slightly lower permeate flux of 55 $L \cdot m^{-2} \cdot hr^{-1}$was recorded after immersed in alkaline solution 12 h. The lignin modified membrane rejected up to 99.30% of oil, while the neat PVDF membrane only rejected 83.30% of oil. The lignin modified membrane showed slightly lower but stable flux than the neat PVDF membrane due to the reduction of membrane fouling.

*Keywords:* lignin; membrane; microfiltration; oil

*Corresponding author.
*E-mail address:* chcpleo@usm.my (C.P. Leo)

## 1. Introduction

Lignin is a biopolymer that can be isolated from a wide range of lignocellulosic waste, representing near to 30% of lignocellulosic waste [1]. It consists of phenylpropanoids such as coniferyl, sinapyl and coumaryl alcohols at a varied ratio and a small amount of lignols, depending on the plant source. More than 50 million tons of lignin and lignin-related chemicals were produced annually [2]. Their emerging applications as bioplastics, adsorbents, anticorrosion coating, adhesive, and more have been extensively reported.

For wastewater treatment, lignin has been developed into flocculant, adsorbents, and membrane filters. The lignin-based flocculants are efficient in the removal of dyes, heavy metals, chemical oxygen demand (COD), phosphate in wastewater after amination, carboxymethylation, crosslinking, sulfonation, and grafting [3]. The lignin-based adsorbent could be prepared through the mentioned modification strategies to remove heavy metal ions in water [4] similarly to porous adsorbents [5]. The adsorption of heavy metals on lignin through ion-exchange could be further improved by increasing the surface area. Lignin derivatives also adsorbed dyes [6] and drugs [7], likewise the porous adsorbents [8–10]. Glycidyltrimethylammonium chloride was used to modify lignin to remove 80% of anionic viruses through flocculation followed by filtration [11]. Polyurathane/lignin composite foam with lignin content up to 50 wt.% was produced through blending followed by polymerization [12]. The hydrophobic polyurethane foam was transformed into the hydrophilic composite foam after incorporating lignin. The adsorption of oil from water into the composite foam increased, and the composite foam showed excellent reusability.

Lignin-modified membranes were studied in recent years due to the continued demand for hydrophilic modification agents in membrane fabrication. Membranes made of hydrophobic polymers could be easily fouled [13]. Yong et al. [14] reported on the blending of lignin into polyvinyl chloride (PVC) dope solution before phase inversion to form an antifouling membrane for the ultrafiltration of oily solution. A high lignin content promoted the increment of the glass transition temperature, as shown in the thermalgravimetric spectra with only a single phase. X-ray diffraction spectra also confirmed the compatibility between lignin and PVC due to the interaction between the hydroxyl groups of lignin and the chlorine groups of PVC, as proven in Fourier-transform infrared spectra. Membrane pore size and porosity were slightly increased, but the surface hydrophilicity was significantly improved for promoting water permeation more than 3 times. Oil rejection, chemical oxygen demand (COD) reduction, and suspended solid removal of PVC membrane was also greatly enhanced beyond 83.92% after lignin incorporation. Using lignin as the additive in the fabrication of polyethersulfone (PES) membrane, Shamaei et al. [15] observed an increment in the underwater oil contact angle and negative surface charge. The lignin modified PES membrane attained about 270% higher water permeability than PES membrane, but rejection of organic pollutants dropped about 9% due to pore size enlargement was reported. The blending of lignin into the dope solution containing polybenzoxazine, the dense membrane formed with the hydrophilic surface [16]. Phenol and tertiary amine groups of polybenzoxazine were released from the hydrogen bondings network constructed between polybenzoxazine and lignin. The water permeation in pervaporation for the dehydration THF and isopropanol aqueous solution increased more than 2-folds. Lavanya and Balakrishna [17] further blended the peanut shell power, which comprises of cellulose, hemicellulose and lignin, into polysulfone (PSf)

membrane dope solution prior phase inversion. Pore formation was greatly enhanced, resulting in large pores and finger-like channels. The lignocellulose modified PSf membrane achieved higher water permeability than PSf membrane due to the improvement of porous structure and surface hydrophilicity. It rejected more BSA and exhibited less fouling even though the negative surface charge increased.

Lignin is an anion polyelectrolyte, and it could be paired with the cationic polyelectrolyte to modify polymeric membranes with a negatively charged surface. Through layer-by-layer assembly, lignin/poly(diallyldimethylammonium chloride) bilayers were coated on the PES ultrafiltration membrane [18]. The water permeability was reduced after coating, while the molecular weight cut-off of PES membrane reduced from 19 kDa to 2 kDa. Gu et al. [19] coated lignin/polyethyleneimine (PEI) bilayers on polysulfone membrane. Increasing the coating numbers reduce surface hydrophobicity and protein adsorption. Although showing the reduced fouling in the filtration of bovine serum albumin (BSA) solution, changes in membrane pore size, rejection, and permeability were not reported.

Alkaline extraction of lignin has been commonly reported. The lignin in alkaline solution was successfully applied as the food coating [20] and packaging materials [21]. Similarly, lignin in the alkaline solution is expected to form a hydrophilic coating on the hydrophobic PVDF membrane to reduce fouling in filtration. In this work, lignin was dissolved in NaOH solution to modify the polyvinylidene fluoride (PVDF) membrane for the improvement of surface hydrophilicity and oily water filtration. Unlike blending, surface modification using lignin allows the improvement of membrane properties without affecting the existing membrane formulation. The effects of NaOH concentration and lignin loading on membrane

morphology and other properties were studied. The modified membranes were further tested in the filtration of oily water.

## 2. Materials and methods

### *2.1. Materials*

PVDF (Solef® 6010 PVDF) from Solvay Solexis (France) was dried at 100 ºC before preparing the membrane dope solution. The solvent, N-methyl-2-pyrrolidone (NMP) (> 99.5%) was supplied by Merck (Darmstadt, Germany), while the other additives such as ortho-phosphoric acid ($H_3PO_4$) (> 85 %), lithium chloride (LiCl) and acetone were acquired from Merck (Darmstadt, Germany). Ethanol acquired from Merck (> 99.9 %, Darmstadt, Germany) was used as the coagulation bath. Lignin in the form of dry powder was provided by the School of Chemical Sciences, Universiti Sains Malaysia. NaOH from Sigma Aldrich (ACS reagent, ≥99.0%, pellets) was used in the pH adjustment of an aqueous solution for preparing lignin solution. Corn cooking oil from ACH Food Companies, Inc and Tween 80 from Merck were used to prepare oily water for the filtration test.

### *2.2. Synthesis and modification of membrane*

PVDF membranes were first prepared as described in the previous work [22]. PVDF (13 wt.%) was dissolved into NMP solvent (77 wt.%) containing acetone (5 wt.%), $H_3PO_4$ (3 wt.%), and $LiCl_2$ (2 wt.%) that work as the non-solvent additives. The dope solution was stirred at 50 ºC for 1 day. After degassing, the dope solution was cast

on the woven support on a glass plate at a casting gap of 400 µm (XB320D, Beijing Jiahang Technology Co. Ltd., China ). The wet film was immersed into the ethanol bath for 20 min, followed by the water bath for 1 day to form a PVDF membrane through phase inversion.

Lignin solution was prepared by dissolved the lignin into NaOH solution with varied concentration (0.25%, 0.5%, 1.0% and 1.5%). Lignin dissolves in alkaline-based aqueous system such as NaOH solution [23]. The dissolution is affected by the cation size and increases drastically above pH 9. A stable coating could be formed after immersing the membrane into lignin solution and rinsing with water. PVDF membranes were modified via surface coating by fully immersed into the lignin solution for 1 day. The modified membranes (NaOH-0.25, NaOH-0.5, NaOH-1.00, NaOH-1.50) were then rinsed with distilled water and kept in distilled water for characterization and filtration test. The lignin concentration was then adjusted between 0.25 wt.% and 1.0 wt% in the NaOH solution with concentration which caused minimum changes on membrane morphology. The samples were designated as Lig-0.25, Lig-0.50, Lig-0.75, Lig-1.0.

### *2.3. Membrane characterization*

The lignin modified PVDF membranes were rinsed with deionized water and dried for 24 h before characterization. The cross-section of membranes modified using lignin solution with varied NaOH concentration was studied using a scanning electron microscope (SEM) (HITACHI S-3000N, Hitachi Ltd., Japan). The cross-section and top surface of membranes modified using lignin solution with varied lignin concentration were studied using a field emission SEM (FE-SEM, Hitachi SU8010

model, Japan). The mean pore size of membranes was measured using a porometer (Porolux 1000, IB-FT GmbH, Germany). For pore size measurement, membrane samples were wetted with Porefil for 30 min before the test. The membrane samples from 600 $cm^{-1}$ to 3,800$cm^{-1}$ were analyzed using Fourier transformed infrared (FT-IR) spectroscopy (Nicolet iS10, Thermo Scientific, USA) to study the chemical properties of membrane samples. The oil adhesion on the membranes was studied using Lauda surface analyzer LSA200.

### *2.4. Oil-water emulsion preparation and separation test*

The water permeate flux of membranes was determined using a dead-end stirred cell, Sterlitech HP4750 (Sterlitech Corporation, WA) and distilled water at room temperature. The membranes with an effective area of 14.6 $cm^2$ were tested in the pressure range of 0.2-1.0 bar after compaction using nitrogen gas. The permeation flux ($J$, $L \cdot m^2 \cdot h^{-1}$) was calculated using the following equation.

$$J = \frac{V}{A \times t} \quad (1)$$

where $V$ is the volume of the permeate, $A$ is the effective area of the membrane, and $t$ is the filtration time. The water permeability was further determined from the graph of water permeate flux versus pressure through linear regression. The oily water was prepared by mixing oil and distilled water with a volume ratio of 1:100. Tween-80 (0.5mg/mL) was added to form the stable emulsion. The oil-water emulsion was ultrasonicated for 15 min before feeding into the dead-end stirred cell for separation test [24]. The membranes were tested at 1.0 bar and the oil rejection was calculated using:

$$r = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where $C_p$ is the oil concentration in the permeate, and $C_f$ is the oil concentration in the feed solutions. The oil concentration in the permeate sample was determined using a UV-visible spectrophotometer (Genesys 20, Thermo Fisher Scientific) at 225 nm [25]. The oil concentration was determined using a calibration curve of 0.0068-0.0543 mol/L ($y = 39.94x$, $r^2 = 0.8452$). The lignin modified PVDF membrane with the highest oil rejection was immersed in NaOH solution (2 wt.%) for 12 h to understand its' stability. The separation performance of alkaline treated membrane in oily water filtration was tested, as mentioned before.

## 3. Results and discussion

### *3.1. Membrane characteristics*

Fig. 1 shows the cross-section morphology of the neat PVDF and PVDF membrane modified with 1 wt.% of lignin dissolved in NaOH solution with varied concentration. The unmodified PVDF membrane showed spongy structure winter interconnected pores as reported in our recent works [26], [27] and other works [28]. The porous structure, pore size and surface roughness are greatly affected by the solvent exchange rate in the coagulating baths. The solvent exchange rate is lower in the ethanol bath compared to the water bath, resulting in a spongy structure. PVDF is less soluble in ethanol, reducing the precipitation rate to form a spongy structure as well [29]. The SEM images in Fig. 1 (b), (c) and (d) shows that the porous structure was not significantly affected after lignin coating except when NaOH solution with 1.5 wt% was used. The membrane sample, NaOH-1.50 turned into a dense membrane after

lignin coating, as shown in Fig. 1 (e). Lignin from different plant sources and processing routes is commonly soluble in alkaline solution [30], but PVDF membrane is susceptible to the morphology changes in alkaline solution [31].

The membrane was further modified using lignin with a varied concentration in NaOH solution with a low concentration of 0.5 wt.%. The morphology of membrane cross-section and surface could be observed from Fig. 2. The porous surface of Lig-0.25, Lig-0.5, Lig-0.75, and Lig-1.0 membranes was filled up with lignin. A very dense surface was observed from the SEM image of Lig-1.0 membrane modified with 1 wt.% of lignin in NaOH solution with a concentration of 0.5 wt.%. However, the surface remains rough. The morphology changes observed in this work are different from the morphology of PES membrane blended with lignin reported by Shamaei et al. [15]. The blending promoted precipitation and the demixing rate. They caused the enlargement of pore size but the reduction of the dense sublayer. On the other hand, the layer-by-layer coating of poly (diallyldimethylammonium chloride) and lignin on PES membrane resulted in a smooth surface [18]. The thickness of membranes without fabric support was measured using SEM images as shown in Fig. 2 (a), (c), (e), and (g). The membrane thickness only reduced greatly when lignin concentration was adjusted to 0.25 wt.%. The anionic lignin solution at low concentration could penetrate into the PVDF membrane with a negative surface charge and densified the membrane after NaOH removal. Hence, the membrane thickness reduced significantly during drying due to severe shrinkage. Yeo et al. [32] commented that the polymer shrinkage was significantly affected by the microvoid formation after incorporating lignin.

The membrane pore size after modification using the varied concentration of lignin solution was further measured. The changes in pore size are summarized in Table 1. The large pore size of the neat PVDF membrane at 0.41 μm was reduced to be smaller

than 0.30 μm when the lignin concentration was varied between 0.25 wt.% to 0.75 wt.%. However, such pore size reduction was not observed for Lig-1.0 sample modified using 1 wt.% of lignin in NaOH solution with a concentration of 0.5 wt.%. The lignin solution is anionic [33], and it was expected to be physically coated on PVDF with a negative surface charge [34]. The high concentration of lignin solution is expected to raise the electrostatic repulsion between lignin and PVDF membrane. Hence, the penetration of lignin into the membrane could be greatly reduced. The lignin coating tends to densify on the membrane surface after removing NaOH in the solvent exchange step, as shown in Fig. 2 (c), (e), and (g). The pore size reduction could be related to the polymer shrinkage caused by microvoid absence [32].

FTIR spectra of the neat PVDF membrane and the PVDF membranes modified using lignin solution containing varied lignin concentration in NaOH solution (0.5 wt.%) are shown in Fig. 3. All the PVDF membrane samples exhibited the bands related to $CH_2$ wagging vibration within 1401 – 1406.39 $cm^{-1}$ and C-C bonding within 1165 - 1171 $cm^{-1}$. These samples also displayed C-F and C-C-C symmetrical stretching vibration peaks within the range of 838 – 840 $cm^{-1}$and 876-878 cm-1, respectively [35]. Syringyl (S), guaiacyl (G) andp-hydroxyphenyl (H) bands are commonly observed in the FTIR spectra of lignin extracted from the alkaline pulping process [36]. Lig-0.25, Lig-0.50, Lig-0.75, and Lig-1.0 samples only showed an additional peak at 1275 $cm^{-1}$ in their FTIR spectra compared to the neat PVDF membrane. The addition peak can be correlated to the stretching vibration of guaiacyl rings. However, the other characteristic peaks of the G band (1029 $cm^{-1}$) and S bands (1330, 1115 and 819.94 $cm^{-1}$) could not be identified due to overlapping with PVDF characteristic peaks. The appearance of G band at 1275 $cm^{-1}$ and the absence of S bands could be induced by demethoxylation

reaction in the alkaline pulping process. This reaction transformed S groups to G groups with higher stability in the lignin.

The water contact angle on the modified membrane samples could not be measured due to the fast penetration of water droplet into the membrane sample with large pores and hydrophilic surface. The oil droplet could not be placed on the membrane surface for underwater contact angle measurement. Hence, the adhesion of the oil droplet on the membrane surface was studied. Fig. 4 shows that the oil droplets did not adhere to the membrane surface either the membrane samples have been modified with lignin solution or not. Unlike our previous works [27, 37] the neat PVDF membrane had not been dried before the oil adhesion test in this work. The neat PVDF membrane with a rough surface could capture a water layer within the hierarchical structure formed using an ethanol bath in phase inversion. The water layer captured by hierarchical structure prevents fouling, as reported by others [38]. The lignin coating further improved the surface hydrophilicity, and oil adhesion was not observed on the lignin modified membrane samples (Lig-0.25, Lig-0.5, Lig-0.75, and Lig-1.0).

### *3.2. Water permeation and oil emulsion rejection test*

The water permeability of the neat PVDF membrane and the lignin modified PVDF membrane using NaOH with varied concentration (NaOH-0.25, NaOH-0.50, NaOH-1.00, NaOH-1.50) was determined. As stated in Table 2, the water permeability was significantly reduced when the PVDF membrane was modified using lignin solution with a high NaOH concentration of 1.50 wt.%. The pore rupture observed in SEM images (Fig. 1(e)) could be the main reason. Hence, the subsequent modification of PVDF membrane was conducted using lignin solution with a NaOH concentration

of 0.50 wt.%. NaOH-0.5 membrane showed the least reduction of water permeability compared to the neat PVDF membrane. By adjusting the lignin concentration to 0.75 wt.% in the NaOH solution with a concentration of 0.50 wt.%, the membrane permeability could be significantly enhanced, about 110% (Table 3). The lignin concentration of 0.75 wt.% was preferred as it also resulted in the membrane with the rejection of oil emulsion up to 99.25%. The milky feed was purified into crystal clear water, as shown in Fig. 5. With an underwater oil contact angle larger than 150 °, the PVDF membranes modified by other researchers [39-42] also rejected more than 98% of oil in water, as shown in Table 4. The neat PVDF membrane only rejected 83.30% of oil emulsion in the feed. However, the permeate flux of oily water through the lignin modified membranes is lower than the permeate flux of oily water through the neat PVDF membrane as displayed in Fig. 6. The oily water permeate flux of Lig-0.75 membrane stabilized after 1 h, but the oily water permeate flux of the neat PVDF membrane reduced continuously. The unrejected oil emulsion could penetrate into the pores of the neat PVDF membrane and fouled the membrane through pore condensation [43]. After being immersed in NaOH solution for 12 h, the lignin modified PVDF membrane (Lig-0.75) could still reject 99.00% oil emulsion. A stable but lower permeate flux was recorded, as shown in Fig. 7.

## 4. Conclusions

PVDF membrane was successfully coated with lignin solution with varied NaOH and lignin concentration. The lignin coated membrane showed slight changes in morphology, but great improvement in separation performance. The excessive NaOH caused the pore collapse due to the instability of PVDF in the highly alkaline solution.

The lignin penetrated into the porous membrane and caused the reduction of pore size. The rough surface was not fully demolished after lignin coating. The FTIR spectra confirmed the existence of guaiacyl groups of lignin on the PVDF membrane. The hydrophilic lignin and rough surface could cause the formation of the water layer on the membrane surface. Hence, the adhesion of the oil droplet on the lignin coated membrane immersed in water was prevented. The increasing lignin content enhanced the water permeability and oil rejection of the lignin modified membranes. Although at lower permeate flux, the lignin coated membranes rejected more oil than the neat PVDF membrane with minimum fouling.

## CRediT authorship contribution statement

**N.A. Zakaria**: Investigation, Writing – original draft. **Hoi-Fang Tan:** Investigation. **M. Hazwan Hussin:** Investigation. **A.L. Ahmad:** Supervision, Writing – review & editing. **C.P. Leo:** Conceptualization, Methodology, Writing - review & editing, Supervision. **Phaik Eong Poh:** Investigation, Conceptualization, Writing – review & editing. **Kourosh Behzadian:** Fund acquisition, Writing – review & editing. **Isaac I. Akinwumi:** Fund acquisition, Writing – review & editing. **Alireza Moghayedi:** Fund acquisition, Writing – review & editing. **Joaquin Diazsolano:** Fund acquisition, Writing – review & editing.

## Declaration of Competing Interest

The authors declare no conflict of interest.

## Acknowledgements

The authors would like to acknowledge the Royal Academy of Engineering for the financial support (Frontiers of Engineering for Development Contract, FoE2021\9\2) to conduct this work.

**References**

[1] M. Hazwan Hussin, A. A. Aziz, A. Iqbal, M. N. M. Ibrahim, N. H. A. Latif, Development and characterization novel bio-adhesive for wood using kenaf core (Hibiscus cannabinus) lignin and glyoxal, Int. J. Biol. Macromol., 122 (2019) 713–722, https://doi.org/10.1016/j.ijbiomac.2018.11.009.

[2] M. Norgren and H. Edlund, Lignin: Recent advances and emerging applications, Curr. Opin. Colloid Interface Sci., 19 (5) (2014) 409–416, https://doi.org/10.1016/j.cocis.2014.08.004.

[3] B. Wang, S.F. Wang, S.S. Lam, C. Sonne, T.Q. Yuan, G.Y. Song, R.C. Sun, A review on production of lignin-based flocculants: Sustainable feedstock and low carbon footprint applications, Renew. Sustain. Energy Rev., 134 (2020) 110384, https://doi.org/10.1016/j.rser.2020.110384.

[4] W. Zhang, H. Duo, S. Li, Y. An, Z. Chen, Y. Ren, S. Wang, X. Zhang, X. Wang, An overview of the recent advances in functionalization biomass adsorbents for toxic metals removal, Colloids Interface Sci. Commun., 38, (2020) 100308, https://doi.org/10.1016/j.colcom.2020.100308.

[5] T. M. Albayati, A.A. Sabri, D. B. Abed, Adsorption of binary and multi heavy metals ions from aqueous solution by amine functionalized SBA-15 mesoporous adsorbent in a batch system, Desalin. Water Treat., 151 (2019) 315-321, https://doi.org/10.5004/dwt.2019.23937.

[6] Y. Ma, D. Zheng, Z. Mo, R. Dong, X. Qiu, Magnetic lignin-based carbon nanoparticles and the adsorption for removal of methyl orange, Colloid. Surface A, 559 (2018) 226-234, https://doi.org/10.1016/j.colsurfa.2018.09.054.

[7] B. Gao, P. Li, R. Yang, A. Li, H. Yang, Investigation of multiple adsorption mechanisms for efficient removal of ofloxacin from water using lignin-based adsorbents, Sci. Rep., 9 (2019) 637, https://doi.org/10.1038/s41598-018-37206-1.

[8] T.M. Albayati, Application of nanoporous material MCM-41 in a membrane adsorption reactor (MAR) as a hybrid process for removal of methyl orange, Desalin. Water Treat., 151 (2019) 138-144, https://doi.org/10.5004/dwt.2019.23878.

[9] A. M. Alkafajy, T. M. Albayati, High performance of magnetic mesoporous modification for loading and release of meloxicam in drug delivery implementation, 23 (2020) 100890, https://doi.org/10.1016/j.mtcomm.2019.100890.

[10] T. M. Albayati, A.A.A. Jassam, Synthesis and characterization of mesoporous materials as a carrier and release of prednisolone in drug delivery system, J Drug. Deliv. Sci. Tec., 53 (2019) 101176, https://doi.org/10.1016/j.jddst.2019.101176.

[11] G. N. Rivière, A. Korpi, M. H. Sipponen, T. Zou, M. A. Kostiainen, M. Österberg, Agglomeration of viruses by cationic lignin particles for facilitated water purification, ACS Sustain. Chem. Eng., 8 (10) (2020) 4167–4177, https://doi.org/10.1021/acssuschemeng.9b06915.

[12] O. S. H. Santos, M. Coelho da Silva, V. R. Silva, W. N. Mussel, M. I. Yoshida, Polyurethane foam impregnated with lignin as a filler for the removal of crude oil from contaminated water, J. Hazard. Mater., 324 (2017) 406–413,

https://doi.org/10.1016/j.jhazmat.2016.11.004.

[13] A. Abdel-Karim, H. Elhaes, A.S. El-Kalliny, M.I. Badawy, M. Ibrahim, T.A. Gad-Allah, Probing protein rejection behavior of blended PES-based flat-sheet ultrafiltration membranes: A density functional theory (DFT) study, Spectrochim. Acta A, 238 (2020) 118399.

[14] M. Yong, Y. Zhang, S. Sun, W. Liu, Properties of polyvinyl chloride (PVC) ultrafiltration membrane improved by lignin: Hydrophilicity and antifouling, J. Memb. Sci., 575 (2019) 50–59, https://doi.org/10.1016/j.memsci.2019.01.005.

[15] L. Shamaei, B. Khorshidi, M. A. Islam, M. Sadrzadeh, Development of antifouling membranes using agro-industrial waste lignin for the treatment of Canada's oil sands produced water, J. Memb. Sci., 611 (2020) 118326, https://doi.org/10.1016/j.memsci.2020.118326.

[16] Y. T. Chen, Y. L. Liao, Y. M. Sun, C. C. Hu, J. Y. Lai, Y. L. Liu, Lignin as an effective agent for increasing the separation performance of crosslinked polybenzoxazine based membranes in pervaporation dehydration application, J. Memb. Sci., 578 (2019) 156–162, https://doi.org/10.1016/j.memsci.2019.02.036.

[17] C. Lavanya and R. Geetha Balakrishna, Naturally derived polysaccharides-modified PSF membranes: A potency in enriching the antifouling nature of membranes, Sep. Purif. Technol., 230 (2020) 115887, https://doi.org/10.1016/j.seppur.2019.115887.

[18] L. Shamaei, B. Khorshidi, M. A. Islam, M. Sadrzadeh, Industrial waste lignin as an antifouling coating for the treatment of oily wastewater: Creating wealth from waste, J. Clean. Prod., 256 (2020) 120304, https://doi.org/10.1016/j.jclepro.2020.120304.

[19] L. Gu, M.Y. Xie, Y. Jin, M. He, X.Y. Xing, Y. Yu, Q.Y. Qu, Construction of antifouling membrane surfaces through layer-by-layer self-assembly of lignosulfonate and polyethyleneimine, Polymers (Basel)., 11 (11) (2019) 9–11, https://doi.org/10.3390/polym11111782.

[20] W. Jonglertjunya, T. Juntong, N. Pakkang, N. Srimarut, C. Sakdaronnarong, Properties of lignin extracted from sugarcane bagasse and its efficacy in maintaining postharvest quality of limes during storage, LWT - Food Sci. Technol., 57 (1) (2014) 116–125, https://doi.org/10.1016/j.lwt.2013.11.042.

[21] A. Javed, H. Ullsten, P. Rättö, L. Järnström, Lignin-containing coatings for packaging materials, Nord. Pulp Pap. Res. J., 33 (3) (2018) 548–556, https://doi.org/10.1515/npprj-2018-3042.

[22] N. Hamzah and C. P. Leo, Fouling prevention in the membrane distillation of phenolic-rich solution using superhydrophobic PVDF membrane incorporated with $TiO_2$ nanoparticles, Sep. Purif. Technol., 167 (2016) 79–87, https://doi.org/10.1016/j.seppur.2016.05.005.

[23] E. Melro, A. Filipe, D. Sousa, A.J.M. Valente, A. Romano, F.E. Antunes, B. Medrohno, Dissolution of kraft lignin in alkaline solutions, Int. J. Biol. Macromol., 148 (2020) 688-695. https://doi.org/10.1016/j.ijbiomac.2020.01.153.

[24] J. Cui, Z. Zhou, A. Xie, Q. Wang, S. Liu, J. Lang, C. Li, Y. Yan, J. Dai, Facile preparation of grass-like structured NiCo-LDH/PVDF composite membrane for efficient oil–water emulsion separation, J. Memb. Sci., 573 (2019) 226–233, https://doi.org/10.1016/j.memsci.2018.11.064.

[25] A. L. Ahmad, T. A. Otitoju, B. S. Ooi, Optimization of a high performance 3-aminopropyltriethoxysilane-silica impregnated polyethersulfone membrane

using response surface methodology for ultrafiltration of synthetic oil-water emulsion, J. Taiwan Inst. Chem. Eng., 93 (2018) 461–476, https://doi.org/10.1016/j.jtice.2018.08.021.

[26] H. F. Tan, W. L. Tan, N. Hamzah, M. H. K. Ng, B. S. Ooi, C. P. Leo, Membrane distillation crystallization using PVDF membrane incorporated with TiO2 nanoparticles and nanocellulose, Water Sci. Technol. Water Supply, 20 (5) (2020) 1629–1642, https://doi.org/10.2166/ws.2020.068.

[27] H. Tan, W. Tan, B. S. Ooi, C. P. Leo, Superhydrophobic PVDF /microfibrillated cellulose membrane for membrane distillation crystallization of struvite, Chem. Eng. Res. Des., 170, (2021) 54–68, https://doi.org/10.1016/j.cherd.2021.03.027.

[28] A. Hai, A. A. Durrani, M. Selvaraj, F. Banat, M. A. Haija, Oil-water emulsion separation using intrinsically superoleophilic and superhydrophobic PVDF membrane, Sep. Purif. Technol., 212 (2019) 388–395, https://doi.org/10.1016/j.seppur.2018.10.001.

[29] P. Sukitpaneenit and T. S. Chung, Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and rheology, J. Memb. Sci., 340 (1–2) (2009) 192–205, https://doi.org/10.1016/j.memsci.2009.05.029.

[30] S. Maitz, W. Schlemmer, M. A. Hobisch, J. Hobisch, and M. Kienberger, Preparation and characterization of a water-soluble kraft lignin, Adv. Sustain. Syst., 4 (8) (2020) 2000052, https://doi.org/10.1002/adsu.202000052.

[31] M. F. Rabuni, N. M. Nik Sulaiman, M. K. Aroua, N. A. Hashim, Effects of alkaline environments at mild conditions on the stability of PVDF membrane: An experimental study, Ind. Eng. Chem. Res., 52 (45) (2013) 15874–15882, https://doi.org/10.1021/ie402684b.

460 [32] J. S. Yeo, J. H. Lee, S. H. Hwang, Effects of lignin on the volume shrinkage and
461 mechanical properties of a styrene/unsaturated polyester/lignin ternary
462 composite system, Compos. Part B Eng., 130 (2017) 167–173,
463 https://doi.org/10.1016/j.compositesb.2017.07.084.
464 [33] Z. Wang, N. Bo, Y. Liu, G. Yang, Y. Liu, Y. Zhao, Preparation of lignin-based
465 anion exchangers and their utilization for nitrate removal, BioResources, 8 (3)
466 (2013) 3505–3517, https://doi.org/10.15376/biores.8.3.3505-3517.
467 [34] Y. Kakihana, L. Cheng, L.F. Fang, S.Y. Wang, S. Jeon, D. Saeki, S. Rajabzadeh,
468 H. Matsuyama, Preparation of positively charged PVDF membranes with
469 improved antibacterial activity by blending modification: Effect of change in
470 membrane surface material properties, Colloids Surfaces A Physicochem. Eng.
471 Asp., 533 (2017) 133–139, https://doi.org/10.1016/j.colsurfa.2017.08.039.
472 [35] H. Bai, X. Wang, Y. Zhou, L. Zhang, Preparation and characterization of
473 poly(vinylidene fluoride) composite membranes blended with nano-crystalline
474 cellulose, Prog. Nat. Sci. Mater. Int., 22 (3) (2012) 250–257,
475 https://doi.org/10.1016/j.pnsc.2012.04.011.
476 [36] N. A. Aziz, A.F.A. Latip, C.P. Leo, N.H.A. Latif, N. Brosse, R. Hashim, M.H.
477 Hussin, Reinforced lignin-phenol-glyoxal (LPG) wood adhesives from coconut
478 husk, Int. J. Biol. Macromol., 141 (2019) 185–196,
479 https://doi.org/10.1016/j.ijbiomac.2019.08.255.
480 [37] N. Hamzah and C. P. Leo, Membrane distillation of saline with phenolic
481 compound using superhydrophobic PVDF membrane incorporated with $TiO_2$
482 nanoparticles: Separation, fouling and self-cleaning evaluation, Desalination,
483 418 (2017) 79–88, https://doi.org/10.1016/j.desal.2017.05.029.
484 [38] J. Ju, T. Wang, Q. Wang, Superhydrophilic and underwater superoleophobic

PVDF membranes via plasma-induced surface PEGDA for effective separation of oil-in-water emulsions, Colloids Surfaces A Physicochem. Eng. Asp., 481 (2015) 151–157, https://doi.org/10.1016/j.colsurfa.2015.01.041.

[39] J. Gao, M. Cai, Z. Nie, J. Zhang, Y. Chen, Superwetting PVDF membrane prepared by in situ extraction of metal ions for highly efficient oil/water mixture and emulsion separation, Sep. Purif. Technol., 275 (2021) 119174, https://doi: 10.1016/j.seppur.2021.119174.

[40] J. Wu, Z. Hou, Z. Yu, J. Lang, J. Cui, J. Yang, J. Dai, C. Li, Y. Yan, A. Xie,, Facile preparation of metal-polyphenol coordination complex coated PVDF membrane for oil/water emulsion separation, Sep. Purif. Technol., 258 (2021) 118022, https://doi: 10.1016/j.seppur.2020.118022.

[41] X. Zeng, J. Lin, W. Cai, Q. Lu, S. Fu, J. Li, X. Yan, X. Wen, C. Zhou, M. Zhang, Fabrication of superhydrophilic PVDF membranes by one-step modification with eco-friendly phytic acid and polyethyleneimine complex for oil-in-water emulsions separation, Chemosphere, 264 (2021) 128395, https://doi: 10.1016/j.chemosphere.2020.128395.

[42] B. Jiang, K. Cheng, N. Zhang, N. Yang, L. Zhang, Y. Sun, One-step modification of PVDF membrane with tannin-inspired highly hydrophilic and underwater superoleophobic coating for effective oil-in-water emulsion separation, Sep. Purif. Technol., 255 (2021), 117724, https://doi: 10.1016/j.seppur.2020.117724.

[43] I. N. H. M. Amin, A. W. Mohammad, M. Markom, C.P. Leo, N. Hilal, Flux decline study during ultrafiltration of glycerin-rich fatty acid solutions, J. Memb. Sci., 351 (1–2) (2010) 75–86, 2010, https://doi.org/10.1016/j.memsci.2010.01.033.

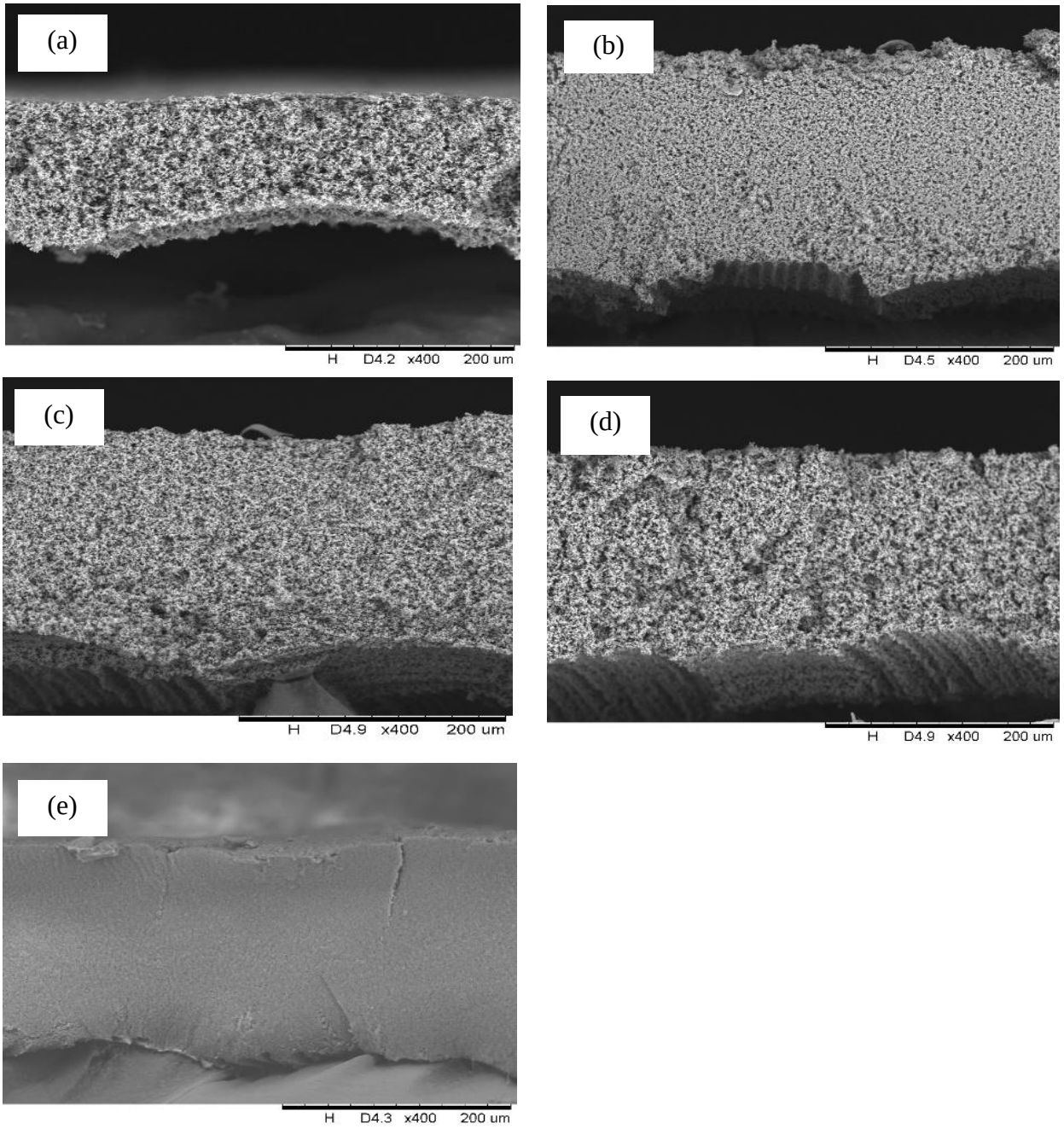



**Fig. 1.** SEM images of (a) PVDF membrane and PVDF membrane modified with 1 wt.% of lignin in NaOH solution with (b) 0.25 wt.%, (c) 0.5 wt.%, (d) 1.0 wt.%, and (e) 1.5 wt.% concentration.

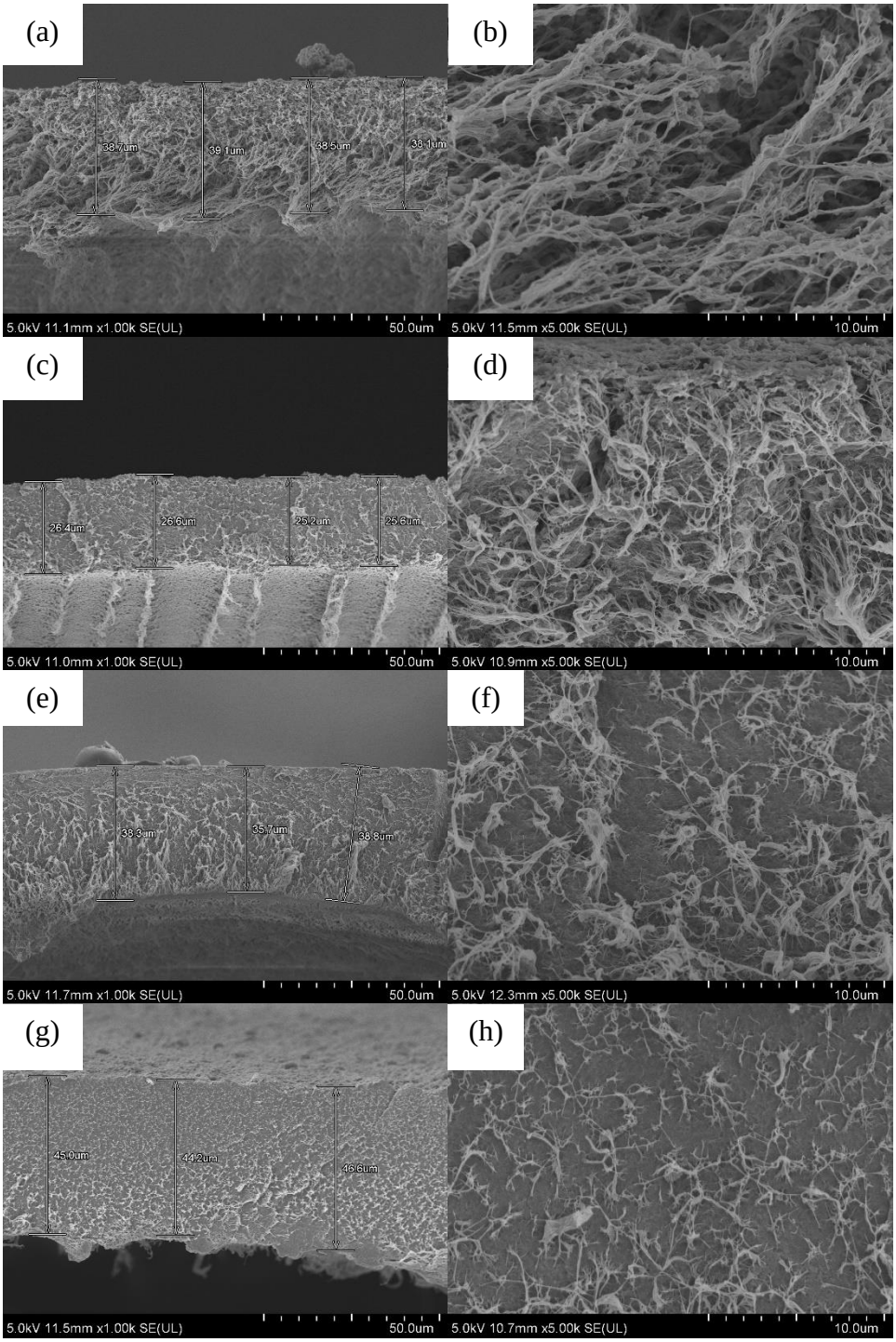



**Fig. 2.** SEM images of (a) PVDF membrane modified with 0.25 wt.% (Lig-0.25), (b) 0.50 wt.% (Lig-0.50), (c) 0.75 wt.% (Lig-0.75) and (d) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

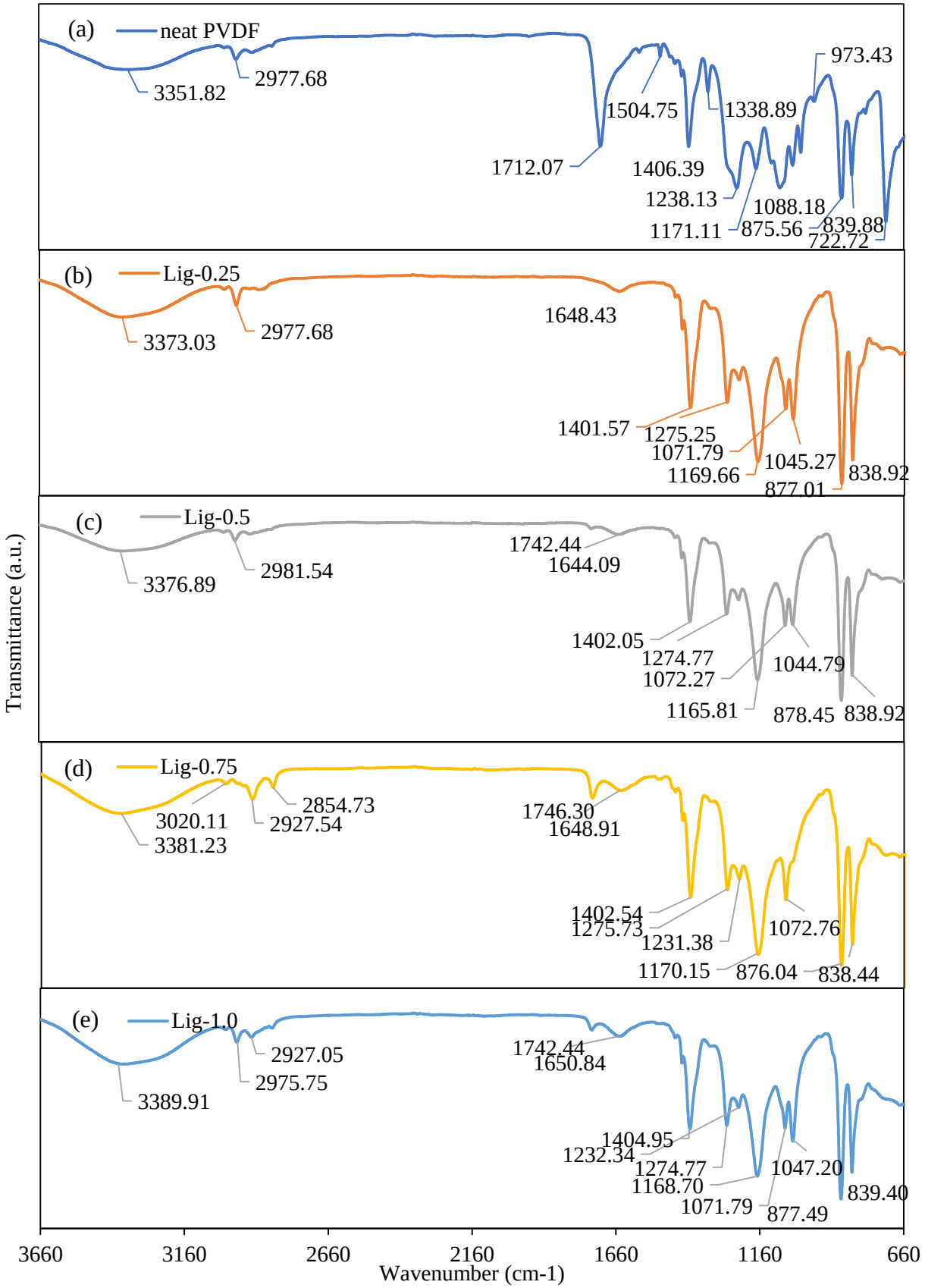



**Fig. 3.** FTIR spectra of (a) neat PVDF membrane and PVDF membrane modified with (b) 0.25 wt.% (Lig-0.25), (c) 0.50 wt.% (Lig-0.50), (d) 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

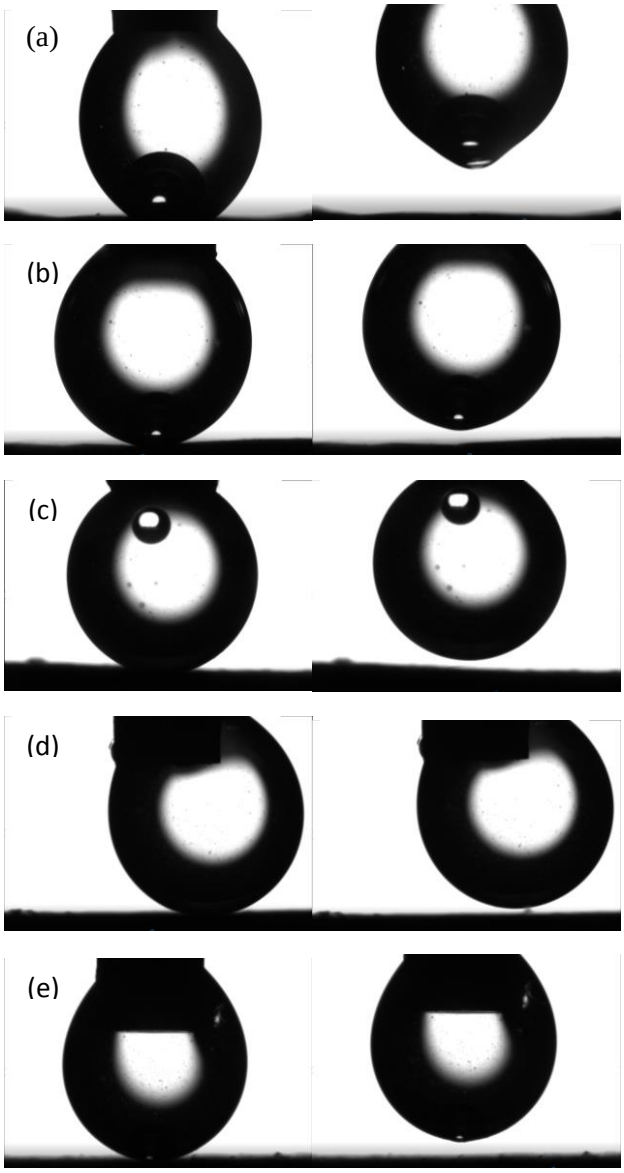



**Fig. 4.** Underwater oil droplets placed on (a) neat PVDF membrane and PVDF membrane modified with (b) 0.25 wt.% (Lig-0.25), (c) 0.50 wt.% (Lig-0.50), (d) 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

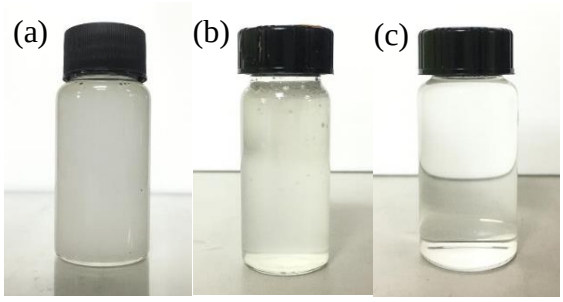



**Fig. 5.** The feed sample and the permeate samples of oily water filtration using b) the neat PVDF membrane and (b) the PVDF membrane modified with 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

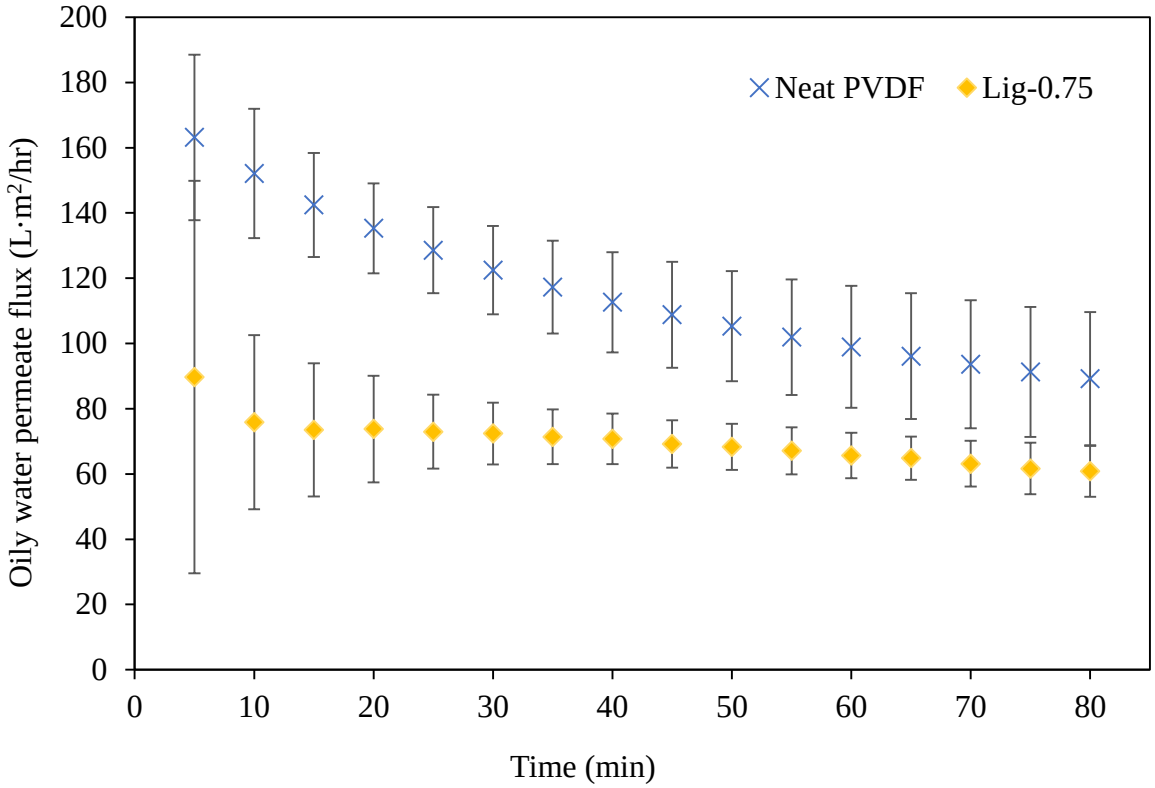



**Fig. 6.** The permeate flux of oily water filtration using the neat PVDF membrane and the PVDF membrane modified with 0.75 wt.% (Lig-0.75) of lignin in 0.5 wt.% of NaOH solution.

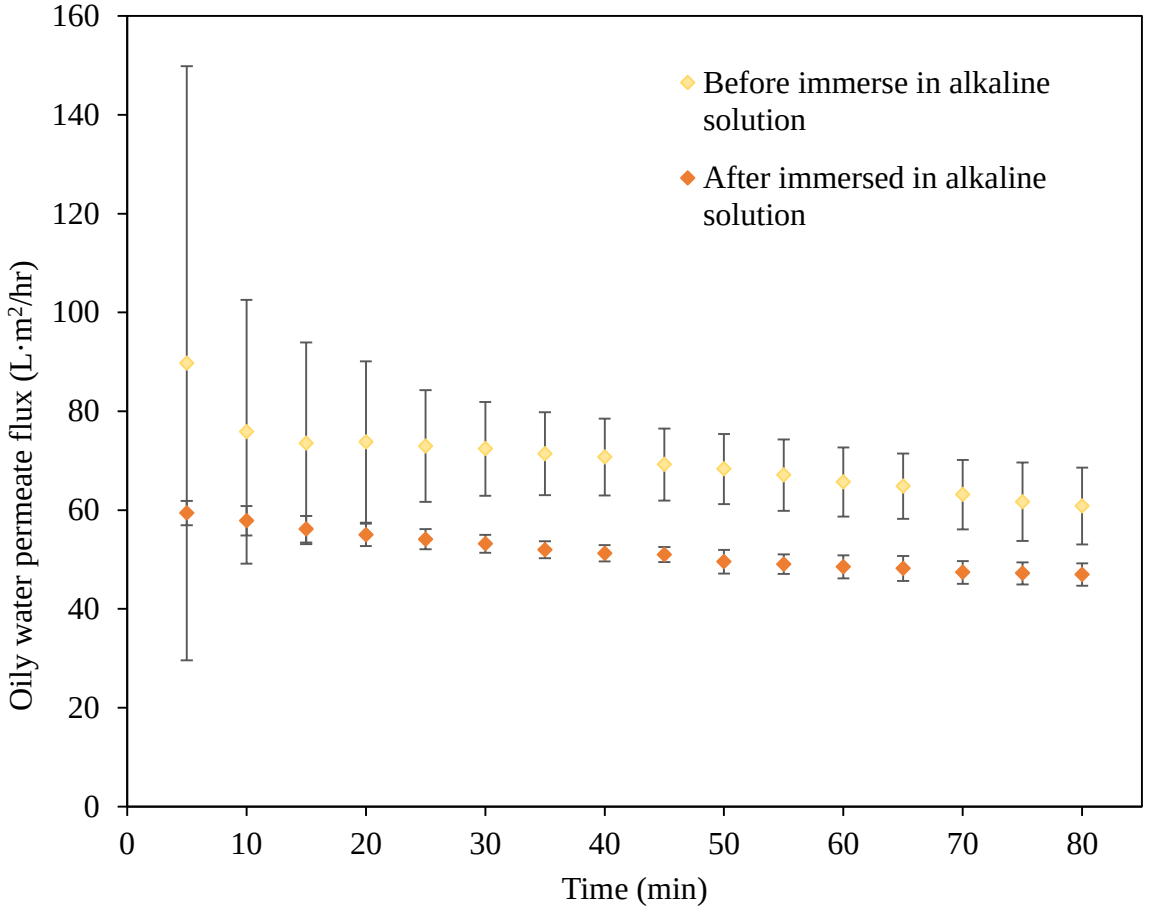



**Fig. 7.** The permeate flux of oily water filtration using PVDF membrane modified with 0.75 wt.% (Lig-0.75) of lignin in 0.5 wt.% of NaOH solution before and after immersed in alkaline solution.

**Table 1**

The pore size of the neat PVDF membrane and the PVDF membranes modified with lignin in NaOH solution.

| Membrane | Lignin content (wt%) | Pore size (μm) |
|---|---|---|
| Neat PVDF | 0 | 0.41 ± 0.22 |
| Lig-0.25 | 0.25 | 0.28 ± 0.18 |
| Lig-0.50 | 0.50 | 0.30 ± 0.01 |
| Lig-0.75 | 0.75 | 0.22 ± 0.13 |
| Lig-1.0 | 1.00 | 0.37 ± 0.27 |

**Table 2**

The pure water permeability of the neat PVDF membrane and the PVDF membrane modified with 1 wt.% of lignin in NaOH solution with varied concentration.

| Membrane | Lignin content (wt.%) | NaOH concentration (wt.%) | Water Permeability ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) |
|---|---|---|---|
| PVDF | 0 | 0 | 525.99 ± 16.28 |
| NaOH-0.25 | 1 | 0.25 | 408.49 ± 20.93 |
| NaOH-0.50 | 1 | 0.50 | 522.44 ± 12.56 |
| NaOH-1.00 | 1 | 1.00 | 296.03 ± 15.89 |
| NaOH-1.50 | 1 | 1.50 | 245.73 ± 19.07 |

**Table 3**

The pure water permeability of the neat PVDF membrane and the PVDF membrane modified with varied lignin content in 0.5 wt.% NaOH solution with varied concentration.

| Membrane | Lignin content (wt.%) | NaOH concentration (wt.%) | Water Permeability ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) |
|---|---|---|---|
| PVDF | 0 | 0 | 525.99 ± 16.28 |
| Lig-0.25 | 0.25 | 0.50 | 595.06 ± 21.94 |
| Lig-0.50 | 0.50 | 0.50 | 607.98 ± 10.74 |
| Lig-0.75 | 0.75 | 0.50 | 1102.60 ± 13.47 |
| NaOH-0.5 or Lig-1.00 | 1.00 | 0.50 | 624.78 ± 24.08 |

**Table 4**

Comparison to other works reporting on the modified PVDF membranes with underwater oil contact angle larger than 150 $^{o}$.

| Modifier | Preparation techniques | Wetting properties | | Performances | | Ref |
|---|---|---|---|---|---|---|
| | | Water contact angle ($^{o}$) | Oil contact angle ($^{o}$) | Oil rejection (%) | Water Permeability ($L.m^{-2}.h^{-1}.bar^{-1}$) | |
| Tannic acid (TA)/ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) | In-situ extraction | 0 | >150 | 99.99 | 2671.60 $^{-1}$ | [39] |
| TA - Titanium (Ti) | Facile layer-by-layer self-assembly | 0 | >150 | 99.35 | 689.6 $^{1}$ | [40] |
| Phytic Acid (PA)@Polyethyleneimine (PEI) | Surface depositing | 37 | 154.9 ± 0.42 | >98.5 | 12203.6 | [41] |
| Tannic acid (TA)/sodium periodate (NaIO4) | Dip-coating | 32 | 162 | >98 | >2400 | [42] |
| PVDF-lignin/sodium hydroxide (NaOH) | Surface coating | - | >150 | 99.25 | 1102.60 ± 13.47 | Present work |

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: