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Improved oily wastewater rejection and flux of hydrophobic PVDF membrane after polydopamine-polyethyleneimine co-deposition and modification

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ABSTRACT

The surface structure and properties of a membrane largely determine its in-service performance during a filtration process. Polyvinylidene fluoride (PVDF) hydrophobic membrane is widely used in the separation of oily wastewater because of its mechanical strength, but is susceptible to oil fouling, whereas hydrophilic membranes are easily damaged in water due to their wettability but are resistant to oil. The advantages of the two membranes are then combined by modifying the hydrophobic membrane to be hydrophilic to maintain stability, mechanical strength, and antifouling performance. PVDF ultrafiltration membranes were modified with a mixture of different concentrations of polydopamine (PDA) and polyethyleneimine (PEI) using different deposition times (6, 12, and 24 h) and characterized using SEM, FTIR, and contact angle. Membrane performance was tested using a dead-end module for 60 min. The PDA-modified membrane showed a decrease in hydrophilicity from 88.1° to 77.7° after being coated with 0.5 g/L PDA for 6 h, while with the addition of 2 g/L PEI, the hydrophilicity reached 64.6° SEM characterization showed the presence of aggregates formed during the PDA polymerization process and decreased with the addition of PEI. This is in line with the results obtained from the performance test with the dead-end module where the smaller the aggregate, the greater the flux produced. FTIR characterization showed a strong bond between PDA and PDA-PEI with the membrane as the concentration and coating time increased.

1. Introduction

Rapid industrial growth such as in the oil and gas, petrochemical, pharmacy, and food industries has led to an increase in oily wastewater (OWW) (Tawalbeh et al., 2018; Yue et al., 2018; Zulfiqar et al., 2019). Disposal of OWW results in various lines of environmental pollution including surface water, underground water, and soil. In addition, there is also a possibility of air pollution due to OWW that evaporates (Ahmad et al., 2020). This OWW pollution has a negative impact on surface water, where the presence of OWW blocks the entry of sunlight and oxygen into the water. Facing these challenges, various technologies have been developed for OWW separation. Meanwhile, the developed technology must have high efficiency, low energy consumption, low cost, and compact size (Fan et al., 2021). The most conventional technology is skimming, which is generally used for the separation of heterogeneous OWWs. Alternative technologies such as

adsorption, absorption, chemical and biological processes were also developed to overcome these problems, but resulted in the low effectiveness of the process, especially for water-oil emulsions which are difficult to process using these conventional techniques (Sun et al., 2020; Yang et al., 2021; Yue et al., 2019). Recently, the exploration of membrane technology as a promising solution to overcome the problems related to water management including the removal of OWW from surface water has attracted many researchers (Bolto et al., 2020). Of concern, OWW itself can be classified as free oil ($>150\mu m$), dispersed oil ($20–150\mu m$), and emulsified oil ($<20\mu m$) (Tanudjaja et al., 2019). It is generally found that OWW in surface water easily interacts with various other impurities, surfactants and forms emulsified oil. Therefore, it is appropriate to use membranes as a separation technology, because of their small droplet ($<10\mu m$) separation capability.

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The selection of the right membrane for the emulsified oil filtration process is important to consider as the smaller pore size than the droplet is one of the main keys to the effectiveness of the separation. In addition to the pore size, chemical and thermal stability and mechanical strength also need to be considered (Hai et al., 2019; Hu et al., 2021; Li et al., 2018; Sun and Feng, 2017; Sun et al., 2020; Zhang et al., 2016). The membrane materials that are commonly synthesized are polysulfone (PS), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), and cellulose acetate (CA) (Padaki et al., 2015; Subasi and Cicek, 2017). In this research, PVDF-based membranes were selected for research and development. This is based on the resistance to chemical compounds and its stability in various operating pressures. Although PVDF membrane has many advantages, it has very hydrophobic properties (Liu et al., 2014). Therefore, PVDF membranes tend to have a higher risk of fouling (Zhao et al., 2013). Moreover, the formation of fouling on the membrane has a fatal effect on decreasing the separation efficiency, so the related issue is always a trend to be discussed (Li et al., 2019). Surface modification is one alternative to reduce membrane hydrophobicity (Tang et al., 2017). The formation of a hydration layer on the surface inhibits the formation of fouling due to the bonding of water with the hydrophilic surface.

Many efforts have been made to improve the properties of PVDF membranes, especially hydrophilicity and resistance to fouling. Almaie et al. have succeeded in reducing the hydrophilicity of PVDF membranes through modification of the active surface of the membrane (Almaie et al., 2022). Several selected studies related to OOW separation using PVDF membranes can be seen in Table 1.

Surface modification using polydopamine (PDA) has attracted much attention because of its strong adhesive properties with abundant functional moieties and excellent biocompatibility. This ability refers to self-polymerization which ensures the formation of bonds (Li et al., 2019). In addition, the nature of PDA which tends to be hydrophilic can prevent the formation of fouling due to organic compounds (McCloskey et al., 2010). However, the deposition of PDA is a time-consuming process, and the resulting hydrophilicity is barely satisfactory (Li et al., 2018; Wardani et al., 2019). PDA oligomers usually form rough surfaces and large aggregate particles because of the non-covalent interaction. Therefore, it is possibly lead to membrane fouling and reduce water permeability.

Polyethyleneimine or PEI could react with amine and catechol causing covalent bonds that lead to strong networks to improve coating stability. Apart from that, PEI is also known as an amine-rich cationic polymer (Zhao et al., 2015). Thus, PEI can combine with PDA through a Michael-addition and Schiff-base reaction mechanism. Therefore, the aggregate formed in solution will contain PDA and PEI, and both will be deposited together into the substrate simultaneously (Lv et al., 2018). The mechanism by which PEI occurs is believed to be able to react with oxidized dopamine and inhibit the interaction of hydrogen bonds and $\pi - \pi$ bonds. The same thing was also reported by Lv et al., who tested the kinetics of PEI/PDA coating on the surface of silicon wafers (Lv et al., 2018). Illustrations of the reaction and coating mechanisms can be seen in Figs. 1.d and 1.e. The addition of PEI significantly accelerated the deposition reaction process between PDA and PEI (Qiu et al., 2018). On the other hand, the addition of PEI also reduced particle size and hinder non-covalent interactions forming a homogenous and loose layer on a substrate during the polymerization process (Ding et al., 2020). PEI also increases the membrane surface wettability causing a more hydrophilic membrane.

In this research, it is hoped that a breakthrough will be obtained related to improving the properties of PVDF membranes through modifications using PDA-PEI. The scope of successful modification includes: hydrophobicity-hydrophilicity, permeability, rejection. The hope is to obtain hydrophilic PVDF membranes with high rejection and flux capabilities.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF) membrane was obtained from Microdyn-Nadir with a nominal pore size of 0.03μm. Dopamine-HCl, Polyethylenimine, and 20mM tris buffer saline were supplied from Sigma Aldrich. NaOH 0.1N was supplied from Emsure, the other chemicals were tween 20, oil, and acetone were used without any further modifications. Commercial palm oil has the following specifications: Density at $40°C = 0.916 \pm 0.005$ g/cm^3, Kinematic viscosity at $40°C = 35.7$ mm^2/s, pH at $25°C = 5.4$. All solutions were prepared by aquadest.

2.2. Coating PVDF membrane

PVDF membrane coating was carried out by immersing the membrane in various modifying solutions. First of all, before the modification process, membrane needs to be washed by soaking in acetone for 30 min. At the same time, PDA solution was prepared by dissolving

Table 1
Selected studies related to oily wastewater separation using PVDF membranes.

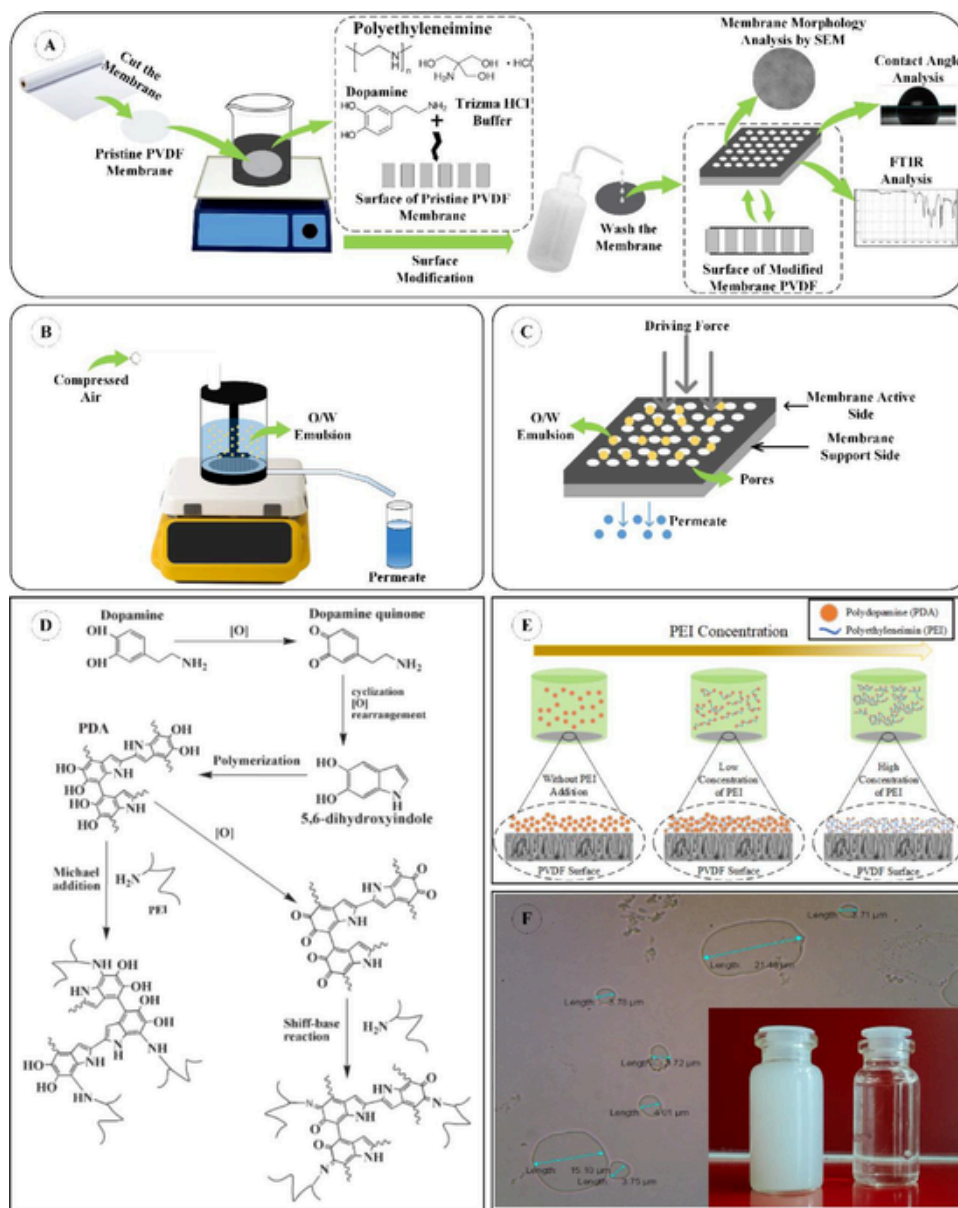| Materials	Synthesis and/or Modified Method	Results		Detail Properties Improvement	Ref
		Permeation Flux (L.m^{-2}.h^{-1})	Separation Efficiencies (%)		
PZGS–PVDF (0, 0.5, 1.0, and 1.5%PZGS)	Phase Immersion (PI)	5.7 – ±71	77.2 – 99.3	The addition of PZGS in the synthesis of PVDF is proven to be able to increase hydrophilicity, which is indicated by a decrease in the contact angle from 84.1° to 58.1° The stability of the membrane separation performance in the acid – neutral – base range was also obtained by the addition of the PZGS.	(Mansha et al., 2022)
PVDF–b–PVI Membrane	Atom transfer radical polymerization (ATRP)	181 ± 1.82 – 420.25 ± 0.96	81.2 ± 2.1 – 98.08 ± 0.5	The modification using [CuBr]:[DMDP] increased the hydrophilicity, which was marked by a decrease in the contact angle from 89.5° to 30.98° In addition, the modification was also successful in the formation of antifouling on the membrane surface.	(Valizadeh et al., 2022)
PVDF–b–P (PEGMA–co–BVIm–Br) membrane	Nonsolvent–induced phase separation (NIPS)	176 – 400	81.2 – 96.1	The successful modification reduced the hydrophobicity of the membrane, indicated by a decrease in the contact angle, which was originally 89.5° ± 1.96 to 33.8° ± 1.55. In addition, the modification also succeeded in increasing the stability of the flux and resistance to fouling.	(Valizadeh et al., 2021)
CCB–Fe/PPnp–PVDF	Phase Immersion (PI)	± 9 – ± 11	~ 99	The successful modification reduced the potential for fouling by reducing hydrophobicity (CA 81° ± 0.9 to 44° ± 1.7).	(Baig et al., 2022)
PVDF/PPAm–TA	Immersing	1184.3	99.47	Properties have improved, especially resistance to fouling, service life, hydrophobicity (135° – 158)	(Jiang et al., 2022)
PVDF/PDA-PEI	Immersing	This will be discussed later			This work

Fig. 1. Schematic illustration of (a) PVDF membrane modification, (b) Dead-end filtration, (c) Filtration process mechanism, (d) PDA–PEI copolymerization mechanism (Reproduced with permission from Zhao et al., 2015), (e) PEI concentration effect on copolymerization, (f) OWW droplet under a microscope.

dopamine – HCL with Trizma – HCL pH 8.5 for concentrations of 0.5, 1, 2, and 3g/L, respectively. Meanwhile, PDA – PEI solution was prepared by adding PDA solution with the addition PEI for each concentration. PEI concentrations were varied at 0.5, 1, 2, and 3g/L at a PDA concentration of 3g/L. For information, acidity control was carried out by adding 0.1N NaOH to the Trizma - HCL solution preparation with a pH of 8.5.

Next, the membrane was immersed in each variation of the PDA and PDA-PEI solutions for 6, 16, and 24 h. Immersion was carried out on a shaker at a speed of 60rpm to homogenize the PDA and PDA-PEI solutions. After the immersion was completed, the membrane was washed and rinsed using distilled water to remove the remaining PDA and PDA-PEI particles that were not tightly bounded. The membrane was then dried for 24 h. Drying is intended to remove residual water from the washing process. As a note, PVDF membrane modification was conducted by immersing the membrane inside PDA-PEI solution. Hence, the possibility of PDA-PEI coverage of both sides of PVDF membrane was clearly possible. In addition, the membranes were applied to treat oily wastewater where high degree of hydrophilicity of membrane is re-

quired and the increase of hydrophilicity on both sides of the membranes actually help to improve the flux and rejection of the membranes.

Functional groups on the membrane were characterized using Fourier Transform Infrared (FTIR) [Shimadzu, IRTracer – 100] at a wavelength range of 500 – 4500 cm^{-1}. The morphological structure of the membrane surface was characterized using Scanning Electron Microscopy (SEM) [Zeiss, EVO MA10]. The hydrophilicity of the membrane was analyzed using contact angle [DataPhysics Instruments, OCA25]. The membrane modification procedure can be seen in Fig 1.a.

2.3. Filtration performance using dead-end modules

The membrane filtration performance was tested using an oil-in-water emulsion (simulated oily wastewater) sample with a concentration of 5000ppm. Samples were prepared by dissolving 0.5g of palm oil in 100mL of water and adding 0.5% Tween 20 as an emulsifier. Homogenization (IKA, T25 digital ULTRA-TURRAX®) was carried

out at room temperature ±20°C for 5 min (15,000rpm). OWW droplets under a microscope (Olympus Microscope, CX21LED) can be observed in Fig 1.f. The droplet images were taken 6 times, which can be seen in Fig S1. The average droplet diameter from various points of collection is around $8.88 \pm 8.066\mu m$. In appearance, the OWW is cloudy white (left) and the permeate is clear (right) (see Fig 1.f). The emulsion stability test was carried out for 60 min and it was found that the emulsion did not experience coalescence.

This dead-end configured filtration module has an active area of 38.5 cm². During the process, the thrust is supplied from the compressed gas pressure, which is controlled and measured every time. Before measuring the performance, each membrane was first tested using 100mL aquadest, and the water flux was measured. Data collection related to water flux was carried out for 30 min. After that, the performance test was carried out by adding 100mL of water-oil emulsion and calculating the flux every 10 min for 60 min.

Rejection measurements were carried out every 10 min by measuring the concentration of permeate. The measured concentration is compared with the initial concentration to obtain the percentage of rejection. As a marker, each performance measurement was carried out at room temperature (±20 °C).

Water flux was measured and calculated by the following equation:

$$J_w = \frac{V_w}{A \cdot t \cdot P}$$

where V_w, t, A, P are volume permeate (L), time (h), active membrane area (m²), and pressure (bar), respectively. Meanwhile, the rejection measurement and calculation followed the following equation:

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

where, C_p and C_f are the permeate concentration (ppm) and the initial feed concentration (ppm), respectively. The procedure for testing the performance of the membrane, and the mechanism for separating the OWW, are shown in Fig 1.b and Fig. 1.c, respectively.

3. Results and discussion

3.1. Membrane characterization with fourier transform infrared (FTIR)

Characterization related to the chemical composition on the surface of the PVDF membrane was carried out using FTIR. In brief, several functional groups that mark the presence of PDA-PEI, including N—H, C—O, C—N, and O—H. These functional groups tend to be hy-drophilic, in which case the H atoms form better hydrogen bonds with water. Thus, water passes through the membrane more easily than oil. Based on the literature, the success of membrane modification using PDA is most evident with -OH and -NH bonds. This bond indicates the attachment of the amine group specifically to the membrane substrate (Li et al., 2022). The results of the characterization in Fig. 2 indicate a change in chemical composition after the PDA coating process. The formation of N—H/O—H bonds gives a stretching vibration response in the absorption wavelength range of 3000 to 3600 cm⁻¹. The presence of these bonds forms stretching vibrations on the C=C aromatic ring and gives a detectable response at 1500 to 1650 cm⁻¹. However, the existence of this bond is quite difficult to observe in this research. This occurs because the peak formed by the bending-shearing N—H vibration at 1600 cm⁻¹ coincides with the peak caused by the C=C bond. Additional evidence for the success of the coating is indicated in the characterization results showing the presence of O—H, C—N and C—O groups found at 1170, 1275, and 1401 cm⁻¹, respectively.

The addition of PEI in the PVDF membrane coating process using PDA is expected to provide changes in surface properties indicated in the FTIR characterization.

The FTIR response from the addition of PEI showed that the C=N bond that should have formed in the 1560 cm⁻¹ range was not visible. However, another response from the addition of PEI was observed that the FTIR response to N—H and O—H bonds tended to be weak. This indicates that the formation of agglomerates on the membrane surface also decreased. In other words, the addition of PEI was successful in preventing the formation of agglomerates.

3.2. Membrane surface morphology using scanning electron microscopy (SEM)

The surface morphology of the membrane using SEM indicated changes due to PDA and PDA-PEI coating. As observed in Fig. 3 (a – h), the surface of the pure membrane is smooth and uniform. PDA and PDA-PEI coating showed changes in the characteristics of the membrane from being smooth to rough and not uniform. The membrane roughness increased with the increase in the amount of DPA agglomerate deposition. Observations on PDA-modified PVDF membranes showed that the coating time affected the roughness of the membrane, this was also observed on PDA-PEI hybrid membranes. The interaction of non-covalent bonds results in an increase in the number of aggregates during deposition, which is accompanied by a rougher surface morphology of the membrane. The amount of aggregate covering the pores on the membrane surface that is affected by the amount of PDA on the surface can be observed in the modified PVDF membrane morphology with 0.5g/L compared to 3g/L.
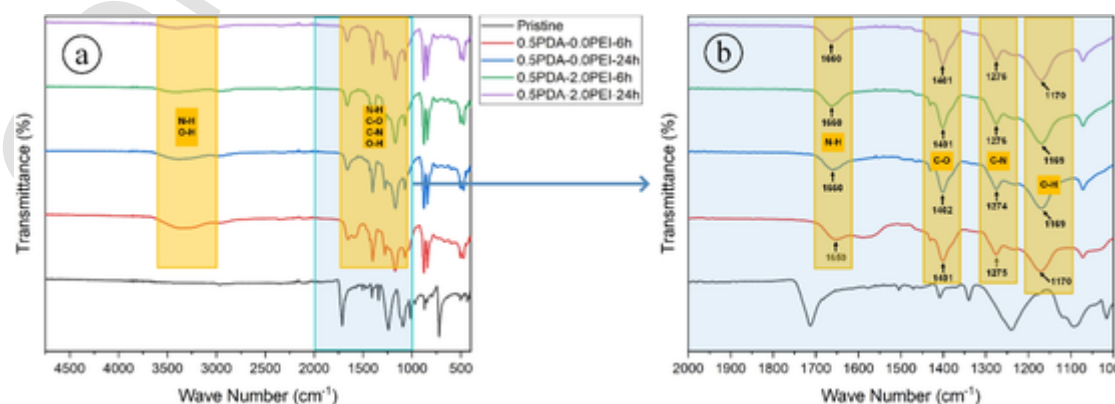

Fig. 2. FTIR spectra of PVDF membrane: Pristine and PDA – PEI hybrid modified. (a) Wave Number 500 – 4500 cm⁻¹, (b) Magnification for wave number 1000 – 2000 cm⁻¹.
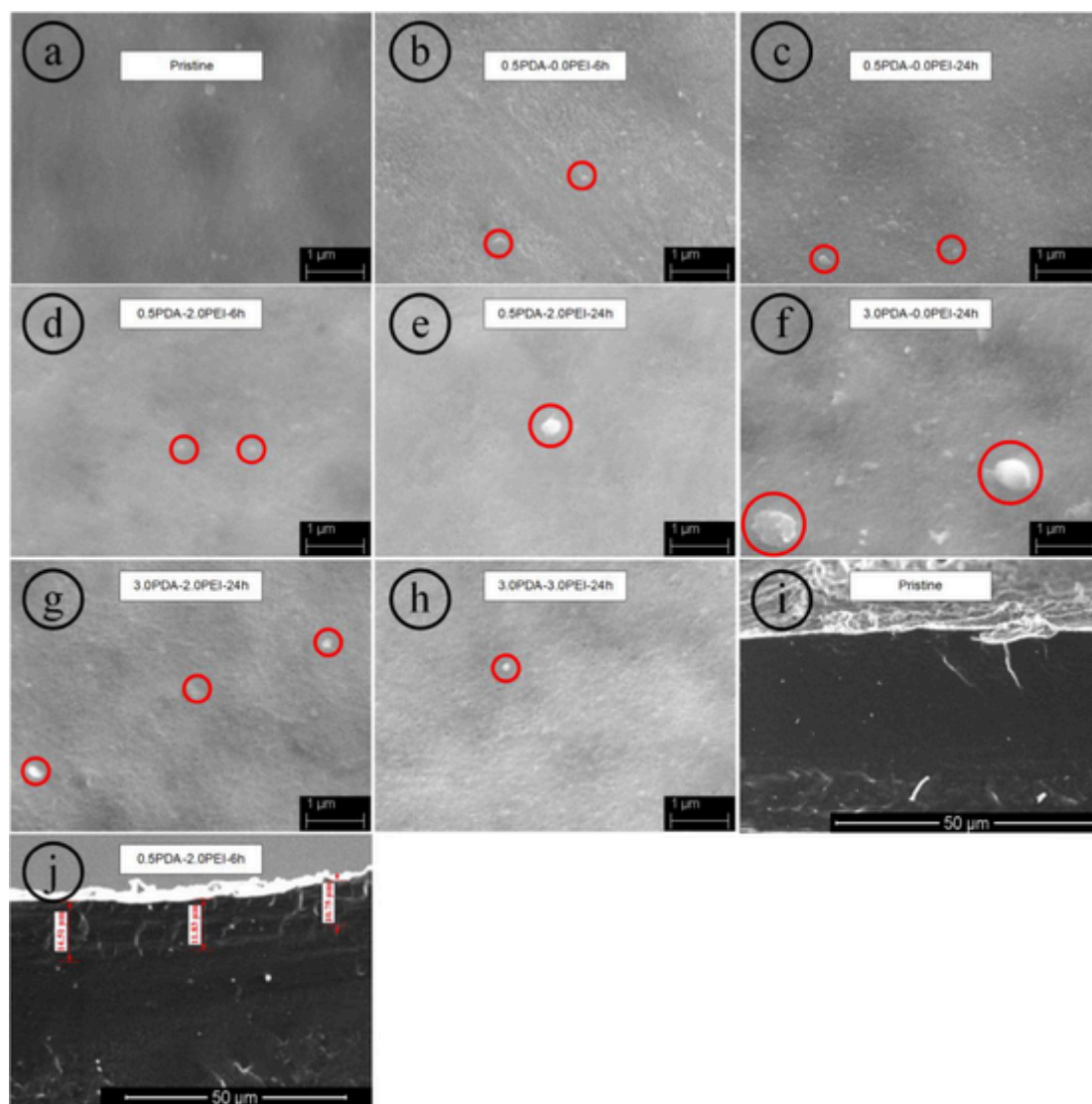
Fig. 3. Morphology of various membranes using SEM; a – h (20,000x magnification): surface, i – j (1,200x magnification): cross section.

On the other hand, the addition of PEI made the membrane smoother due to the destruction of non-covalent bonds in the PDA aggregates. The impact of the addition of PEI was observed on the PDA-PEI hybrid membrane, both at 0.5g/L and 3g/L PDA. The addition of 2g/L PEI stabilized the polymerization process, and the agglomerates on the membrane surface were minimized. PEI concentration also affects the polymerization process, this can be observed in PDA-PEI hybrid membranes with 2g/l and 3g/L PEI. It shows that with the addition of PEI the membrane is smoother. This proves that the greater the PEI concentration, the smoother the membrane surface because the destruction of non-covalent bonds in PDA aggregates is a lot. Research conducted by Wang et al. and Lv et al. both found that the addition of PEI played a role in stabilizing PDA polymerization. The indication appears on the surface of the membrane as a result of their SEM characterization (Lv et al., 2015; Wang et al., 2017). Apart from the membrane roughness, the coating thickness of the membrane was also measured by means of SEM. In Fig. 3 (i – j) it is observed the comparison between the thickness of the membrane before and after modification with a change of around $12.36 \pm 1.94\mu m$.

3.3. Contact angle test (CA)

The nature of the membrane surface related to the contact angle is one of the focuses and indicators of the successfulness of membrane modification. In line with this, coating using PDA-PEI resulted in a decrease in the contact angle, or in other words, the membrane tends to be more hydrophilic. The presence of PDA gives a hydrophilic shade because the functional groups are amine, imine, and catechol. Interestingly, the presence of a PEI layer on the membrane surface contributed to the decrease in the contact angle due to the amino groups (Yang et al., 2014). The experimental data of membrane's contact angles in this study is presented in Fig 4

Pristine PVDF membrane has a contact angle of 88.1°, which indicates its high hydrophobicity. The presence of functional groups obtained from PDA coating showed a decrease in contact angle, which has proved by the 0.5g/L coatings that succeeded in reducing the contact angle to 77.7° with a coating time of 6 h. The decrease in contact angle with respect to coating time can also be observed when 24 h of processing has obtained a decrease to 75.2° In addition, the amount of mass of the superimposed PDA also gives a finite contact angle reduction, which indicates the presence of functional groups that play an important role in changing the surface properties of the membrane. The results showed that coating using 3g/L succeeded in reducing the contact
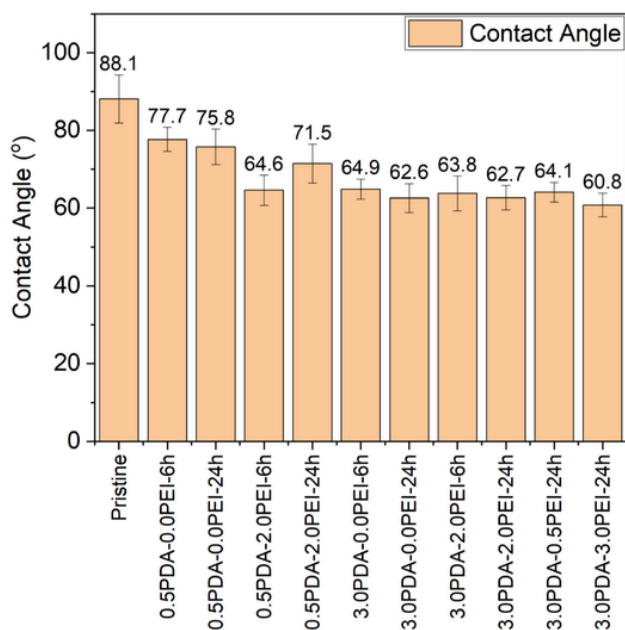
Fig. 4. Contact Angle on Modified PDA, PDA-PEI, and Pristine PVDF Membranes.

angle up to 64.9° for 6 h of coating time, while for 24 h of coating it decreased to 62.6° These results indicate the amount of PDA mass for coating is more dominant than the coating time.

The presence of PEI as a stabilizer of PDA polymerization has an effect due to the presence of functional groups, in addition to reducing the possibility of agglomeration formation. It appears that the addition of 2g/L PEI to a fix of 0.5g/L PDA resulted in a decrease in the contact angle to 71.5°, which was originally 75.8° for a 24-hour immersion time. However, this trend of adding PEI as a stabilizer needs to be reviewed at different PDA concentrations, the addition of various PEIs to the 3g PDA fixation did not give similar results. At first, the immersion with 3g/L of PDA without adding PEI was originally 62.6°, and the addition of 2g/L of PEI actually increased to 62.7° Also, the addition of 0.5g/L PEI actually resulted in a small increase in membrane's contact angle. As a reason, the rate of polymerization that occurs at a fairly high PDA concentration cannot be fully controlled by the addition of PEI. In particular, this phenomenon is supported by variations in PEI at a concentration of 3g/l PDA.

The best decrease in contact angle at the fixation concentration of PDA 3g/L was observed in the combination of PEI 3g/L with a contact angle of 60.8° The exposure indicates that combined PDA-PEI concentrations should be considered to provide the intended results. This refers to the consideration of PEI's ability as a stabilizer which is expected to control the polymerization rate and inhibit the emergence of agglomeration.

3.4. Dead-end system membrane performance test

Various criteria related to membrane performance are also indicators of the success of modified membranes. In this study, the membrane performance was evaluated through the value of flux and rejection. Often, these two things contradict each other and are inseparable due to various factors. As previously discussed, surface properties such as hydrophobicity and size play an important role in the resulting performance. Meanwhile, membrane modification is expected not to affect these properties but to prevent membrane fouling. Observations on various membrane coating times using 0.5g/L PDA have been carried out. The results prove that the formation of a PDA layer on the surface of the membrane is able to prevent fouling, this can be observed in Fig 5.a. In general, the longer coating time results in the formation of agglomerates. The presence of this aggregate actually results in the formation of blocking on the membrane which results in a lower flux initially, but on the other hand, the flux stability is more guaranteed. When related to the rejection value, the presence of PDA on the membrane surface increases the achievable rejection. The rejection is found in Fig 5.b, a pristine membrane, which initially had 86% rejection, increased with an achievement range of 96–98%. This finding provides valuable information which states that the addition of 0.5g/L PDA resulted in better membrane's performance compared to membrane without PDA addition.

Apart from rejection, the permeate flux also indicates an increase in the stability of the OWW separation (see Fig. 5.a). In the membrane without PDA modification, it was shown that the flux tended to decrease suddenly at sometime early in the filtration process and tended to be stable at some time afterward. Different things were shown due to the addition of PDA, in which the flux decreased gradually. This phenomenon indicates the presence of PDA helps membrane stability against fouling due to oily water. Meanwhile, the decrease in rejection and flux with increasing polymerization time is indicated by the ongoing polymerization and the tendency to form aggregates in the process.
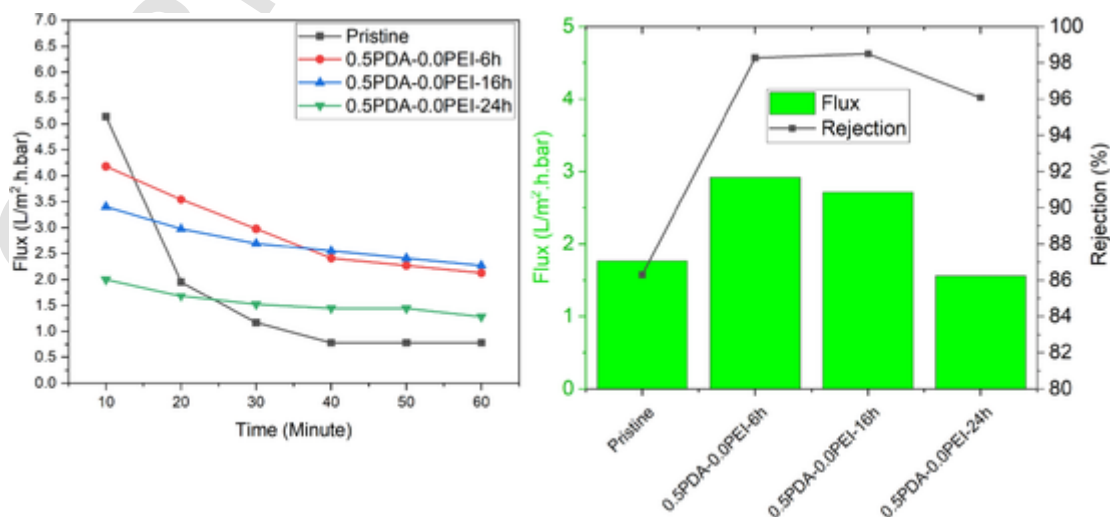

Fig. 5. PDA-modified PVDF membrane water flux (a) and rejection capability (b) at various coating times.
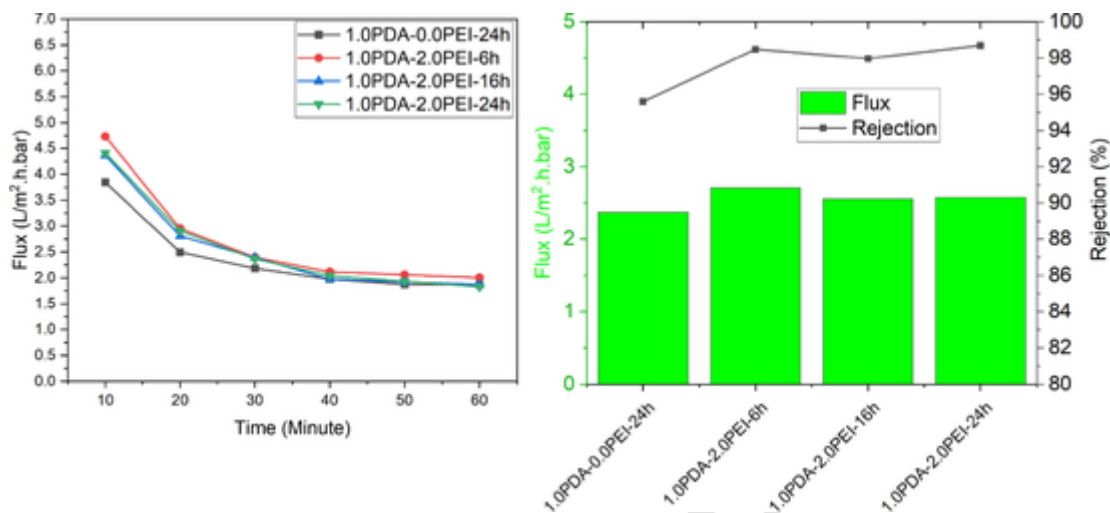
Fig. 7. PDA-PEI modified PVDF membrane water flux (a) and rejection capability (b) at various PEI concentrations when concentration PDA constant at 1 g/L.

Observations on the effect of PDA concentration need to be carried out to measure its effect on the initial coating. A coating time of 24 h was chosen, in which the most agglomerates were formed on the membrane surface compared to 6 and 16 h. As shown in Fig 6.a, the flux tends to be stable at increasing PDA concentration. This indicates that the presence of PDA is beneficial for flux stability. However, this finding was not supported by the rejection trends which in fact decreased with the presence of more PDA at the beginning of the coating as shown in Fig 6.b. Apart from that, the indication of excessive PDA concentration encourages polymerization that is too fast, and the growth of aggregates becomes unavoidable.

Consideration of adding polymerization stabilizer becomes an attractive option. In this research, PEI was added to prevent the formation of agglomerates in PDA polymerization. The SEM images on Fig. 3f-h with various PEI concentrations indicated the decrease in PDA aggregate formation. This decrease in aggregate formation should alter the membrane performance during separation. From Fig. 7a and b the addition of PEI could increase the initial flux and also oil rejection capacities of the membranes. The formation of PDA aggregates should be avoided because aggregates might plug the support's pores and also alter the rejection efficiency of the membrane (Lv et al., 2018). It was previously mentioned that a concentration of 1g/L PDA gives the best condition in terms of flux and rejection. Thus, the effect of coating time on

certain PDA-PEI concentrations was carried out first. In this observation using 2g/L PEI, the attached flux shows that increasing coating time does not always result in a decrease in flux. This indicates that the existing PDA-PEI interaction has already experienced saturation at 16 and 24 h. Rejection as another review showed the same thing, the addition of time did not increase the rejection. The two performance parameters are presented in Fig 7.a and 7.b. In addition, the role of PEI as a stabilizer is also insignificant at a concentration of 1g/L PDA. This is indicated by the more controlled polymerization of dopamine compared to high concentrations. Moreover, the excess PEI will form aggregates, which are highly water soluble and free to move.

The results of the comparison related to the coating time of PDA-PEI show that the trend towards the stability of the fusion has been achieved. However, further investigation of the ability of PEI as a stabilizer for various concentrations of PDA still needs to be conducted. Reflecting on the previous values, the variation starts from 0.5g/L PDA and ends with 3g/L PDA. As shown in Fig 8.a, 0.5g/L PDA gave the best initial flux, but up to 60min, the filtration time trended downward. On the other hand, at 1 and 2g/L PDA, the flux was initially lower, but at 60 min the filtration seemed to have stabilized. Nonetheless, 0.5g/L PDA remains a leading candidate in this process. This is inseparable from the trend that allows achieving stability in the near future. Rejection was achieved up to 98% with the lowest value for 3g/L PDA. It is
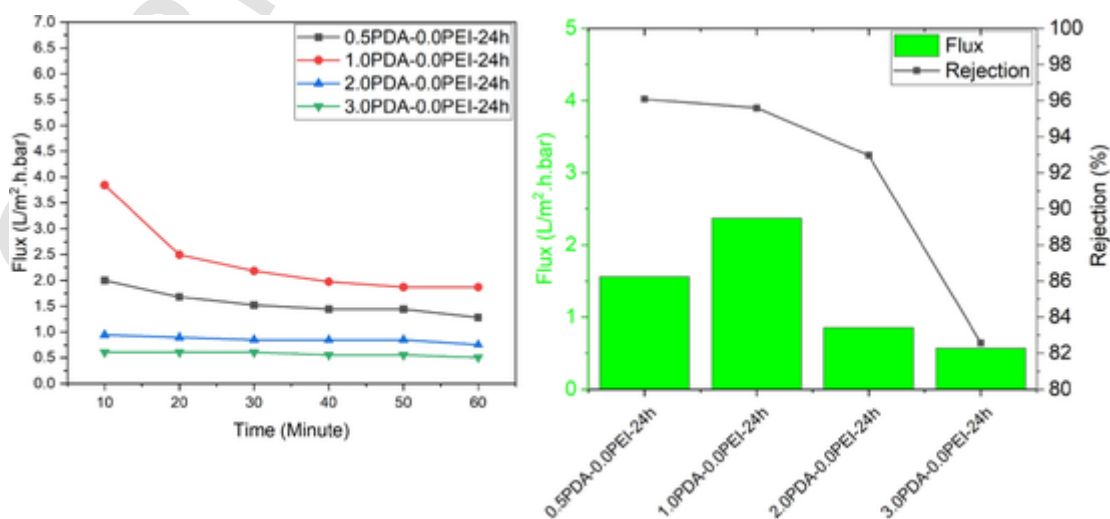

Fig. 6. PDA-modified PVDF membrane water flux (a) and rejection capability (b) at various PDA concentrations when coating time fixed at 24 h.
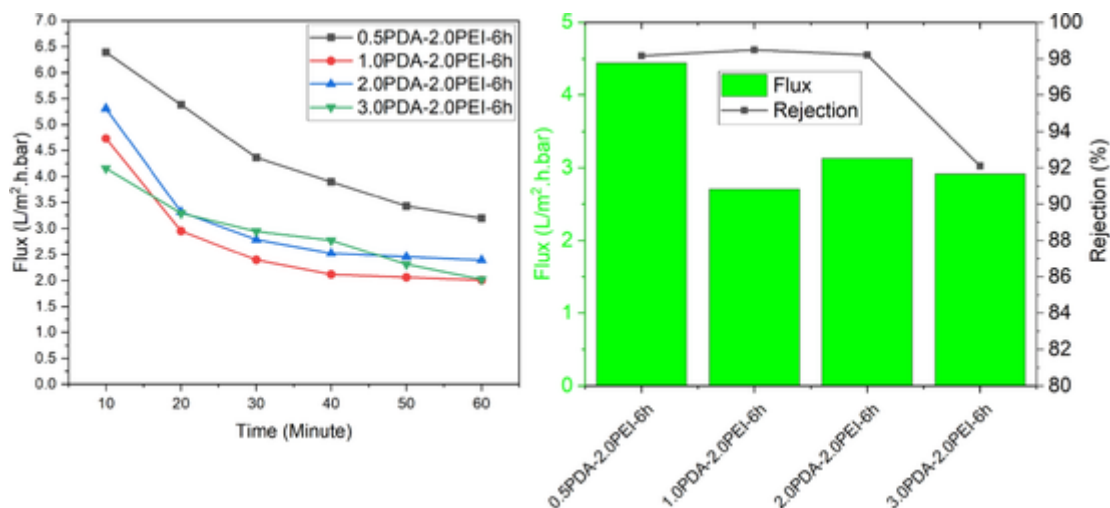
Fig. 8. PDA-PEI modified PVDF membrane water flux (a) and rejection capability (b) at various PDA concentration when concentration PEI constant at 2 mol.

possible that the PDA concentration is too high and it binds to PEI more dominantly before it sticks to the surface of the membrane which results in a less than optimal coating process.

4. Conclusion

In summary, it is shown that the addition of PDA-PEI as a PVDF membrane modifying agent has a measurable physical effect. Among them, the surface properties in the form of hydrophilicity which has increased markedly by a decreased contact angle (88.1° to 64.6° for 0.5g/L PDA - 2g/L PEI for 6 h copolymerization), and membrane roughness which also increased was observed through SEM. FTIR supports the fact that PDA-PEI has successfully coated the surface of PVDF membranes. Meanwhile, the measured filtration performance in flux stability and rejection showed satisfactory results. In general, the modification of the membrane is capable of rejecting more than 90% of the OWW, with increased stability against fouling. Based on various reviews, it is concluded that 0.5g/L PDA - 2g/L PEI for 6 h is the best blend with an average flux around $\pm 4.4 \text{L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ and 98% rejection.

CRediT authorship contribution statement

Putu Doddy Sutrisna : Conceptualization, Methodology, Resources, Supervision, Writing – review & editing, Project administration, Funding acquisition. **Pra Cipta Buana W. Mustika :** Writing – original draft, Software, Formal analysis. **Ronaldo Pangestu Hadi :** Writing – review & editing, Formal analysis. **Caren :** Investigation, Formal analysis, Writing – review & editing. **Yosia Elenio Gani :** Investigation, Formal analysis, Writing – review & editing.

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at https://doi.org/10.1016/j.sajce.2023.01.006.

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