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Case Report

Exploring the effect of CNTs and pluronic on characteristics and stability of polyethersulfone (PES) and polyvinylidene fluoride (PVDF) membranes

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ABSTRACT

The accumulation of organic matter and colloidal particles on the membrane surface during the filtration process requires periodic chemical cleaning, potentially impacting the membrane properties and characteristics. Unfortunately, in recent years research into membrane stability against cleaning agents has often been neglected. This should be a crucial part to be prepared as membrane use in the industrial world, therefore this research aims to study the aging of polyethersulfone (PES) and polyvinylidene fluoride (PVDF) membranes modified with single-walled carbon nanotubes (CNTs) and Pluronic (PF). Membranes were prepared using phase inversion method and then treated by soaking in a 5 % sodium hypochlorite (NaClO) solution for 1 hour. Changes in the properties and performance of each membrane were investigated before and after treatment. Overall, the results show that the modified CNTs/PF-PES has better stability in various aspects of analysis such as functional groups, chemical composition, morphology, and hydrophilicity. The CNTs/PF-PES water contact angle increases from 59.4° to 64.7° while CNTs/PF-PVDF water contact angle increases until 69.1°. In addition, CNTs/PF-PES performance also shows more stable results with a flux decrease of 1.31 L/m^2.h only, while CNTs/PF-PVDF experiences a decrease of up to 16.31 L/m^2.h. Therefore, it can be concluded that CNTs and PF modification is better and more stable on PES membrane matrix compared to PVDF.

1. Introduction

Membrane technology has achieved significant advancements and is extensively implemented across a multitude of industrial sectors to date. These include haemodialysis, desalination, surface water treatment, chloro-alkali electrolysis, sterile filtration, food and beverage processing, together with gas separation processes including nitrogen and hydrogen separation [1]. Membrane-based methods are often regarded as innovative and distinctive water and wastewater treatment technologies as they possess several advantages, for example greater efficiency, ease of use, no change in phase, excellent selectivity, normal operating temperature conditions and low energy consumption [2–4]. It has attracted considerable attention as a replacement for traditional separation procedures on account of its specific advantages, such as the ability to selectively separate substances, automatic operation, minimal space requirements, besides no chemical consumption while processing [5–8]. Despite the advantages of membranes, there are certain issues that need to be resolved. Fouling is the principal challenge in membrane

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technology, which can presents a barrier to further deployment since it drastically decreases membrane productivity and increases energy consumption [9–12].

The main aim of developing an antifouling membrane is to alter its surface characteristics, for instance surface charge, surface roughness, and toxicity toward foulants, and hydrophobicity. This is achieved by including either nanoparticles (NPs) [13,14] or organic molecules as additives [15,16]. An extensive range of methods have been utilised to modify membranes, such as matrix blending [17], surface coating [18], interfacial polymerisation [19], chemical induced graft polymerisation [20], photoinduced graft polymerisation [21], plasma graft copolymerisation [22], in addition to initiated chemical vapour deposition (iCVD) [23].

Lately, membrane modification using organic and inorganic materials as additives has become incredibly popular in relation to overcoming fouling problems. Particular studies have successfully improved membrane performance by using ingle-walled carbon nanotubes (CNTs). For example, [24] modified PES membranes using polyvinylpyrrolidone (PVP) coated on the surface of multiwalled carbon nanotubes (MWCNTs). The modified PES membrane with PVP and MWCNTs 0.1 wt%, exhibited the most optimal overall performance, encompassing flux recovery ratios until 95 %. Arahman et al. (2022) reported similar results by incorporating pluronic and CNTs into the PES matrix, increasing the water permeability by up to 40 %. [26] reported AAF-MWCNTs in NF membranes generated improved stability of the active polyamide (PA) layer in high acid media, resulting in higher performance.

By enhancing membrane hydrophilicity, prolonged use of the membrane is susceptible to fouling as the filtration process progresses. Fouling causes a continuous decrease in flux over time, reduces filtration efficiency, generates higher operating costs and shortens membrane life, thus extensive implementation of membrane technology in water treatment is impeded [27,28]. Excess organic matter and colloidal particles must be physically removed from the membrane's surface and pores through water flushing and backflushing [29–31]. Nonetheless, some of these impurities cannot be removed by physical cleaning [32,33]. Therefore, the utilization of chemical cleaning is crucial for ensuring the effective functioning of the membrane system in operation [34–36].

In regard to chemical cleaning of low-pressure membranes, sodium hypochlorite (NaClO) is a popular agent on account of its economical price, accessibility and effective remediation of organic and biological contamination [37]. Apart from cleaning, NaClO is also frequently used for aging in particular studies, with the aim of determining the durability of the membrane after cleaning. Various studies, for example [38], observed three types of commercial hollow fibre PVDF membranes against NaClO aging. The SMM-1010 and MEMCOR® CS II membranes improved slightly after exposure to NaClO, while the ZeeWeed 500 membrane revealed a more significant decrease in flux using humic acid filtration. [39] noted that PVDF reinforced hollow fibre membranes exhibit mechanical strength used for membrane bioreactor (MBR) applications. Weathering did not significantly affect the mechanical strength; however, after 524,000 ppm.h (~13.1 years) of NaClO exposure, the membrane failed to function and increased the transmembrane pressure (TMP). Likewise, [40] examined PES aged by experiencing chemical and structural changes to the surface of the membrane during exposure to NaClO. The aged membrane has a permeability value 1.6 times greater than the pristine membrane.

Given the divergent findings in previous research regarding aging with NaClO, it becomes imperative to conduct a comparative analysis of the aging solutions employed for further assessment. For instance, research conducted by [41] compared sodium hypoclorite and sodium hydroxide as aging agents. The results confirmed that NIPS-PVDF using NaClO removes hydrophilic additives on the surface, while NaOH focuses on the dehydrofluorination process which results in the formation of conjugated polyene chains in the membrane structure. Conversely [42], used five separate chemicals to age membrane including water, NaClO as well as three types of bleach products, Bayclin, Soclin and Proclin. The results demonstrated that the highest flux recovery was obtained by the membrane using NaClO, with a FRR value of 95 %. Furthermore [43], compared aging for different types of pristine Polyethylene, PES, and PVDF membranes using two different types of aging solutions, NaClO and citric acid (CA). Overall, results show that NaClO has a higher cleaning efficiency, up to 100 % compared to CA. Based on the result, NaClO reported satisfactory results for each study. Thus, NaClO was used as an aging solution in this study.

This study focuses on developing the stability of the modified PES and PVDF membranes with CNTs and PF. PES, recognized for its robust polymer properties, serves as a key material in the fabrication of a wide range of filtration membranes. Renowned for its high-temperature resilience, broad pH tolerance, and impressive mechanical and structural strength [44].On the other hand, PVDF is a pure thermoplastic fluoropolymer that is highly unreactive, possesses excellent thermal stability, and can be used in a relatively high pH range [45]. Therefore, it is highly suitable for use in various situations and conditions. Both polymers have been extensively studied in membrane fabrication and application for water, and wastewater treatment. CNTs are incredibly strong and lightweight materials. When incorporated into membranes, they can enhance the mechanical strength of the membrane, making it more robust and durable, and exhibit distinctive structural characteristics that can be customized to improve membrane selectivity [46]. Pluronic, a triblock copolymer, is known for its amphiphilic nature and ability to form micelles in polymer solution. When blended to polymer solution, Pluronic can help mitigate fouling by forming a protective layer on the membrane surface, reducing the adhesion of foulants such as proteins, bacteria, or organic compounds [47,48]. CNTs has been investigated as an additive to improve the properties of PVDF membranes [49], while Pluronic has been used to improve the properties and filtration efficiency of PES membranes [47]. Regarding literature review, there is no research report on the effect of combining Pluronic and CNTs as membrane additive.

This research aims to determine membrane aging on the characteristics and performance of the modified membrane. The membrane was modified by incorporating Pluronic and CNTs into PES and PVDF, both of which function as anti-fouling agents that are important for long-term membrane performance and efficiency. Four types of membranes were prepared, including pure PES and PVDF membranes as control variables, and CNTs/PF-PES and CNTs/PF-PVDF membranes as independent variables. This membrane is then contacted with sodium hypochlorite (NaClO) as aging agent for a certain period of time, after which its characteristics and performance are evaluated. This work is a first implementation of the modification of PES and PVDF membranes with pluronic and CNTs for resistance to aging agents. It is expected to provide valuable insight into membrane aging in industrial applications.

2. Experimental

2.1. Material

The chemical components required include Polyethersulfone (PES, Average Mw: 65 kDa, Ultrason E6020 P, BASF, Ludwigshafen, Germany), Polyvinylidene Fluoride powder (PVDF, average Mw ~ 534,000) sourced from Sigma Aldrich, Single-walled carbon nanotubes (CNTs) and Pluronic F127 (PF) as the membrane modifying agent, and Dimethylformamide (DMF) as the solvent, all obtained from WAKO, Pure Chemical Industries, Ltd., (Osaka, Japan). Distilled water for the membrane coagulation media was provided by the chemical operation unit laboratory, University of Syiah Kuala. Sodium hypochlorite, acquired from CV. Gemilang Jaya, Medan, serves as the aging agent.

Table 1
Membrane composition.

Membrane	Composition (wt%)				
	PES	PVDF	CNTs	Pluronic	DMF
A_1	18	–	–	–	82
A_2	18	–	0.05	3	78.99
B_1	–	18	–	–	82
B_2	–	18	0.05	3	78.99

2.2. Membrane preparation

Membrane fabrication started by sonicating a small amount (0.05 wt %) of CNTs in DMF solvent, then 18 wt% of polymers (PES and PVDF) and PF 3 wt% were added. The membrane composition is shown in Table 1. After stirring for 24 hours, a homogeneous solution achieved. The solution was then spread onto a glass plate using membrane applicator, resulting in a wet thickness of 300 μm. Subsequently, the casted membrane was immersed into a non-solvent (distilled water) bath. The wet thickness is the thickness set on the casting knife at the time of membrane molding. Actual membrane thickness may be less owing to shrinkage. Membrane solidification was performed in a coagulation bath at room temperature (26°C) with a 2-min immersion time. The membrane underwent rinsing three times with tap water and was then stored in a container filled with distilled water.

2.3. Aging agent preparation

Sodium hypochlorite (NaClO) with a concentration of 5 % was prepared by diluting 209 ml of 12 % NaClO into 500 ml of distilled water solution and stirring until the color of the solution is completely clear (homogeneous). The membrane was soaked in NaClO for 1 hour, then further analysis of its characteristics and performance was conducted.

2.4. Membrane characterisation

2.4.1. Functional group analysis

Analysis of functional groups aims to determine the membrane's chemical bonds. The experiment was conducted utilizing a Fourier Transform Infrared instrument (PerkinElmer Inc.) at Kobe University, Research Centre for Membrane and Film Technology with a wave number range of 500–4000 cm^{-1}. The membrane's chemical groups can be identified through the wave number of the peak absorbed by the membrane.

2.4.2. Chemical composition and morphology analysis

SEM and EDS analysis were performed using SEM-EDX (Phenom ProX, Thermo Scientific, Japan). The membranes were dried using nitrogen and then coated using platinum (Pt) on the surface and cross-sectional area to generate electrical conductivity prior to being monitored under vacuum conditions. Electron energy with a power of 15 kV is fired at the membrane sample enabling the membrane chemical compound and morphology to be observed.

2.4.3. Membrane hydrophilicity

The assessment of membrane hydrophilicity was performed using the Water Contact Angle instrument (Drop Master DMo-502, Kyowa, Japan). A membrane segment measuring 0.5 cm × 5 cm was dried using a freeze dryer for 24 hours. Subsequently, a 1 μL water droplet was dispensed onto the membrane surface, and the angle formed between the membrane surface and water was automatically determined on the monitor display. This process of measuring the water contact angle was repeated three times for each sample, and the average value along with the standard deviation was calculated.

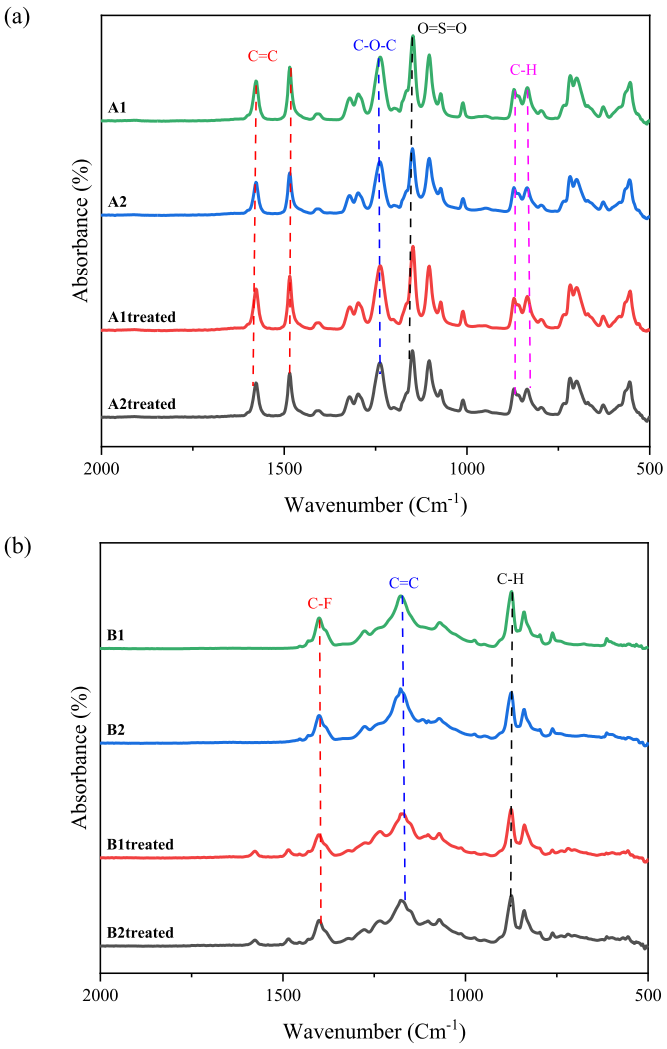

Fig. 1. IR-spectra of (a) PES and (b) PVDF membrane.

2.4.4. Porosity and analysis of pore size

The porosity and pore size of the membrane were determined by measuring the difference in weight of the membrane after drying. The membrane was dried in an oven at 60 °C until its weight reached a constant value. Porosity and pore size were then calculated by gravimetric method using Equation (1) and Equation (2) respectively [25].

$$\varepsilon = \frac{W_1\text{-}W_2}{\rho\, A\, l} \times 100\% \quad (1)$$

where ε is membrane porosity (%), W_1 is membrane wet weight (g), W_2 membrane is dry weight (g), ρ is water density (g/cm^2), A is membrane surface area (cm^2) and l is membrane thickness (cm).

$$rm = \sqrt{\frac{(2.9\text{-}1.75) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \quad (2)$$

where rm is mean pore size of membrane (μm), η is water viscosity, Q is permeate flow rate (cm^3/s), and ΔP is pressure difference (Pa).

2.4.5. Evaluation of membrane performance

The assessment of membrane permeation performance, specifically in terms of water flux, involved several steps. First, the membrane sample sheet was placed into the cross-flow filtration module. Subsequently, deionized water was flowed through the module using a peristaltic pump at a pressure of 0.2 MPa for 1 hour until compression occurred. Finally, the pressure decreased to 0.1 MPa, and the volume of

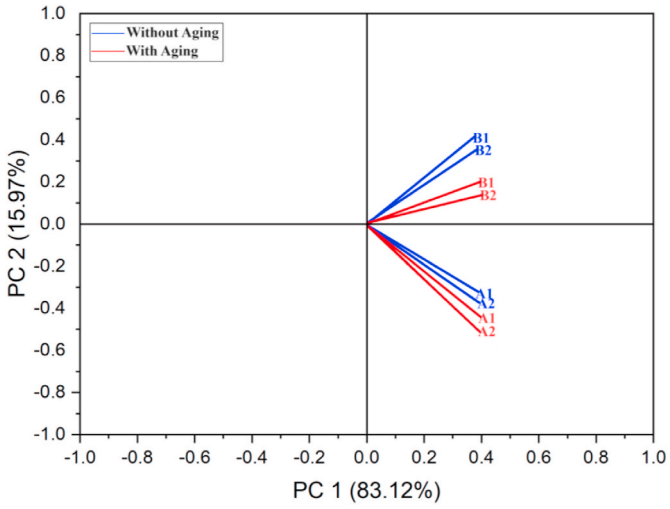

Fig. 2. PCA result of membranes.

permeate passing through the membrane was calculated every 10 minutes until the flux reached a constant value. Water flux value was estimated using an equation (3) [25].

$$J = \frac{V}{A \times t} \tag{3}$$

where J is pure water flux (L.m^2/h), V is permeate volume (L), and t is filtration time (h).

The membrane rejection performance was evaluated using humic acid as a model foulate with a concentration of 50 ppm. Following the permeation process, the yield of humic acid in the permeate was analyzed employing a UV–Vis spectrometer (DR 5000 Hach Lange). Afterward, the rejection percentage is calculated using equation (4) [25].

$$R = 1\frac{C_p}{C_f} \times 100\% \tag{4}$$

where R is rejection percentages (%), C_p is Feed concentration (ppm) and C_f is permeate concentration (ppm).

3. Result and discussion

3.1. Membrane functional group

The findings related to the FTIR for the PES membrane samples are shown in Fig. 1a). It can be noted that each membrane sample exhibited the same absorption peak. The stretching vibration of the benzene ring C═C is observed at 1570 cm^{-1} and 1480 cm^{-1}. The next stretching vibration, indicating the ether bond with the phenyl group C–O–C, is noted at 1420 cm^{-1}. The stretching vibration of the sulfone group O═S═O, which is a specific group of PES, is detected at 1150 cm^{-1}, while the C–H aromatic bonds can be seen at wave values of 871 cm^{-1}and 836 cm^{-1} [50]. The incorporation of CNTs and the addition of PF did not result in any alterations to the membrane's functional groups. This occurs because all the vibration bands related to the PES functional groups coincide with the additives. Conversely, in the additive membrane, all polymeric bands are present without any notable alterations compared to the pure polymer spectrum.

The PVDF membrane also experienced a similar situation, as shown in Fig. 1b. The peaks appearing at wave number 875 cm^{-1} and 1178 cm^{-1} are the C═C functional group of C–H and C═C respectively,

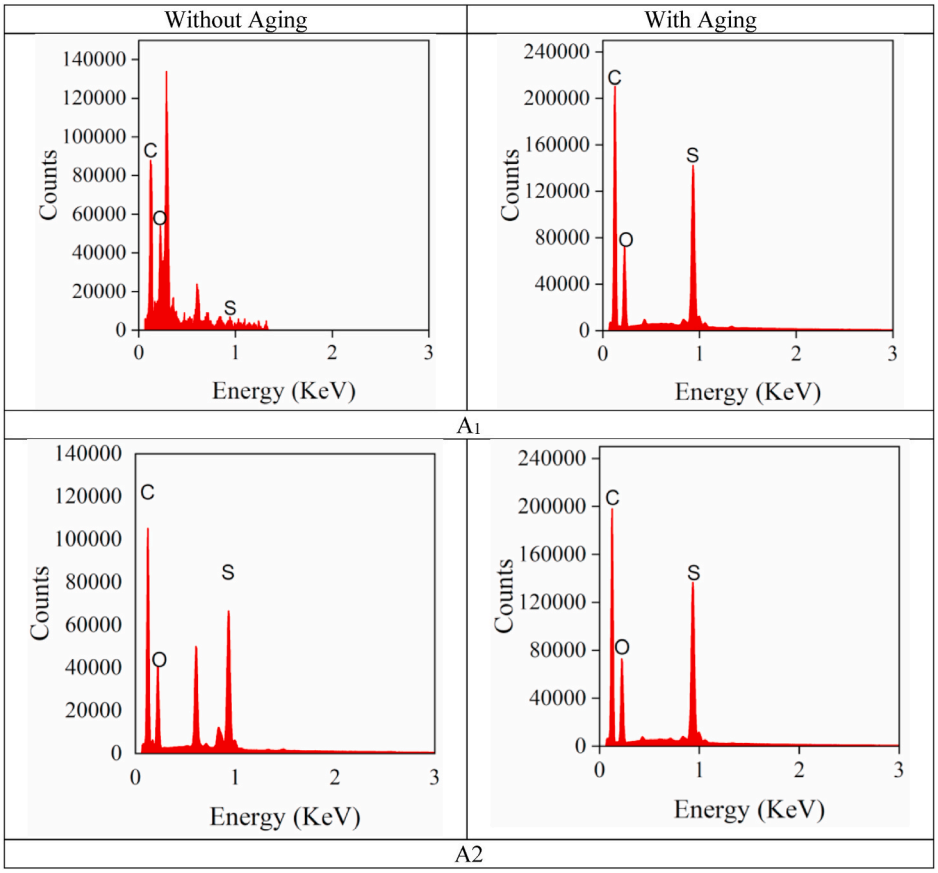

Fig. 3. EDS spectrum of PES membrane.

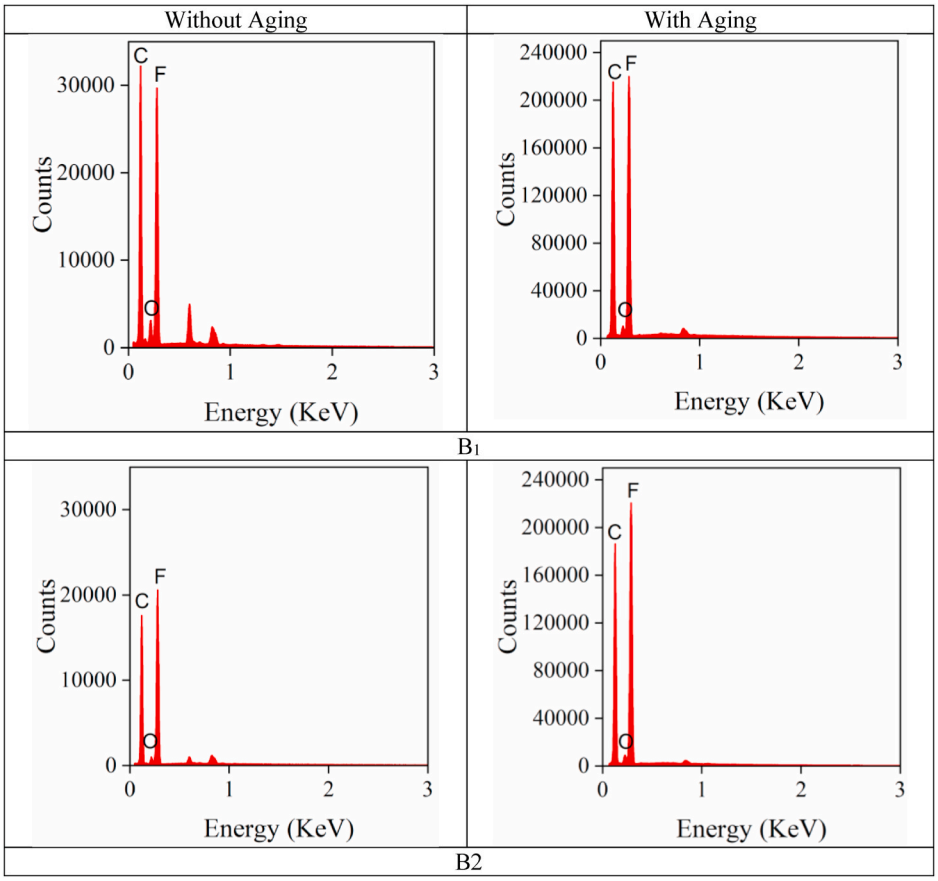

Fig. 4. EDS spectrum of PVDF membrane.

indicating PVDF polymer as the main component of the PVDF membrane [42,51]. Interpretation of the FTIR is challenging because the peaks are identical between each membrane. Therefore, further analysis is required using principle component analysis (PCA) to cluster variables that have a close relationship [52].

The results of the PCA analysis for the eight different membrane types are explained in Fig. 2. The results show A_1 and A_2 without aging are close to A_1 and A_1 with aging treatment, indicating that these four membranes are based on PES polymer. Moreover, B_1 and B_2 without aging reveal close proximity to B_1 and B_2 with aging, denoting the similarity of the membrane composition, PVDF.

In addition, the PES membrane demonstrates closeness concerning each component, indicating that the peak changes are not significant. Hence, this can be interpreted as a high level of stability. Nonetheless, in the PVDF membrane comprising code B_1, B_2 without aging and B_1, B_2 with aging, a gap is evident between the membrane both before and after aging which could be caused by release of chemical components, thereby reducing the similarity of the absorption intensity formed. This confirms that the level of stability of the PVDF membrane is lower than the PES membrane [53].

3.2. Membrane chemical composition

Figs. 3 and 4 depicts the Energy Dispersive X-ray Spectroscopy (EDS) spectra showcasing various chemical constituents and their quantitative evaluation within the PES and PVDF membrane. The qualitative analysis of the EDS spectrum revealed consistent presence of four components in both membranes: Carbon (C) and Oxygen (O). Additionally, S indicated the characteristics of PES, while F suggested the presence of PVDF. Carbon nanotubes primarily consist of Carbon (C), Oxygen (O), and Hydrogen (H), with carbon constituting over 98 % of their composition.

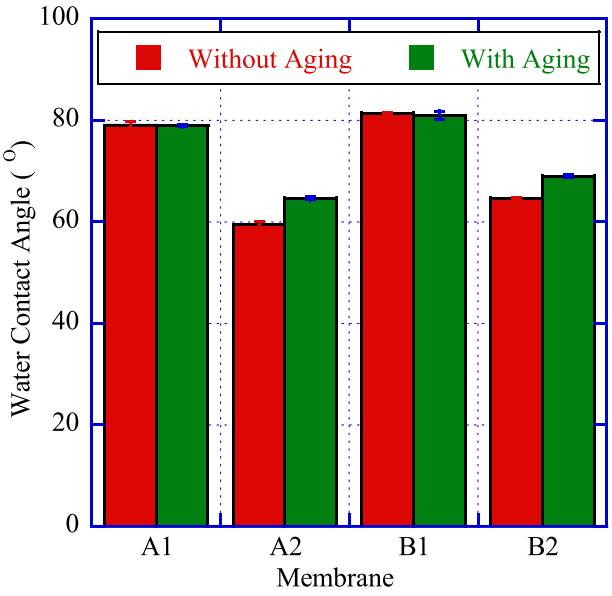

Fig. 5. Water contact angle of membranes.

Furthermore, Pluronic predominantly comprises Carbon (C) and Hydrogen (H) as its principal chemical compounds.

The increase in C and O concentrations in PES membrane is clearly presented in Fig. 3, which indicates that CNTs and PF are integrated into the membrane matrix, the same also occurs in the PVDF membrane in Fig. 4 where the C and O components can be clearly seen to increase, with an indication of an increase in the intensity of the EDS peak

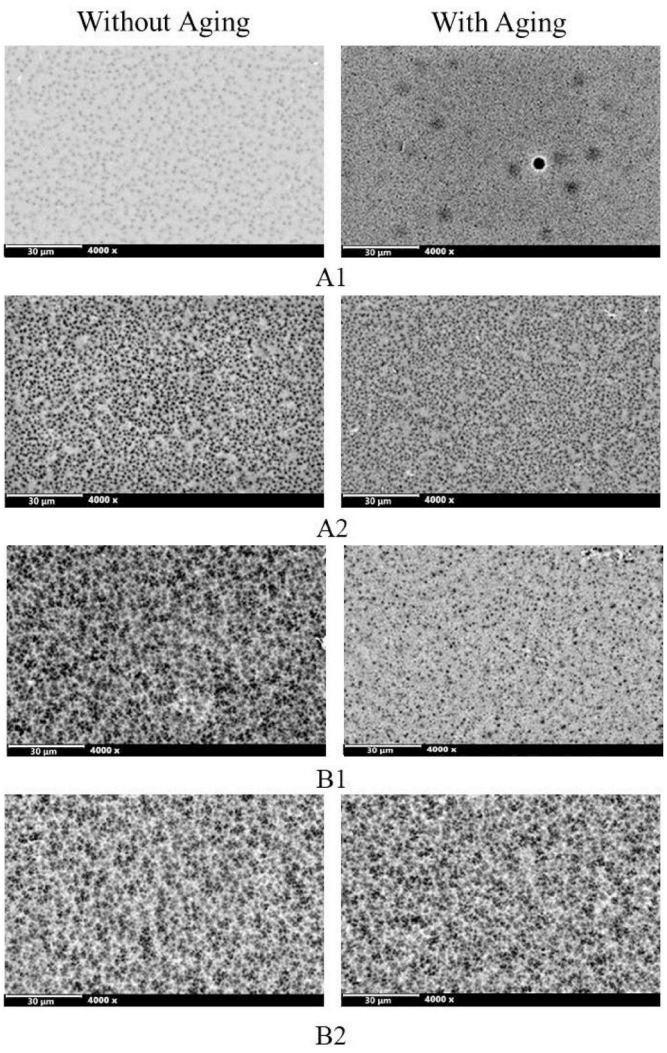

Fig. 6. SEM images of membrane surface.

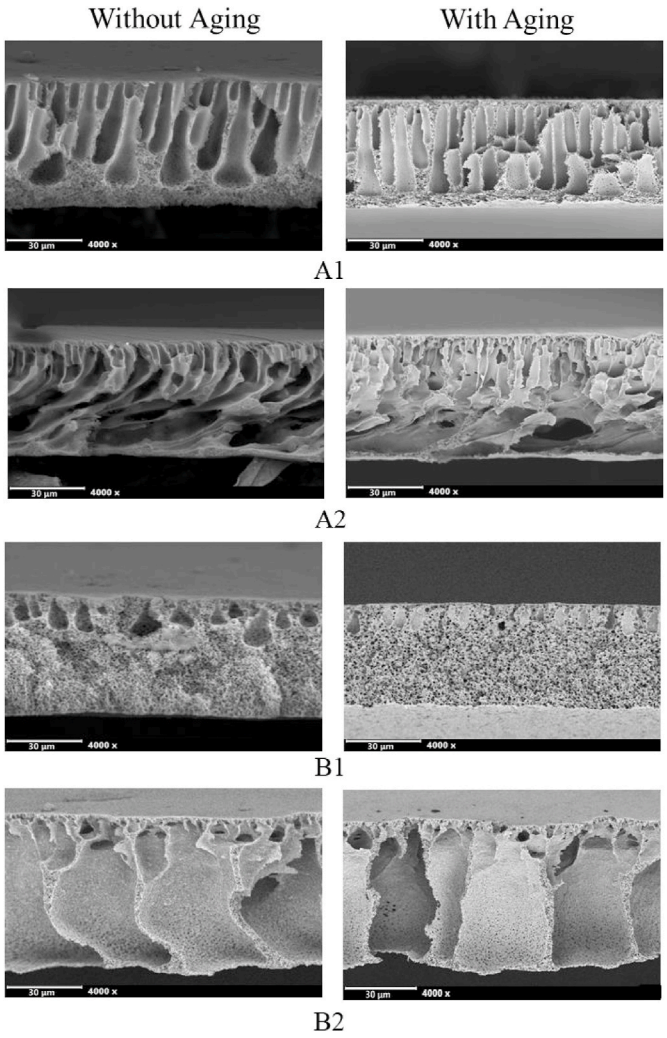

Fig. 7. SEM images of membrane cross-section.

spectrum [54]. After the aging process is carried out, the four membranes tend to experience a decrease in the overall chemical composition. This is because the use of chemicals such as NaClO can leach out additives which are hydrophilic during the aging process [55]. PES membrane shows better stability compared to PVDF with peak intensity in the EDS spectrum that does not decrease too drastically, the comparison of the decrease in chemical composition can be compared through Figs. 3 and 4. These results are in agreement (linear) with the FTIR spectrum analysis, as discussed in the previous section.

3.3. Membrane hydrophilicity

The results of the water contact angle (WCA) analysis are shown in Fig. 5, investigating the water contact angle plays a crucial role in assessing the hydrophilicity of membranes, typically, a reduction in contact angle suggests an enhancement in hydrophilicity. The results show that the addition of carbon nanotubes and pluronic additives have a significant impact on the WCA. The addition of CNTs to the membrane has an impact on increasing hydrophilicity caused by –COOH and OH-groups as a result of acid functionalization which increases the formation of water groups [56], as well as the addition of plurnoic which plays an important role in increasing hydrophilicity because it has a hydrophilic PEO segment. During the phase inversion process, the hydrophilic segments within the polymer matrix gather at the surface. Afterward, hydrogen bonding occurs between the PEO block and water molecules, resulting in the creation of a hydration layer on the membrane surface. This process effectively increases the membrane's affinity for water [57].

In this work, PES membrane has a lower WCA compared to PVDF membrane with values of 79.1° and 81.5° respectively, signifying that the PES membrane has better hydrophilicity, when compared to PVDF. The aging process had less impact on the pure PES membrane when in comparison to the modified PES as well as the PVDF membrane. Fig. 5 explains that the PES and PVDF membranes experienced almost no changes, whereas the modified PES and PVDF experienced an increase from 59.4° to 64.7° and 64.7°–69.1° respectively. This relates to the previous EDS discussion, which exhibited a reduction in the hydrophilic component (O) of the membrane.

3.4. Membrane morphology

Morphological structure is an important characteristic used to evaluate membrane separation efficiency and examine pore structure more precisely. Fig. 6 reveals surface morphology of membrane, the addition of nano carbon and pluronic additives shows an increase in pores on the membrane surface for both samples. Nonetheless after aging, A_1 exhibits the presence of several faint black dots on the surface which are believed to be pores formed after the washing process. A_2 with aging also exhibits practically the same phenomenon, although there are more pores on the membrane surface compared to A_2 without aging. Meanwhile, in B_1 and B2 membrane, the pores on the surface are shown almost similar without

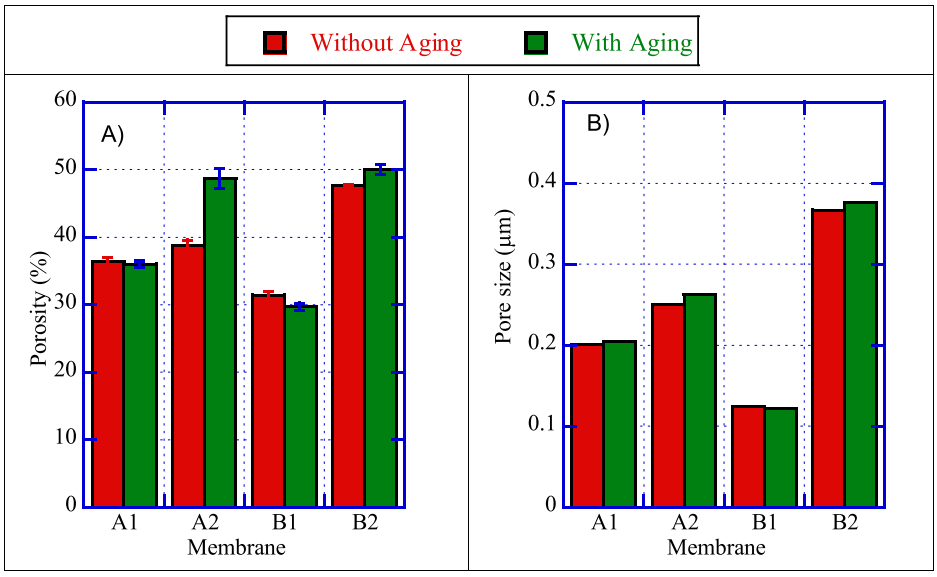

Fig. 8. Porosity (a) and mean pore size (b) of membranes.

and with aging, which do not reveal changes before and after aging. Likewise, it can be realised that there is no noticeable difference in the two membrane samples after the membrane aging process.

To delve deeper into the analysis, SEM examination was carried out on the cross-section of the membrane to investigate any alterations in pore structure. Fig. 7 illustrates the cross-section morphology of the membrane fabricated in this study. The membrane exhibits asymmetric pores comprising two layers: an active layer and a support layer. As depicted in the SEM cross-section image, the morphology of the PES-based membrane showcases a finger-like pore structure, whereas the PVDF-based membrane displays a sponge-shaped pore structure.

However, after the addition of additives, both membranes demonstrate changes in their morphological structure. PES with a finger-like pore structure consisting of larger pores and PVDF with a larger open pore structure with macrovoids inside. Similarly, the aging process barely has any impact on the morphological structure of the membrane; there are no prominent differences in both types of samples both before and after the addition of additives. The enlargement of pore structures observed in both membrane samples is attributed to the inclusion of 3% wt of pluronic amphiphilic surfactant polymer (PF) into the dope solution.

3.5. Porosity and mean pore size

The porosity and pore size of membranes are depicted in Fig. 8. Membranes with added additives (A_2 and B_2) exhibit higher porosity and pore size compared to pristine membranes. The incorporation of additives into the membrane can expedite phase inversion between solvent and nonsolvent, resulting in enhanced pore formation and consequently leading to an increase in membrane flux [58].

The aging process exclusively impacted on the porosity and pore size of membranes containing additives (A2 and B2), while minimal alterations were observed in pure PES or PVDF membranes (A1 and B1). This phenomenon may stem from the displacement of hydrophilic compounds within the A2 and B2 membrane during the soaking process. Consequently, during NaClO soaking, the hydrophilic compounds are liberated from the membrane, leading to the formation of new cavities. This is further supported by the emergence of new pores observed on both the surface and cross-section of the membrane (see Figs. 6 and 7).

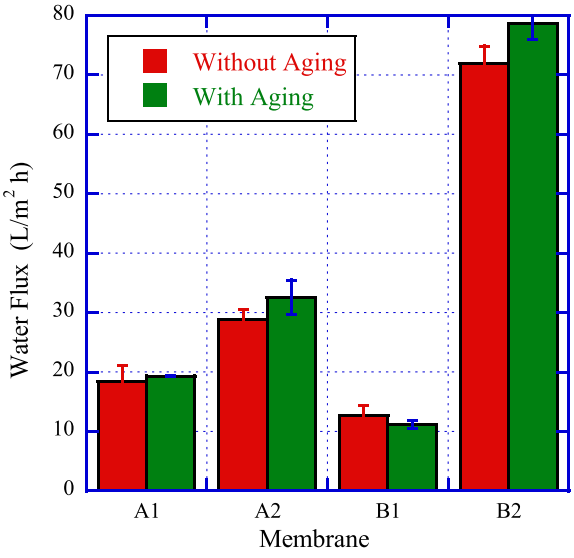

Fig. 9. Water flux of membranes.

3.6. Water flux

The pure water flux (PWF) test results for PES and PVDF membranes are shown in Fig. 9. It can be seen that the modified membrane has a higher WF compared to the pure membrane. The PES membrane integrated with CNTs and pluronic (A_2) showed an increase in WF of 56.8 % compared to pure PES (A_1). This is due to changes in membrane properties after modification, including an increase in hydrophilicity (Fig. 5) and an increase in the number of pores. These results are linear with SEM images both on the surface (Fig. 6) and on the cross-sectional structure of the membrane (Fig. 7). Similarly, the PVDF membrane modified with CNTs and pluronic (B_2) showed a very high increase in WF, up to 466.6 %. This increase was largely influenced by changes in the morphological structure of the cross section (Fig. 7), where the sponge-like structure on the B_1 membrane changed to a finger-like structure on the B_2 membrane, with a larger channel size. These two results confirm that the combination of CNTs and pluronic has a positive effect on increasing the rate of membrane permease.

An interesting finding was observed in the changes of the WF after

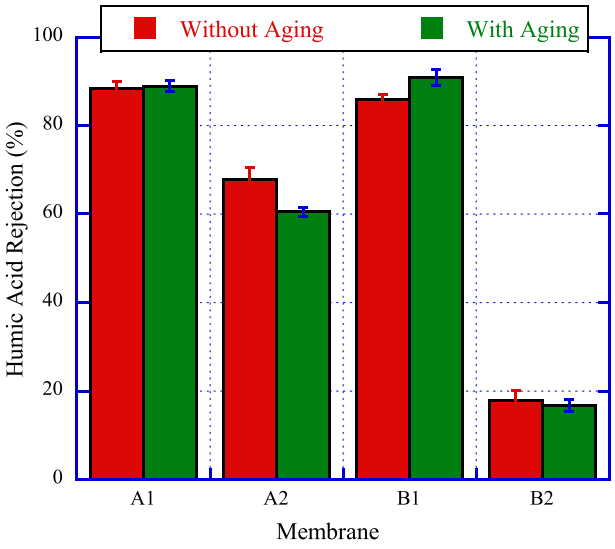

Fig. 10. Humic acid reduction.

aging treatment with NaOCl solution. The unmodified membrane (A_1 and B_1) showed a slight change in flux. This aligns with the minimal alterations in membrane characteristics, particularly in terms of porosity and pore size changes (Fig. 8). Meanwhile, in the modified membrane (A_2 and B_2), the change in flux was more noticeable as can be seen in Fig. 9. However, the change in flux of the modified PVDF membrane was greater than that of the modified PES membrane. This finding is in accordance with the statement made by Mohammad et al., which asserted that the PES membrane is more resistant to NaClO than PVDF [53].

3.7. Solute rejection

The results of the solute rejection evaluation (in this case, humic acid) for the PES and PVDF membranes are shown in Fig. 10. It can be seen that the modified membrane has a lower HA rejection compared to the pure membrane. Compared to pure PES (A_1), the PES membrane integrated with CNTs and pluronic (A_2) showed a 23 % reduction in rejection. This is due to an increase in pore size after modification, from 0.200 to 0.251 μm. The larger membrane pore size allows foulants to be released into the permeate. The same trend was found for PVDF membranes modified with CNTs and pluronic (B_2), where the rejection reduction was very high, up to 79 %. This reduction was also influenced by changes in the morphological structure, which had very large finger-like channels, so that the rejection obtained for B_2 was very low, only 17.87 %. In general, an increase in the flux will have an effect on the rejection capability, so even though the combination of CNTs and pluronic has a positive effect on the flux, it is the opposite for the rejection in this study.

Fig. 10 also shows the solute rejection after aging on the four membranes. In particular, it can be seen that there is no significant difference in the rejection of humic acid in each membrane. The unmodified PES membrane (A_1) showed a quite stable rejection, meanwhile, the modified PES membrane (A_2) presented a slight decrease in rejection. Unlike the pure PES membrane, the rejection of the pure PVDF membrane (B_1) changed slightly after aging. Changes in humic acid rejection in the four membranes after aging may occur due to changes in pore size of the membrane.

4. Conclusion

The improved stability of the PES and PVDF membranes has been positively discussed by examining their characteristics and performance. The results of the FT-IR analysis indicated no difference, although after further testing using PCA, it was determined that PES has excellent stability compared to PVDF. Stability is profoundly influenced by the hydrophilic compound the membrane possesses. Hence, the reduction in hydrophilic compounds, such as O in the membrane, can reduce the stability of the membrane. This is supported by the increase in hydrophilicity for each membrane after the aging process. These alterations affect certain structures both on the surface and the cross-section of the membrane, consequently influencing porosity and pore size. Although the membrane B_2 exhibited the highest Pure Water Flux (PWF) at 86.92 L/m2.h, its rejection capability for humic acid was approximately 20 %. Conversely, the pristine membrane demonstrated the highest rejection rate, up to 90 % for humic acid. Thus, it can be inferred that the additive modification involving CNTs and pluronic is more effective and stable within the PES membrane matrix compared to PVDF. These findings are anticipated to provide valuable insights for membrane aging in industries such as sewage treatment, water treatment, and related fields.

CRediT authorship contribution statement

Nasrul Arahman: Writing – review & editing, Supervision, Conceptualization. **Cut Meurah Rosnelly:** Supervision, Project administration. **Muhammad Prayogie Aulia:** Formal analysis, Data curation. **Rinal Dia'ul Haikal:** Investigation, Formal analysis. **Yusni:** Conceptualization. **Aulia Chintia Ambarita:** Formal analysis. **Poernomo Gunawan:** Writing – review & editing. **Ismail Koyuncu:** Resources. **Hideto Matsuyama:** Resources. **Noriaki Kato:** Resources. **Ryosuke Takagi:** Resources.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

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References

[1] S.P. Nunes, P.Z. Culfaz-Emecen, G.Z. Ramon, T. Visser, G.H. Koops, W. Jin, M. Ulbricht, Thinking the future of membranes: perspectives for advanced and new membrane materials and manufacturing processes, J. Membr. Sci. 598 (2020) 117761, https://doi.org/10.1016/j.memsci.2019.117761.
[2] W. Chen, J. Mo, X. Du, Z. Zhang, W. Zhang, Biomimetic dynamic membrane for aquatic dye removal, Water Res. 151 (2019) 243–251, https://doi.org/10.1016/j.watres.2018.11.078.
[3] S. Meng, X. Meng, W. Fan, D. Liang, L. Wang, W. Zhang, Y. Liu, The role of transparent exopolymer particles (TEP) in membrane fouling: a critical review, Water Res. 181 (2020) 115930, https://doi.org/10.1016/j.watres.2020.115930.
[4] N. Nasrollahi, L. Ghalamchi, V. Vatanpour, A. Khataee, Photocatalytic-membrane technology: a critical review for membrane fouling mitigation, J. Ind. Eng. Chem. 93 (2021) 101–116, https://doi.org/10.1016/j.jiec.2020.09.031.
[5] S. Chellam, M.A. Sari, Aluminum electrocoagulation as pretreatment during microfiltration of surface water containing NOM: a review of fouling, NOM, DBP, and virus control, J. Hazard Mater. 304 (2016) 490–501, https://doi.org/10.1016/j.jhazmat.2015.10.054.
[6] Z. Huang, J. Liu, Y. Liu, Y. Xu, R. Li, H. Hong, L. Shen, H. Lin, B.-Q. Liao, Enhanced permeability and antifouling performance of polyether sulfone (PES) membrane via elevating magnetic Ni@MXene nanoparticles to upper layer in phase inversion process, J. Membr. Sci. 623 (2021) 119080, https://doi.org/10.1016/j.memsci.2021.119080.
[7] R. Li, J. Li, L. Rao, H. Lin, L. Shen, Y. Xu, J. Chen, B.-Q. Liao, Inkjet printing of dopamine followed by UV light irradiation to modify mussel-inspired PVDF

membrane for efficient oil-water separation, J. Membr. Sci. 619 (2021) 118790, https://doi.org/10.1016/j.memsci.2020.118790.
[8] J. Teng, L. Shen, Y. He, B.-Q. Liao, G. Wu, H. Lin, Novel insights into membrane fouling in a membrane bioreactor: elucidating interfacial interactions with real membrane surface, Chemosphere 210 (2018) 769–778, https://doi.org/10.1016/j.chemosphere.2018.07.086.
[9] F. Meng, S. Zhang, Y. Oh, Z. Zhou, H.-S. Shin, S.-R. Chae, Fouling in membrane bioreactors: an updated review, Water Res. 114 (2017) 151–180, https://doi.org/10.1016/j.watres.2017.02.006.
[10] Y. Xiao, W. Zhang, Y. Jiao, Y. Xu, H. Lin, Metal-phenolic network as precursor for fabrication of metal-organic framework (MOF) nanofiltration membrane for efficient desalination, J. Membr. Sci. 624 (2021) 119101, https://doi.org/10.1016/j.memsci.2021.119101.
[11] Y. Xu, Y. Xiao, W. Zhang, H. Lin, L. Shen, R. Li, Y. Jiao, B.-Q. Liao, Plant polyphenol intermediated metal-organic framework (MOF) membranes for efficient desalination, J. Membr. Sci. 618 (2021) 118726, https://doi.org/10.1016/j.memsci.2020.118726.
[12] X. You, J. Zhang, L. Shen, R. Li, Y. Xu, M. Zhang, H. Hong, L. Yang, Y. Ma, H. Lin, Thermodynamic mechanisms of membrane fouling during filtration of alginate solution in coagulation-ultrafiltration (UF) process in presence of different ionic strength and iron(III) ion concentration, J. Membr. Sci. 635 (2021) 119532, https://doi.org/10.1016/j.memsci.2021.119532.
[13] N. Arahman, Fabrication of polyethersulfone membranes using nanocarbon as additive, Int. J. GEOMATE 15 (2018), https://doi.org/10.21660/2018.50.95424.
[14] S. Mulyati, S. Muchtar, M. Yusuf, N. Arahman, S. Sofyana, C.M. Rosnelly, U. Fathanah, R. Takagi, H. Matsuyama, N. Shamsuddin, et al., Production of high flux poly(ether sulfone) membrane using silica additive extracted from natural resource, Membranes 10 (2020) 17, https://doi.org/10.3390/membranes10010017.
[15] F. Saffarimiandoab, B. Yavuzturk Gul, R. Sengur Tasdemir, S. Erkoc Ilter, S. Unal, B. Tunaboylu, Y.Z. Menceloglu, I. Koyuncu, A review on membrane fouling: membrane modification, Desalination Water Treat. 216 (2021) 47–70, https://doi.org/10.5004/dwt.2021.26815.
[16] N. Arahman, A. Fahrina, S. Amalia, R. Sunarya, S. Mulyati, Effect of PVP on the characteristic of modified membranes made from waste PET bottles for humic acid removal, F1000Research 6 (2017) 668, https://doi.org/10.12688/f1000research.11501.2.
[17] R.D. Haikal, A.Z. Marom, M.P. Aulia, A.C. Ambarita, A. Azwar, A. Fahrina, M. R. Bilad, S. Mulyati, M.E. Pasaoglu, I. Koyuncu, et al., Morphology and characteristics of polyethersulfone membrane modified with Polyethylene glycol hexadecyl ether and nanocarbon, Appl. Chem. Eng. 7 (2023), https://doi.org/10.24294/ace.v7i1.2291.
[18] Y. Wang, Q. Li, W. Miao, P. Lu, C. You, Z. Wang, Hydrophilic PVDF membrane with versatile surface functions fabricated via cellulose molecular coating, J. Membr. Sci. 640 (2021) 119817, https://doi.org/10.1016/j.memsci.2021.119817.
[19] M. Adamczak, G. Kamińska, J. Bohdziewicz, Preparation of polymer membranes by in situ interfacial polymerization, Int. J. Polym. Sci. 2019 (2019) 1–13, https://doi.org/10.1155/2019/6217924.
[20] D. Huang, The Study of Chemical Induced Polyolefin-Based Ion Exchange Membrane for Electrodialysis Application, Michigan Technological University, 2020. Doctoral Dissertation.
[21] I.V. Korolkov, Y.G. Gorin, A.B. Yeszhanov, A.L. Kozlovskiy, M.V. Zdorovets, Preparation of PET track-etched membranes for membrane distillation by photo-induced graft polymerization, Mater. Chem. Phys. 205 (2018) 55–63, https://doi.org/10.1016/j.matchemphys.2017.11.006.
[22] M. Dufay, M. Jimenez, M. Casetta, F. Chai, N. Blanchemain, G. Stoclet, F. Cazaux, S. Bellayer, S. Degoutin, PCL covered PP meshes plasma-grafted by sulfonated monomer for the prevention of postoperative abdominal adhesions, Mater. Today Commun. 26 (2021) 101968, https://doi.org/10.1016/j.mtcomm.2020.101968.
[23] G. Ozaydin-Ince, A. Matin, Z. Khan, S.M.J. Zaidi, K.K. Gleason, Surface modification of reverse osmosis desalination membranes by thin-film coatings deposited by initiated chemical vapor deposition, Thin Solid Films 539 (2013) 181–187, https://doi.org/10.1016/j.tsf.2013.04.133.
[24] K. Zhu, G. Wang, S. Zhang, Y. Du, Y. Lu, R. Na, Y. Mu, Y. Zhang, Preparation of organic–inorganic hybrid membranes with superior antifouling property by incorporating polymer-modified multiwall carbon nanotubes, RSC Adv. 7 (2017) 30564–30572, https://doi.org/10.1039/C7RA04248E.
[25] N. Arahman, W.P. Sari, I.M. Sari, C.M. Rosnelly, S. Mulyati, A. Fahrina, M.R. Bilad, P. Gunawan, M.E. Pasaoglu, O.O. Teber, et al., The effectiveness of polyvinylidene fluoride membranes modified with poloxamer and single/multi-walled carbon nanotubes for lactalbumin purification, ChemEngineering 6 (2022) 88, https://doi.org/10.3390/chemengineering6060088.
[26] S. Gholami, J. López, A. Rezvani, V. Vatanpour, J.L. Cortina, Fabrication of thin-film nanocomposite nanofiltration membranes incorporated with aromatic amine-functionalized multiwalled carbon nanotubes. Rejection performance of inorganic pollutants from groundwater with improved acid and chlorine resistance, Chem. Eng. J. 384 (2020) 123348, https://doi.org/10.1016/j.cej.2019.123348.
[27] S. Huang, R.H.A. Ras, X. Tian, Antifouling membranes for oily wastewater treatment: interplay between wetting and membrane fouling, Curr. Opin. Colloid Interface Sci. 36 (2018) 90–109, https://doi.org/10.1016/j.cocis.2018.02.002.
[28] J.M. Ochando-Pulido, V. Verardo, A. Segura-Carretero, A. Martinez-Ferez, Technical optimization of an integrated UF/NF pilot plant for conjoint batch treatment of two-phase olives and olive oil washing wastewaters, Desalination 364 (2015) 82–89, https://doi.org/10.1016/j.desal.2014.10.040.
[29] J.M. Dickhout, J. Moreno, P.M. Biesheuvel, L. Boels, R.G.H. Lammertink, W.M. De Vos, Produced water treatment by membranes: a review from a colloidal perspective, J. Colloid Interface Sci. 487 (2017) 523–534, https://doi.org/10.1016/j.jcis.2016.10.013.
[30] G. Mustafa, K. Wyns, A. Buekenhoudt, V. Meynen, Antifouling grafting of ceramic membranes validated in a variety of challenging wastewaters, Water Res. 104 (2016) 242–253, https://doi.org/10.1016/j.watres.2016.07.057.
[31] J. Zhang, X. Pan, Q. Xue, D. He, L. Zhu, Q. Guo, Antifouling hydrolyzed polyacrylonitrile/graphene oxide membrane with spindle-knotted structure for highly effective separation of oil-water emulsion, J. Membr. Sci. 532 (2017) 38–46, https://doi.org/10.1016/j.memsci.2017.03.004.
[32] S. Shao, W. Fu, X. Li, D. Shi, Y. Jiang, J. Li, T. Gong, X. Li, Membrane fouling by the aggregations formed from oppositely charged organic foulants, Water Res. 159 (2019) 95–101, https://doi.org/10.1016/j.watres.2019.05.004.
[33] Z. Yan, F. Qu, H. Liang, H. Yu, H. Pang, H. Rong, G. Fan, B. Van Der Bruggen, Effect of biopolymers and humic substances on gypsum scaling and membrane wetting during membrane distillation, J. Membr. Sci. 617 (2021) 118638, https://doi.org/10.1016/j.memsci.2020.118638.
[34] J. Ding, S. Wang, P. Xie, Y. Zou, Y. Wan, Y. Chen, M.R. Wiesner, Chemical cleaning of algae-fouled ultrafiltration (UF) membrane by sodium hypochlorite (NaClO): characterization of membrane and formation of halogenated by-products, J. Membr. Sci. 598 (2020) 117662, https://doi.org/10.1016/j.memsci.2019.117662.
[35] S. Tang, L. Zhang, Y. Peng, J. Liu, Z. Zhang, Fenton cleaning strategy for ceramic membrane fouling in wastewater treatment, J. Environ. Sci. 85 (2019) 189–199, https://doi.org/10.1016/j.jes.2019.06.010.
[36] A. Xie, J. Cui, J. Yang, Y. Chen, J. Lang, C. Li, Y. Yan, J. Dai, Photo-fenton self-cleaning PVDF/NH2-MIL-88B(Fe) membranes towards highly-efficient oil/water emulsion separation, J. Membr. Sci. 595 (2020) 117499, https://doi.org/10.1016/j.memsci.2019.117499.
[37] W. Cai, J. Han, X. Zhang, Y. Liu, Formation mechanisms of emerging organic contaminants during on-line membrane cleaning with NaOCl in MBR, J. Hazard Mater. 386 (2020) 121966, https://doi.org/10.1016/j.jhazmat.2019.121966.
[38] M. Han, Q. Han, S. Wu, H. Xiao, L. Zhang, Y. Lin, F. Meng, S. Zhao, Unveiling the impacts of sodium hypochlorite on the characteristics and fouling behaviors of different commercial polyvinylidene fluoride hollow fiber membranes, Membranes 12 (2022) 965, https://doi.org/10.3390/membranes12100965.
[39] C.J.M. Lye, H. Xu, R. Wang, Impact of NaOCl ageing on reinforced PVDF hollow fiber membranes used in membrane bioreactor, J. Water Process Eng. 44 (2021) 102408, https://doi.org/10.1016/j.jwpe.2021.102408.
[40] B. Pellegrin, F. Mezzari, Y. Hanafi, A. Szymczyk, J.-C. Remigy, C. Causserand, Filtration performance and pore size distribution of hypochlorite aged PES/PVP ultrafiltration membranes, J. Membr. Sci. 474 (2015) 175–186, https://doi.org/10.1016/j.memsci.2014.09.028.
[41] Q. Wu, X. Zhang, G. Cao, Impacts of sodium hydroxide and sodium hypochlorite aging on polyvinylidene fluoride membranes fabricated with different methods, J. Environ. Sci. 67 (2018) 294–308, https://doi.org/10.1016/j.jes.2017.07.014.
[42] S. Mulyati, C.M. Rosnelly, Y. Syamsuddin, A.C. Ambarita, S. Muchtar, Household bleach products as high-performance and cost-effective cleaning agents for membrane fouling, South Afr. J. Chem. Eng. 46 (2023) 35–41, https://doi.org/10.1016/j.sajce.2023.07.005.
[43] L. Vanysacker, R. Bernshtein, I.F.J. Vankelecom, Effect of chemical cleaning and membrane aging on membrane biofouling using model organisms with increasing complexity, J. Membr. Sci. 457 (2014) 19–28, https://doi.org/10.1016/j.memsci.2014.01.015.
[44] M. Fadli, A. Khausar, S. Sofyana, U. Fathanah, Karakteristik membran komposit polietersulfon, polivinilpirolidon Dan Kitosan, J. Serambi Eng. 6 (2021), https://doi.org/10.32672/jse.v6i4.3476.
[45] J.E. Marshall, A. Zhenova, S. Roberts, T. Petchey, P. Zhu, C.E.J. Dancer, C. R. McElroy, E. Kendrick, V. Goodship, On the solubility and stability of polyvinylidene fluoride, Polymers 13 (2021) 1354, https://doi.org/10.3390/polym13091354.
[46] M. Dong, J. Guo, Q. Liu, J. Zeng, X. Xiong, X. Gai, Y. Wang, Y. Wu, Low-pressure carbon nanotube membrane with different surface properties for the removal of organic dyes and PPCPs, J. Environ. Chem. Eng. 11 (2023) 110131, https://doi.org/10.1016/j.jece.2023.110131.
[47] J. Chen, C. Gao, S. Zhao, S. Liu, S. Ji, Y. Xing, T. Wu, J. Wu, H. Chen, P. Zou, et al., Construction of PES membranes using NH2-MIL-125 and pluronic F127 via RTIPS method toward elevated ultrafiltration, antifouling and self-cleaning performance, J. Environ. Chem. Eng. 10 (2022) 107162, https://doi.org/10.1016/j.jece.2022.107162.
[48] S.I. Jeon, J.H. Lee, J.D. Andrade, P.G. De Gennes, Protein—surface interactions in the presence of Polyethylene oxide, J. Colloid Interface Sci. 142 (1991) 149–158, https://doi.org/10.1016/0021-9797(91)90043-8.
[49] S. Gholami, J.L. Llacuna, V. Vatanpour, A. Dehqan, S. Paziresh, J.L. Cortina, Impact of a new functionalization of multiwalled carbon nanotubes on antifouling and permeability of PVDF nanocomposite membranes for dye wastewater treatment, Chemosphere 294 (2022) 133699, https://doi.org/10.1016/j.chemosphere.2022.133699.
[50] A.C. Ambarita, N. Arahman, S. Mulyati, A synergistic approach to improving antifouling and antibacterial properties of Ag/DBR/PES membrane, South Afr. J. Chem. Eng. 48 (2024) 30–39, https://doi.org/10.1016/j.sajce.2024.01.002.
[51] K. Li, Q. Su, S. Li, G. Wen, T. Huang, Aging of PVDF and PES ultrafiltration membranes by sodium hypochlorite: effect of solution pH, J. Environ. Sci. 104 (2021) 444–455, https://doi.org/10.1016/j.jes.2020.12.020.
[52] A.C. Ambarita, N. Arahman, M.R. Bilad, B.Y. Gül, S. Korkut, A. Yüksekdağ, O. O. Teber, İ. Koyuncu, S. Mulyati, Polyethersulfone membrane coated with dragon blood resin: effect of input parameters and optimization using response surface

methodology, South Afr. J. Chem. Eng. 45 (2023) 30–41, https://doi.org/10.1016/j.sajce.2023.04.005.
[53] A.W. Mohammad, Y.H. Teow, W.C. Chong, K.C. Ho, Hybrid processes: membrane bioreactor, in: Membrane Separation Principles and Applications, Elsevier, 2019, pp. 401–470. ISBN 978-0-12-812815-2.
[54] N. Rarokar, R. Agrawal, S. Yadav, P. Khedekar, C. Ravikumar, D. Telange, S. Gurav, Pteroyl-γ-l-Glutamate/Pluronic® F68 modified polymeric micelles loaded with docetaxel for targeted delivery and reduced toxicity, J. Mol. Liq. 369 (2023) 120842, https://doi.org/10.1016/j.molliq.2022.120842.
[55] F. Russo, M. Bulzomì, E. Di Nicolò, C. Ursino, A. Figoli, Enhanced anti-fouling behavior and performance of PES membrane by UV treatment, Processes 9 (2021) 246, https://doi.org/10.3390/pr9020246.
[56] M.M. Ngoma, M. Mathaba, K. Moothi, Effect of carbon nanotubes loading and pressure on the performance of a polyethersulfone (PES)/Carbon nanotubes (CNT) membrane, Sci. Rep. 11 (2021) 23805, https://doi.org/10.1038/s41598-021-03042-z.
[57] L. Zhang, Y. Shi, T. Wang, S. Li, X. Zheng, Z. Zhao, Y. Feng, Z. Zhao, Fabrication of novel anti-fouling poly(m-phenylene isophthalamide) ultrafiltration membrane modified with pluronic F127 via coupling phase inversion and surface segregation, Sep. Purif. Technol. 282 (2022) 120106, https://doi.org/10.1016/j.seppur.2021.120106.
[58] E.H. Alosaimi, H.M.A. Hassan, I.H. Alsohaimi, Q. Chen, S. Melhi, A.A. Younes, W. H. El-Shwiniy, Fabrication of sulfonated polyethersulfone ultrafiltration membranes with an excellent antifouling performance by impregnating with polysulfopropyl acrylate coated ZnO nanoparticles, Environ. Technol. Innov. 25 (2022) 102210, https://doi.org/10.1016/j.eti.2021.102210.