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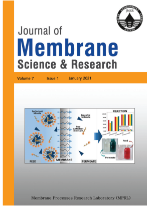

Research Paper

Performance Evaluation of PES-ZnO Nanohybrid using a Combination of UV Irradiation and Cross-linking for Wastewater Treatment of the Rubber Industry to Clean Water

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Keywords

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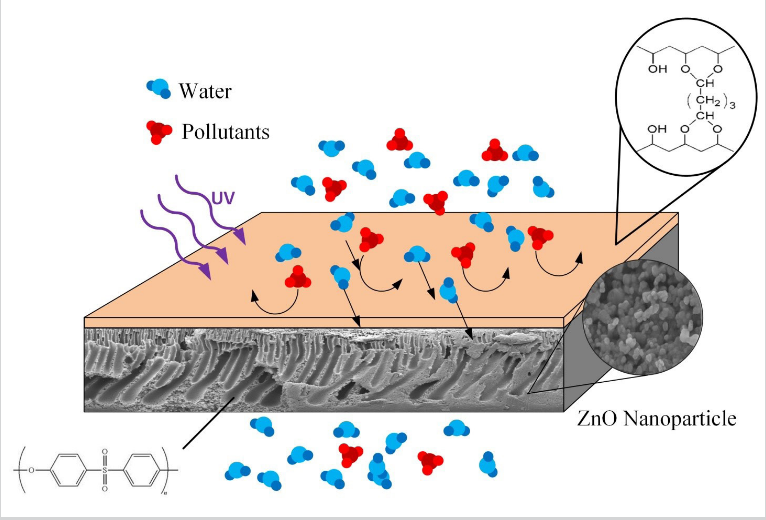
Highlights

- Multi-steps membrane modification was performed for rubber wastewater treatment
- UV irradiation and PVA coating synergistically enhanced pollutants rejection
- Modified membranes exhibited better antifouling behaviour than pristine PES membrane

Graphical abstract



Abstract

Polyethersulfone (PES) membrane can be easily fouled during wastewater treatment as it is slightly hydrophobic. Consequently, several modifications are required to improve membrane surface properties to avoid membrane fouling. UV irradiation and cross-linked polyvinyl alcohol coating on nanohybrid membranes were performed in this study, and PES was combined with ZnO nanoparticles as an inorganic additive. Also, the PES-ZnO nanohybrid membrane was treated under the UV irradiation for a specific exposure time followed with membrane coating using polyvinyl alcohol (PVA) by the dip-coating method. Then, rubber wastewater filtration tests were performed using a cross-flow filtration system. The results revealed that the modifications significantly improved permeability and selectivity. As the duration of the UV irradiation increased, the higher mean flux value increased up to 14.55 $L.m^{-2}.h^{-1}$, but it was sacrificing the rejection efficiency. While the PVA coating decreased the water permeability up to 10.5 $L.m^{-2}.h^{-1}$ and increased the PVA concentration, the contaminant rejection increased up to 82%. The best membrane composition based on this study consisted of 17 wt.% of PES, 1 wt.% of ZnO nanoparticles, 5 wt.% Polyethylene glycol (PEG), 2 minutes UV irradiation, and 3% PVA coating.

1. Introduction

The rubber industry significantly contributes to the human life, while 70–80% of raw rubber is produced in the world, primarily from Thailand, Indonesia, and Malaysia [1]. However, the high production of natural rubber is followed by the large amount of contaminated wastewater discharge. Usually, the waste produced consists of water from the rubber washing process containing latex and noncoagulated serum in small quantities such as protein, carbohydrates, lipids, carotenoids, and salt [2]. Ascending the rubber industry must employ cleaner production technologies, waste minimisation, waste utilisation, resource recovery, and water recycling. The waste treatment may include several methods such as coagulation and adsorption, electrochemical methods, anaerobic, aerobic pond, physicochemical and ozonation processes [3].

In particular, the process of membrane-based separation has become an attractive alternative instead of conventional methods in wastewater treatment. The use of membrane technology has high efficiency, low cost, lack of secondary pollution, excellent thermal properties, high mechanical properties and high chemical stability [4]. In addition, the corresponding membrane technology is widely used in water treatment with various types of membranes such as polysulfone membranes (PSf) [5], cellulose membranes (CA) [6], polyvinylidene fluoride (PVDF), and polyethersulfone (PES) [7].

Furthermore, PES is a high performance amorphous polymer which is usually used in membrane-based water treatment. PES membranes show

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chemical stability, excellent thermal properties, exceptional hydrolysis, and excellent mechanical strength [8]. PES has semi-hydrophonic nature which makes the membrane easily to be fouled during filtration process. The fouling phenomenon in membrane is related to polymer type, surface morphology, pore structure, surface property, and hydrophilicity/hydrophobicity property, and many studies examining fouling reduction in membrane PES have been reported in the literature using a variety of additives to improve the stability of PES for a long time and in industrial applications [9]. Polymer-based layers can be mixed with inorganic particles such as (Carbon nanotubes) CNTs, Ag-NP, TiO_2, ZnO, Al_2O_3, and ZnO_2, and the inorganic compounds improve the chemical and physical properties of the membrane [10]. Films with inorganic particle content can develop antibacterial, photocatalyst, absorptive, and mechanical properties [11], and this condition can be achieved by combining the polymeric membrane with ZnO and SiO_2 nanoparticles [12,13]. However, the utilization of inorganic compounds into polymeric membranes causes the formation of microvoids between the surfaces of inorganic compounds and PES polymeric chains, causing a decrease in membrane selectivity [14]. This problem needs a modification of membrane properties.

Polyvinyl alcohol (PVA) is a very hydrophilic polymer that has excellent mechanical strength and thermal stability [15]. This polymer is usually employed as a modifier polymer in membrane fabrication. The surface modification using PVA was reported to be able to increase the resistance to bio-fouling [16]. Furthermore, there are three approaches in PES membrane modification: (1) bulk modification, (2) blending with other hydrophilic polymer, and (3) surface modification via grafting, coating, irradiation, etc. Surface modifications such as plasma treatment, plasma-induced grafting, UV irradiation, and coating with hydrophilic materials have also been reported [17]. Development of antifouling behavior of the membrane can be achieved by modifying the hydrophilic membrane surface [18]. In addition, modification of membranes using UV irradiation increases the flux value but decreases the rejection value, while using PVA can increase the rejection value [19].

Recently, Rahimpour et al. [20] reported that modification of the PES UF membrane through immersion precipitation by TiO_2 nanoparticles and UV irradiation significantly improves their performances. However, the previous membrane showed a lower reduction in flux than neat PES membranes. Finally, PES-nanoTiO_2 membranes are modified with UV irradiation. The results of the experiment indicated that coating TiO_2 on the membrane surface is a superior technique for modifying PES membranes to minimize membrane contamination. Ma et al. [21] superimposed the PES membrane active surface with polyvinyl alcohol (PVA) as a polymer coating agent followed by the PVA crosslinking to increase the membrane anti-fouling property. As mentioned in the previous studies, the utilization of PVA as membrane coating agent effectively enhanced the anti-fouling behavior of PES-based membranes.

Because previous research only used a single modification technique, in the present study was focused on a combination modification treatments of UV irradiation and crosslinked PVA coating on PES nanohybrid membrane surface. The mixture is expected to be able to increase the performances in terms of permeability and pollutant rejections in rubber wastewater treatment. It is expected that the combined modification treatments of UV irradiation and PVA coating could produce membranes with higher performances.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES) Veradel® PESU 3100P was purchased from Solvay Advanced Material, USA, and was used as the membrane material in this study. *N*-methyl-2-pyrrolidine (NMP), as the solvent, and Polyethylene glycol (PEG), 12 kDa, were both purchased from Merck, Germany. The ZnO nanoparticles powder was supplied from Nano Center Indonesia, Indonesia (average particle size: 341.7 nm). PVA was obtained from Brataco Chemica, Indonesia. The original rubber wastewater was taken from raw rubber processing industry PTPN VII, Bengkulu, Indonesia. The characteristics of the liquid waste samples from PTPN VII BENGKULU are presented in Table 1, and the parameters of wastewater were analyzed in the laboratory.

2.2. Membrane preparation

Both unmodified and modified nanohybrid membrane were fabricated via dry phase inversion followed by wet phase inversion [22]. For bare PES membrane, an appropriate amount of PES was dissolved in NMP. The mixture was stirred for 12 h until a homogenous solution was acquired and the solution was degassed. The polymer solution was then cast onto a clean glass plate with outlet gap of 150 µm and subsequently soaked into a non-solvent (demineralized water) after 60 s dry phase inversion. The preparation for PES-ZnO nanohybrid membrane were first prepared by mixing the ZnO nanoparticles (0.1; 0.5; 1.0 wt.%) with NMP solvents. The ultrasound process was then carried out on the nanoparticle suspension for 3 hours to avoid nanoparticle aggregation [7]. The nanoparticles suspension was then mixed with polymer solution containing 17 wt-% PES in NMP solvent. The dope solution was constant stirred for 12 h to obtain homogeneous and stable polymer solution and then the solution was degassed under vacuum condition.

The polymer solution was cast and coagulated via non-solvent induced at ambient temperature (26 ± 2°C). When the membranes have separated completely, the membranes were immersed into another water bath for 24 h to release all water-soluble component in membrane [22]. After immersion in demineralized water, the excess water on the membrane surface was cleaned, the membrane was let to dry under ambient temperature for 24 h. After obtaining the best membrane with a specific concentration of ZnO nanoparticles based on the performance evaluation, the membrane composition was then used to evaluate the effect of PEG as additive with concentrations of 2, 3, 5 wt.% mixed into the doped solution. The selection of PEG concentration variation was based on the previous study [14]. The membranes properties were characterized and their performance were evaluated based on the permeate flux and pollutant removal efficiency in rubber wastewater filtration process.

2.3. UV Irradiation and PVA coating procedures

UV irradiation was carried out before phase separation process. The casted polymer solution on glass plate was subjected under UV lamp type C (254 nm, 10 watts) for 30, 60, and 120 s to modify the membrane surfaces. Membrane coagulation processes to obtain a dry membrane were conducted the same way as the method in the previous section. The coating solution was made by dissolving an appropriate amount of PVA (1, 2, and 3 wt.%) in demineralized water at 90°C. The nanohybrid PES-ZnO membrane was dip-coated using PVA solution [23], the excess PVA solution was removed. The coated membrane was dried at 60°C for an hour. Crosslinking of PVA with glutaraldehyde was carried out to avoid membrane swelling. The PVA coated membrane was soaked in crosslinking solution containing glutaraldehyde 1.84 wt.% and sulfuric acid 5 wt-% as catalyst. The immersion was left for 1 h at 40°C to let the crosslinking reaction occur. The coated membrane was then dried under ambient condition for 24 h. The modified membranes were characterized and evaluated for their properties and performances.

2.4. Membrane characterization

2.4.1. Membrane porosity measurement

The porosity of the membrane was determined by soaking the membrane in deionized water 24 hours in a specific size of the membrane sample (5 cm x 5 cm). Furthermore, the wet membrane sheet was wiped using filter paper and then weighed as wet membrane weight. The membrane drying was performed at 60°C in vacuum condition for 24 h. The dry membranes were stored in desiccator for 1 h before being weighed [24]. The estimated membrane porosity was calculated using Eq. 1:

$$\varepsilon = \frac{w_i - w_0}{\rho_w \times A \times \delta} \times 100\% \tag{1}$$

where wt_0, and w_t are the masses of wet and dry membranes, respectively (g), ε is the membrane porosity, A is the membrane surface area (cm^2), δ is the membrane thickness (cm), and ρ_w is the density of pure water (g/cm3) [14].

Table 1
Characterisation of feed rubber wastewater from PTPN VII before filtration

Parameters	Value
Biochemical oxygen demand (BOD), mg/L	85
Chemical oxygen demand (COD), mg/L	262
Total dissolved solid (TDS), mg/L	208
Ammonia total, mg/L	25.6
pH	5.24

2.4.2. Water contact angle measurement

The static water contact-angle on the membrane surface was a common method to evaluate the hydrophilicity property of membranes. The contact angle was performed using sessile-drop method and the droplet angles were measured using an anglemeter (RACE anglemeter, Japan).The distilled water with a temperature of 25°C was used as a probe liquid. The water contact angle was measured from both the right and left sides [25].

2.4.3. Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM)

SEM analysis was performed to investigate the membrane morphologies. In SEM analysis, a narrow electron beam was scanned on the membrane surface and deep inside [26]. A small piece membrane sample was soaked in liquid N2 to make the membrane becomes brittle. The membrane was the immediately fractured using tweezer to avoid structural damage. Then, the membranes were sputter-coated with gold to avoid the effect of electrostatic charging for SEM examination. The membrane surface and cross-section were observed under SEM (Merk FEI, Type: Inspect-S50) at specific magnification. FT-IR was used to investigate the change in the chemical structures of membranes. The FT-IR spectra of fabricated membranes were recorded using the FT-IR device (Spectrum 100-Perkin Elmer). The FT-IR spectra of the tested membranes were recorded from 4000 until 400 cm^{-1} wavenumbers.

2.4.4. Antifouling property

The antifouling properties were characterized by recording a continuous decrease in flux. The tested membrane was applied for pure water permeation to obtain pure water flux (J_0). The membrane with the same formula was used to filter rubber wastewater to obtain treated water flux (J_1). The filtration experiment was performed under 5 bar trans-membrane pressure for 150 min with the permeate collection was conducted every 30 min. The flux decrease ratio was calculated using the Eq. (2):

$$M\% = \frac{J_0 - J_1}{J_0} \times 100\% \tag{2}$$

2.5. Membrane performance

The performance of the membranes were evaluated for their permeate water flux and contaminant rejection rate. The rejection performance was studied thorugh the measurement of the TDS, pH, COD, BOD, and $N\text{-}NH_3$ in both feed and permeate water. The membrane filtration test were conducted in a cross-flow filtration system as shown in Figure 1. The membrane sample with a surface area of 12.57 cm^2 were used for filtration test. The filtration experiment was operated under 6 bar trans-membrane pressure for 2.5 h and the permeate water was collected periodically. The permeate water flux and pollutants rejection were calculated using Eqs. (3) and (4) [6].

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

where J_W is permeate water flux ($L.m^{-2}h^{-1}$), V is the volume of collected permeate (L), A is the effective area of the membrane (m^2), and t is the operating time interval (h). The rejection performance of the membranes was evaluated based on the removal efficiencies for contaminant constituents in rubber wastewater.

$$R = \left(1 - \frac{C_P}{C_f}\right) \times 100\% \tag{4}$$

where C_p (mg/L) and C_f (mg/L) are the solute concentrations in the permeate and feed, respectively.

3. Results and discussion

3.1. Morphologic analysis of PES-ZnO nanohybrid membrane

Membrane morphology characterization using SEM is necessary to be performed because it provides the visual information of the surface and cross-sectional structure of membranes that are related with perm-selectivity behavior. Figure 2A illustrates the surface of the 17% PES membrane. Figure 2B is a cross-sectional image of a 17% PES membrane with 1% ZnO, 5% PEG, and has been modified by irradiation of UV as well as the coating with 3% PVA. The surface of bare PES membrane is smoother and denser than the membrane with ZnO nanoparticles loading, PEG addition, and UV irradiation (Figure 2C) at a magnification of 10,000x. Cross-section SEM image of UV irradiated and PVA coated nanohybrid membrane is presented in Figure 2B. A thin and dense layer on the top surface of the membrane was considered as PVA layer while the intermediate layer was typical finger-like micro-voids as supporting structure. These results may be related to membrane permeability and selectivity, which may increase the rejection ability, and the density of the surface may reduce the flux value. Hydrophilicity and cross-linking occur with the addition of PVA, which reduces the accumulation of impurities on the membrane surface.

Many white spots in Figure 2C are observed which are considered as ZnO nanoparticles. The nano particle clumps on the membrane surface is an agglomerate of the nanoparticles as the effect of PEG presence that attracted the ZnO nanoparticles. Compared with bare PES membrane surface (Figure 2A), the nanohybrid membrane exhibits more visible pores on the membrane surface. The incorporation of ZnO nanoparticles and PEG in PES membranes increases the number of pores and pore size, as well as the influence of UV irradiation. Then, UV irradiation in PES membranes was used to increase the hydrophilicity of the membrane because the hydroxyl groups on the membrane surface are more comfortable attaching to ZnO nanoparticles. Then, the presence of ZnO nanoparticles leads to a looser sublayer membrane structure [27]. This result can affect the increase of flux values on the membrane.

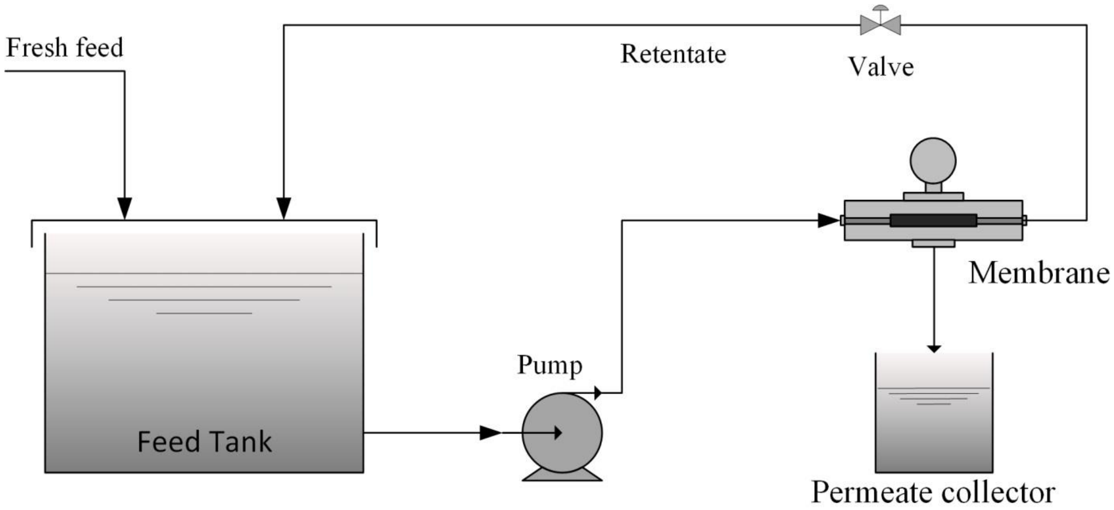

Fig. 1. A general scheme of the experimental membrane filtration system.

The UV irradiation on nanohybrid membrane also improves the affinity ZnO nanoparticles with the membrane to prevent the de-attachment of nanoparticle surface with polymer matrices which could forms unselective gap. However, in Figure 2C, agglomerate formation of nanoparticles might be created by an inhomogeneous dope solution. Besides, the shape as well as ZnO nanoparticles affinity with PES polymers are also essential factors in agglomerate formation [24]. The agglomerate of nanoparticles in the polymeric membrane can cause the formation of non-selective voids that lead to decreasing the rejection performance of the membrane. The agglomeration also induces the rougher surface, which leads to fouling. This phenomenon increases the number of foulants attached at both membrane surface (cake formation) and internal walls (internal fouling), as shown in Figure 2D.

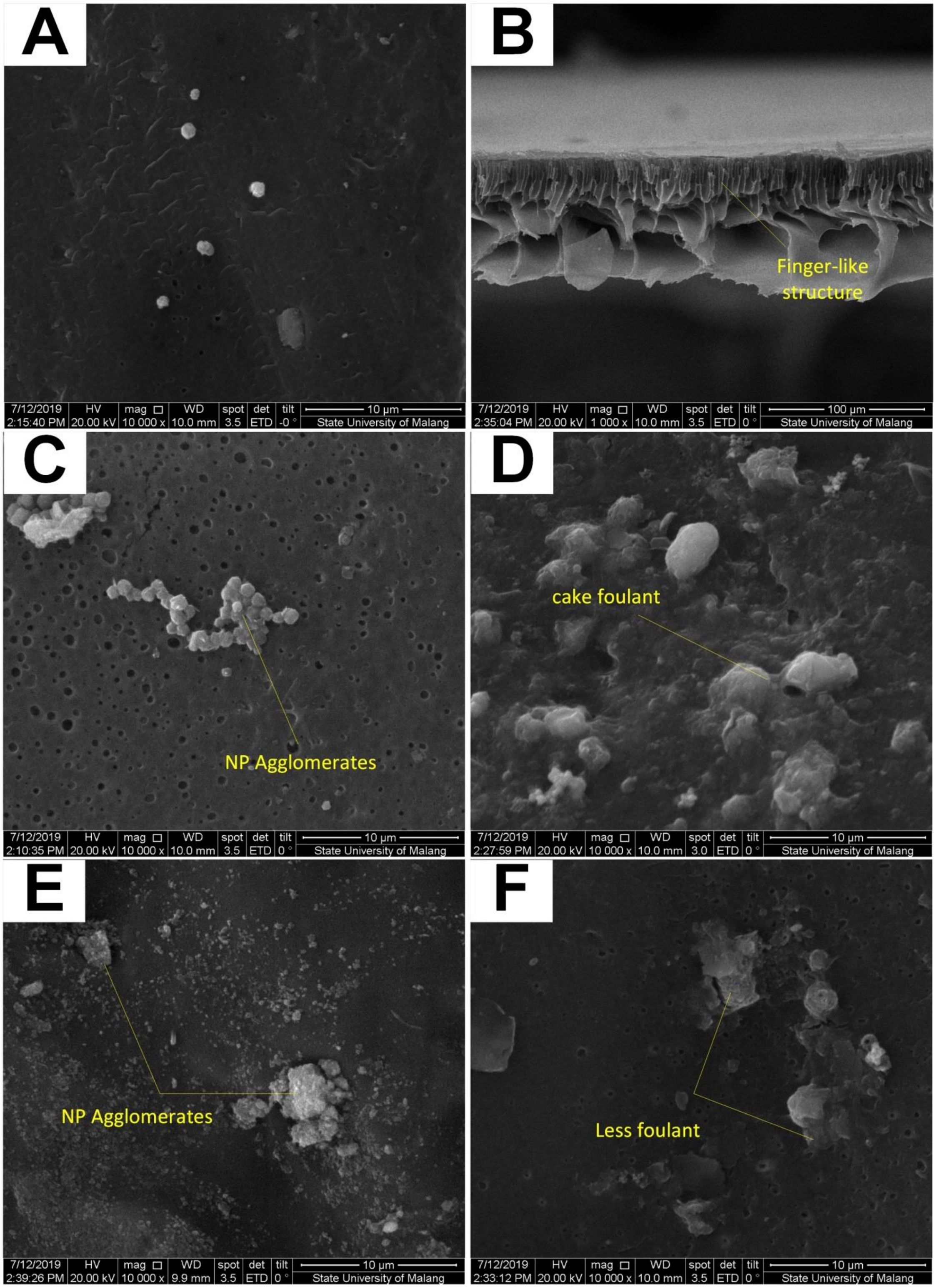

Fig. 2. SEM images of A) neat PES membrane surface B) cross-section image of PES-ZnO membrane C) clean surface membrane of PES-ZnO 1 wt-%, PEG 5 wt-%, 2 min UV irradiation, D) fouled surface membrane of PES-ZnO 1 wt-%, PEG 5 wt-%, 2 min UV irradiation, E) clean membrane surface PVA coated hybrid PES-ZnO membrane, F) fouled surface of PVA coated nanohybrid PES-ZnO membrane.

Figure 2D presents a 17% PES membrane surface, 1% ZnO nanoparticles, 5% PEG, and 2-min irradiation after rubber liquid waste filtration. The cake layer formed on the membrane surface is because of the accumulation of impurities held on the surface. Contaminants originating from liquid wastes allow the rubber to be held on the surface, and some may pass through the membrane pore due to the large size and number of pores based on the image (2D). This result was also because of the presence of PEG and UV irradiation that can form the sublayer cavities that seem to have narrow finger-like structure and large cellular void in the bottom layer. Figure 2E presents the surface image of the 3 wt.% PVA coated PES-ZnO nanohybrid membrane. The visual appearance of the PVA coated membrane surface was denser than that of uncoated membrane. The spreaded white spots are also found on the membrane surface which are considered as ZnO nanoparticles. The PVA coating on nanohybrid membrane helps eliminate unselective voids formed by agglomeration of nanoparticles, besides that PVA modifies the surface pores to be tighter so that the pores are not visible as shown by uncoated membrane in Figure 2C.

Figure 2F presents the fouled surface SEM image of the UV irradiated PES-ZnO nanohybrid membrane with PVA coating. In Figure 2F, it was less formation of cake-layers on the surface of the membrane compared with that of uncoated one. PVA coating successfully modifies the membrane surface by increasing its hydrophilicity, reducing the surface roughness, and gives the surface positive electrostatical charge. The presence of Polyvinyl alcohol (PVA) can reduce fouling as well as increases the selectivity performance without reducing the flux.

3.2. X-ray diffraction analysis of the fabricated membrane

The critical stage in fabricating nanohybrid membrane is coagulation process using non-solvent (demineralized water) because the nanoparticles might be leached out as a result of the affinity with a nonsolvent. XRD analysis was conducted in this study to confirm the presence of the embedded nanomaterial in the polymeric membrane.

Figure 3 shows the XRD diffraction patterns of neat PES membrane, nanohybrid membrane, and ZnO nanoparticles. The XRD pattern of neat PES membrane scatters and forms hill-like patterns at 2θ of 17.93°, indicating the polymer is amorphous. The XRD pattern of ZnO nanoparticles shows the pattern of crystalline type with typical sharp peaks at 2θ of 31.78°, 34.51°, 36.28°, 47.51°, 62.85°, 66.37°, 67.90°, and 69.07°. The diffractogram corresponding to the nanohybrid PES-ZnO membrane is formed by the characteristic ZnO peaks in addition to the PES XRD pattern. The small sharp peaks at 2θ of 31.86°, 34.53°, 36.25°, 47.53°, and 64.74° are attributed to the ZnO nanoparticles incorporated in nanohybrid PES-ZnO membrane, while the presence of a wide broad peak at 2θ of 18.16° is the characteristic of PES. There is a maximum peak shifting between the ZnO nanoparticles diffraction pattern in PES polymer and pure ZnO. The maximum typical peak of pure ZnO is at 36.28°, while the highest peak of ZnO in PES is at 34.53°. This result could be due to the interaction between ZnO nanoparticles with PES polymer. The results show that ZnO nanoparticles were successfully embedded into the PES polymer to produce a nanohybrid membrane. These results also reveal that ZnO has a strong affinity with PES polymer so that the particles are not leached out during the phase inversion process.

3.3. Porosity and contact angle analysis

Structural property such as porosity and surface property such as hydrophilicity play important role in influencing separation performance of the fabricated membranes. The membrane surface hydrophilicity can be evaluated through water contact angle value of the membrane surface. The porosity and water contact angle value of fabricated membranes with various ZnO nanoparticle loading and PEG concentrations are presented in Table 2.

The porosity of the PES-ZnO nanohybrid membrane reached 48.7% after adding 1% ZnO nanoparticles and increased after 1% ZnO nanoparticles reached 45.8%. The phenomenon happens because ZnO nanoparticles was located inside the polyethersulfone (PES) chain segment and causes the chain segment to not spread during membrane composition [27]. The porosity of membrane reached 73.3% after 5% PEG was added on the PES-ZnO nanohybrid membrane so that membrane permeability increased. The contact angle value decreases to 49.9° when adding 1 wt-% ZnO nanoparticles to 17 wt-% PES and decreases to 39.6° after adding 5 wt-% PEG to the PES-ZnO nanohybrid membrane. These results indicate that adding ZnO nanoparticles and additive PVA can improve hydrophilic properties so that membrane permeability increases.

The porosity of PES-ZnO nanohybrid membranes reached 80.89% after UV irradiation for 2 minutes as shown in Table 3. The contact angle in the PES-ZnO nanohybrid membrane with 0.5 minutes UV exposure reached 52.75° higher than that of unirradiated nanohybrid membrane. The value of the contact angle was 45.4° after UV irradiation for 2 minutes. The results show that nanohybrid membrane hydrophilicity is increased with the increasing of irradiation time. The possible answer of this phenomenon is the short time of UV irradiation induces the polymer grafting that makes the membrane pores becomes narrower; however, the longer irradiation time the UV light initiates the formation of free radicals on many sites on the surface thus increase the hydrophilicity [28].

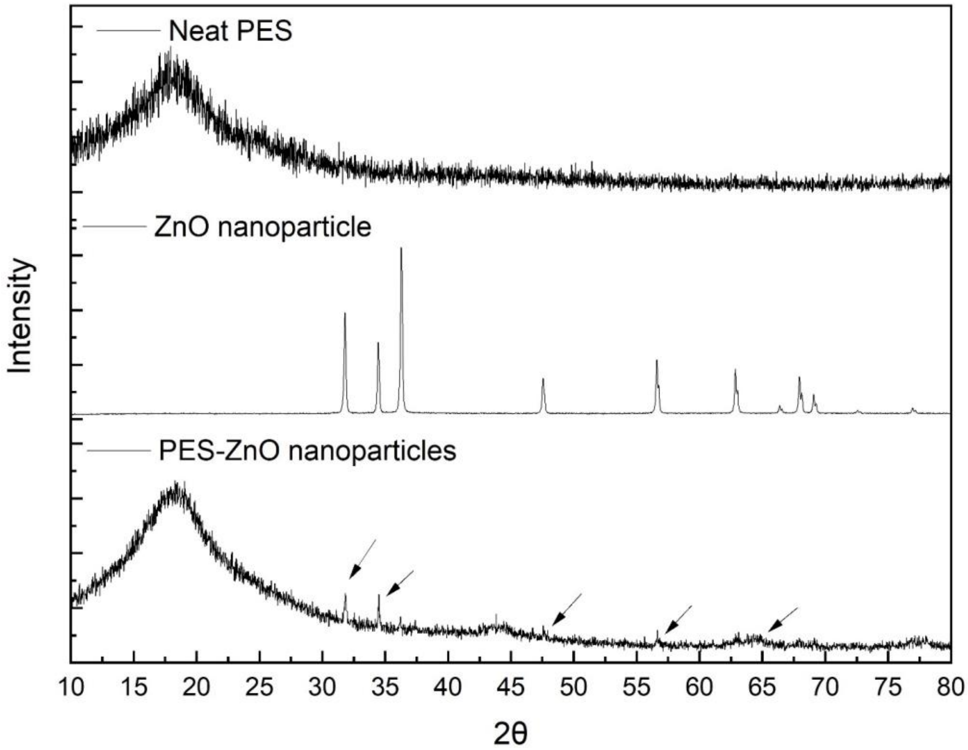

Fig. 3. XRD diffraction patterns of neat PES membrane, ZnO nanoparticles, and nanohybrid PES-ZnO 1 wt-% membrane.

Table 2
Effect of addition of ZnO nanoparticles and PEG on porosity and contact angle values.

Type of membrane	ε (%)	WCA (°)
17% PES	33.5	56.35 ± 0.01
17% PES+0,1%ZnO	48.7	56.9 ± 0.01
17% PES+0.5%ZnO	45.9	51.9 ± 0.05
17% PES+1%ZnO	45.8	49.9 ± 0.05
17%PES+1%ZnO+2%PEG	50.0	49.83 ± 0.13
17%PES+1%ZnO+3%PEG	56.5	46.16 ± 0.17
17%PES+1%ZnO+5%PEG	73.3	39.6 ± 0.03

ε: porosity
WCA: water contact angle

The porosity of the PES-ZnO nanohybrid membrane with 1% PVA becomes 77.7% lower than that of uncoated membrane that reaching 80.8%. A low concentration of PVA additive can enter the substrate of the PES membrane, thereby reducing membrane porosity. Otherwise, high concentrations of PVA additives can cause a thicker surface layer [25] and cross-linking on the membrane matrix and become a thin layer on the membrane surface. The contact angle value of 1 wt.% PVA dip-coated nanohybrid membrane significantly decreases up to 27.1°. This value explains that the hydrophilicity of the nanohybrid membrane surface increases after adding the PVA additive.

3.4. Fourier transform infrared (FT-IR) analysis

The FT-IR spectra as depicted in Figure 4 describe the vibration of sulfonates (R-SO_2-R) and ether (R-O-R) groups by indications of strong peaks at 1135 cm^{-1} and 1240 cm^{-1}, respectively. The presence ZnO nanoparticles was indicated by the band at around 3320 cm^{-1} and a peak change at a wavelength of 543 cm^{-1}, showing a stretching formed from ZnO nanoparticles [12]. Meanwhile, two strong reactions around in 1485 cm^{-1} and 1570 cm^{-1} indicate a vibrational group (C = C) aromatic benzene circle in PES molecules. The stretching of ZnO bond is indicated by the absorption band at 500 cm^{-1}, and the FT-IR spectrum confirms that the presence of ZnO nanoparticles and PEG on PES membranes does not change the backbones in polymers. Another two peaks were also observed at 1365 and 1488 cm^{-1} that corresponded to symmetric deformation vibration and asymmetric deformation vibration of –OH (Leo et al. 2012). UV light induces polymer chains restructuring and grafting that makes the membrane denser [28]. Furthermore, a widening of the peak around 2745–2710 cm^{-1} because of stretching vibrations of hydrogen in carbonyl groups are radical. The modification of membranes by UV irradiation-based on the FT-IR spectrum does not eliminate the backbones in the PES-ZnO nanohybrid membrane. Thus, the FT-IR spectrum shows a broad peak around 3350 cm^{-1} illustrating the vibration of hydroxyl from PVA and absorbed hydroxyl from ZnO that leads on strong water adsorption [12]. In contrast, a peak change at a wavelength of 1725–1735 cm^{-1} because of vibration –C–O– aldehyde from PVA. This phenomenon shows the occurrence of cross-linking between matrix membranes of PVA and PES-ZnO nanohybrid. Consequently, the hydroxyl group increases on the surface of the membrane.

3.5. Effect of ZnO and PEG loading on the performance of PES-ZnO nanohybrid membrane

Original rubber wastewater was used as wastewater feed in the performance evaluation experiment. The membranes with various concentrations fo ZnO nanoparticles and PEG were evaluated for their permeate flux profile and pollutant rejection efficiencies. The calculated permeate flux and pollutant rejection are shown in Figure 5 for variation of ZnO concentration and Figure 6 for variation of PEG concentration.

Table 3
Effect of UV irradiate on porosity and contact angle values.

Fabricated membranes	ε (%)	WCA (º)
17%PES+1%ZnO+5%PEG	73.33	39.6 ± 0.03
17%PES+1%ZnO+5%PEG+0.5UV	76.47	52.75 ± 0.75
17%PES+1%ZnO+5%PEG+1UV	78.41	46.67 ± 0.01
17%PES+1%ZnO+5%PEG+2UV	80.90	45.48 ± 0.01
17%PES+1%ZnO+5%PEG+2UV+1%PVA	77.77	27.15 ± 0.19
17%PES+1%ZnO+5%PEG+2UV+2%PVA	76.93	34.80 ± 0.03
17%PES+1%ZnO+5%PEG+2UV+3%PVA	77.01	38.67 ± 0.17

ε: porosity
WCA: water contact angle

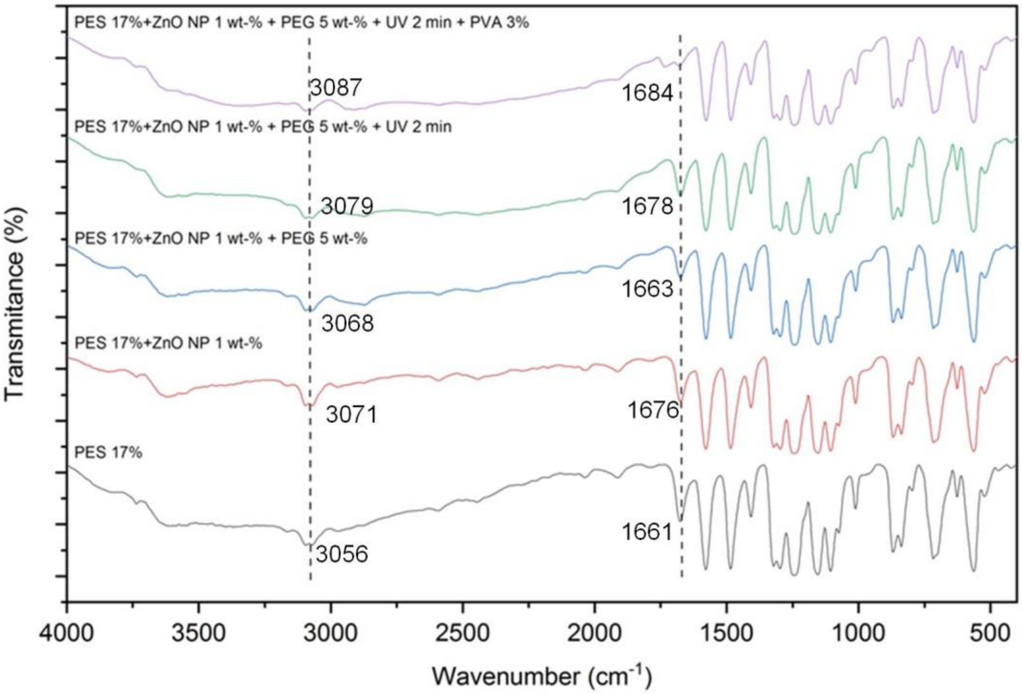

Fig. 4. FT-IR spectra of the pristine PES and modified PES-ZnO nanohybrid membranes.

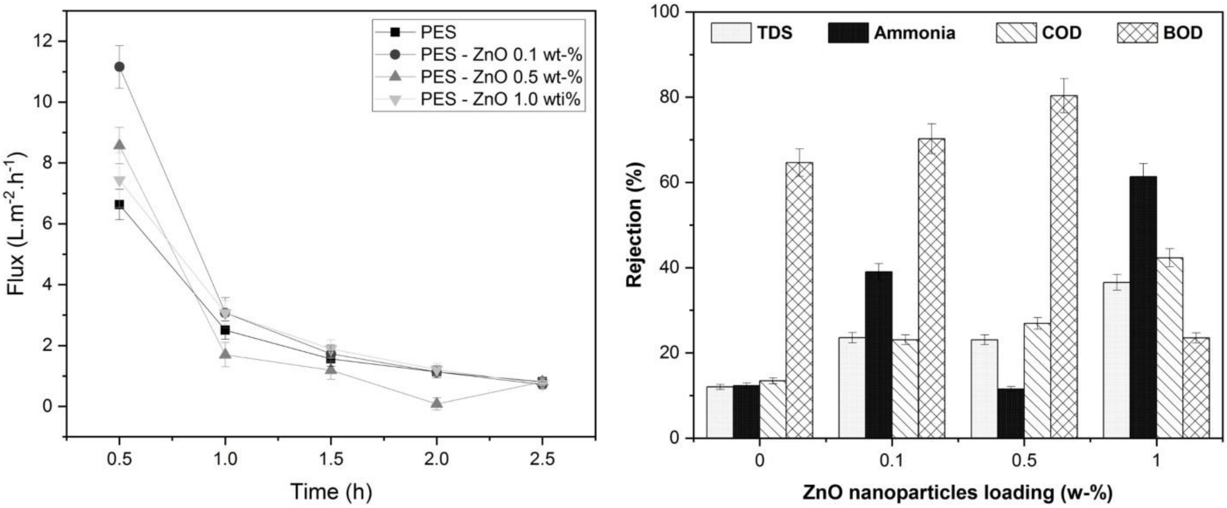

Fig. 5. Flux and pollutants rejection at various ZnO loading in the PES membrane.

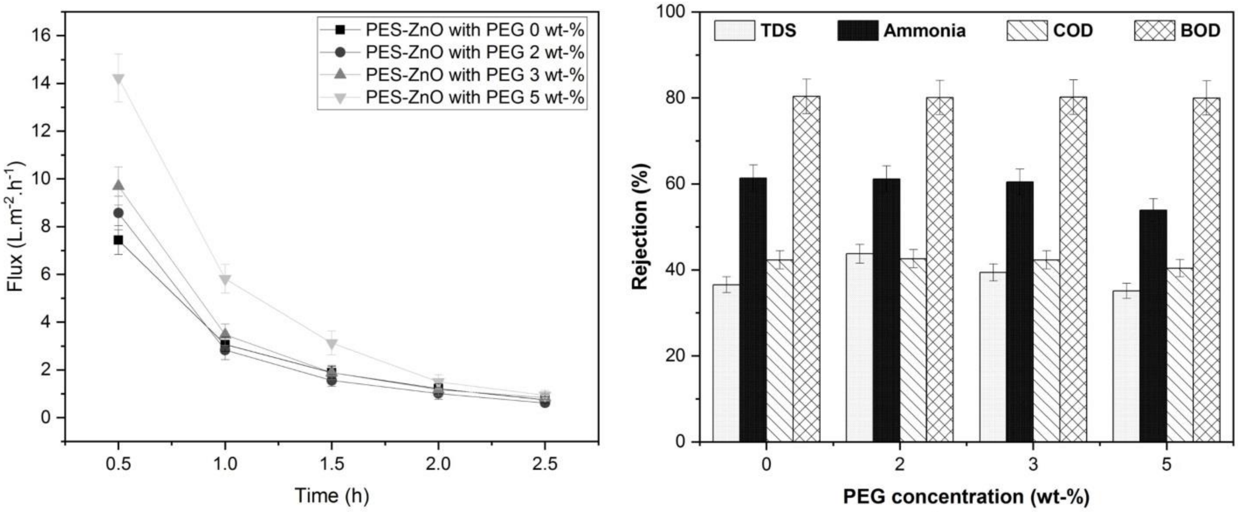

Fig. 6. Flux and pollutants rejection nanohybrid PES membrane with various PEG cocentration.

Figure 5 shows that the highest flux value at 17% PES membrane and 0.1% ZnO nanoparticles concentration reached 11.15 L.m-^{2}h^{-1} compared to the pristine PES membrane, which only reached 6.62 L.m-^{2}.h^{-1}. Figure 6 (left) shows that the highest flux value occurs in the addition of 5% PEG achieved 14.22 L.m-^{2} h^{-1} higher than that of nanohybrid membrane without PEG. PEG is considered as a hydrophilic polymer that is usually used as pore-forming agent as well as increasing the membrane hydrophilicity; thus, the increasing of PEG concentration the more porous membrane will be acquired. Also, microvoids form in the pore structure on the surface so that porosity increases [29]. ZnO nanoparticles give the same effect; microvoid was formed due to the overloading of ZnO nanoparticles which induces the formation of agglomerate on the membrane selective layer. The membrane layer forms two phases, namely, the PES phase and the ZnO phase. These two phases cause defects on the surface of the membrane so they form microvoids [27]. The permeate flux profile of all the fabricated membranes showed high values of permeate water flux then decrease gradually as time passes. The permeate flux profile reached pseudo-steady state after 90 minutes filtration time. The flux decline phenomenon at initial filtration is explained by the membrane compaction due to trans-membrane pressure. The highest rejection value on the Figure 5 at an addition of 1% ZnO with BOD rejection value reached 80.3%, ammonia rejection 61.3%, COD rejection 42.3%, and TDS rejection 36.5%. However, the increasing of PEG concentration decreases the rejection performance of the tested membrane. Figure 6 (right), in BOD rejection to 79% after adding 5% PEG, the value was lower with the PES-ZnO nanohybrid membrane without PEG reaching 80.3%. Also, 61.3% ammonia rejection with a membrane without PEG decreased to 53.8% after adding 5% PEG. These events cause unwanted waste components through the membrane and cause the rejection value to decrease. The formation of micro-void in the pore structure on the surface so that porosity increases [29]. However, an increase in flux is more significant than a decrease in rejection. Therefore, the introduction of 1 wt-% ZnO nanoparticles and 5 wt-% PEG additives to PES membrane was considered as the composition for obtaining the best performance in rubber wastewater treatment.

3.6. Effect of UV irradiation on the performance of PES-ZnO nanohybrid membranes

The best concentration of ZnO nanoparticles loading and PEG-based on the performance evaluation was followed by modification using UV irradiation. Membrane modification by UV irradiation is a simple technique; PES is a membrane material that efficiently functioned under UV irradiation [30]. The flux and rejection values of the best concentrations of PES-ZnO nanohybrid membranes were modified by UV irradiation and are shown in Figure 7.

Figure 7 shows the value of permeate water flux increases along with the increasing of UV exposure time. The initial flux values for 2 minutes UV irradiation reached of 14.55 L.m^{-2}.h^{-1} were higher than 1 min UV irradiation and without irradiation. The value of flux was related to the value of the contact angle and porosity, which states that permeability and hydrophilic properties increase after UV irradiation. This result occurs because UV irradiation induces the formation of free radicals on membrane surface and grafting of the polymer chain become denser after UV light irradiation [31]. Meanwhile, the degradation of polymer chains resulted in greater pore size and increased hydrophilicity and flux value [32]. The impact on the selectivity of PES-nano-ZnO membranes with the rejected value of the membrane decreases with the increasing duration of UV irradiation. The rejection of the membrane at 2 minutes UV irradiation demonstrated that BOD rejection reached 80.1%, ammonia rejection reached 53.7%, and COD rejection achieved 65.3%. While irradiation UV for 0.5 minutes BOD rejection reached 81.6%, COD rejection reached 71.1%. UV irradiation gave the highest flux value at the duration of 2-minute UV irradiation compared to the decreasing rejection value.

3.7. Effect of adding PVA as surface modification to the performance of PES-ZnO nanohybrid membranes

PVA is a polymer that possesses very hydrophilic properties and the coating of crosslinked PVA on the membrane top layer is expected to improve the hydrophilic property due to PVA is highly hydrophilic polymer [33]. The permeate water flux and pollutant rejection performances of the PVA coated nanohybrid membranes are presented in Figure 8.

Figure 8 exhibits that the PES-ZnO nanoparticles membrane flux value added by PVA additive decreases compared to that of uncoated nanohybrid membrane. The initial flux of 3 wt-% PVA coated nanohybrid membrane only reached of 10.52 $L.m^{-2}.h^{-1}$ slightly lower than that of uncoated nanohybrid membrane which reached up to 14.5 $L.m^{-2}.h^{-1}$. Overall pattern as shown in Figure 8 is the permeate flux decrease as the increasing of PVA concentration as membrane coating agent. Ma and co-workers [21] reported that PVA coated PES membranes followed by crosslinking to improve antifouling property enhanced the membrane hydrophilicity; however, the spreading of PVA polymer chain made substantial decline of the permeate flux. The rejection value of the PES-ZnO nanohybrid membrane with 3% PVA concentration resulted in COD rejection reaching 82.6%, BOD rejection reaching 82.11%, ammonia rejection of 57%, and TDS rejection of 51%. pH changes occur, starting from 5.2 to 6.8 in the final filtration results using the PES-ZnO nanohybrid membrane by adding 3% PVA. These changes, because of the electrostatic force repulsion between positively charged speciments. Since the PVA is a positively charged polymer [34], it could reject the positive ions such as proton (H^+) or Brønsted-Lowry acids though Donnan exclusion mechanism. This value is higher than the PES-ZnO nanohybrid membrane without PVA. This phenomenon is because of membrane recycling and the ability to cross-link the adsorption process [35]. As a result, the best performance membrane is the PES-ZnO nanohybrid membrane with 5 wt.% PEG, 2 min. UV irradiation, and 3 wt% PVA. The increase in the rejection value was more significant than the value of the flux, so the concentration of 3% PVA performed the best in this experiment.

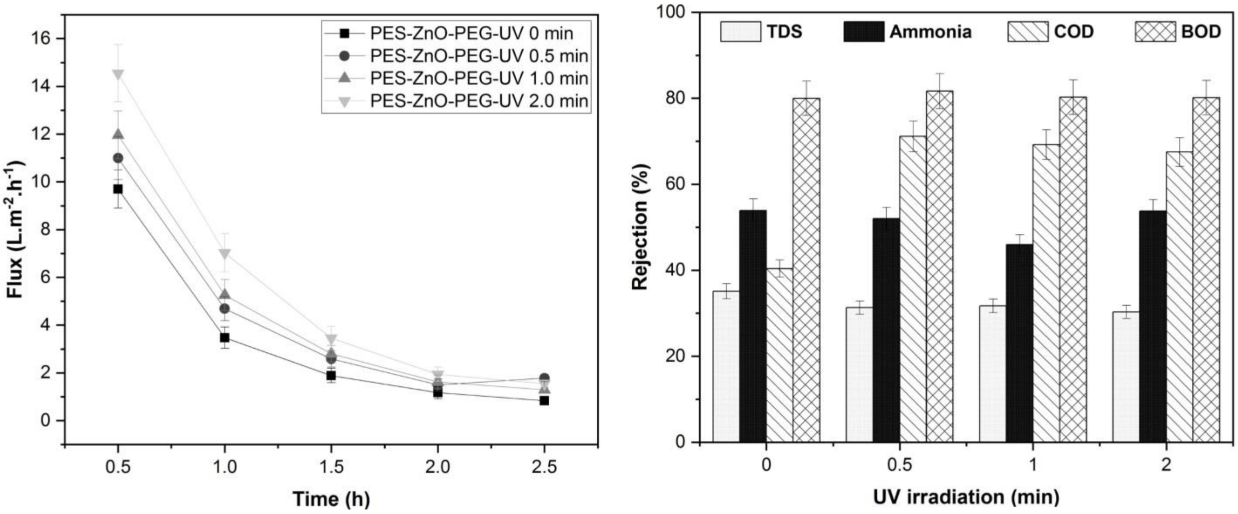

Fig. 7. Flux and pollutants rejection at various UV irradiation times in PES membrane.

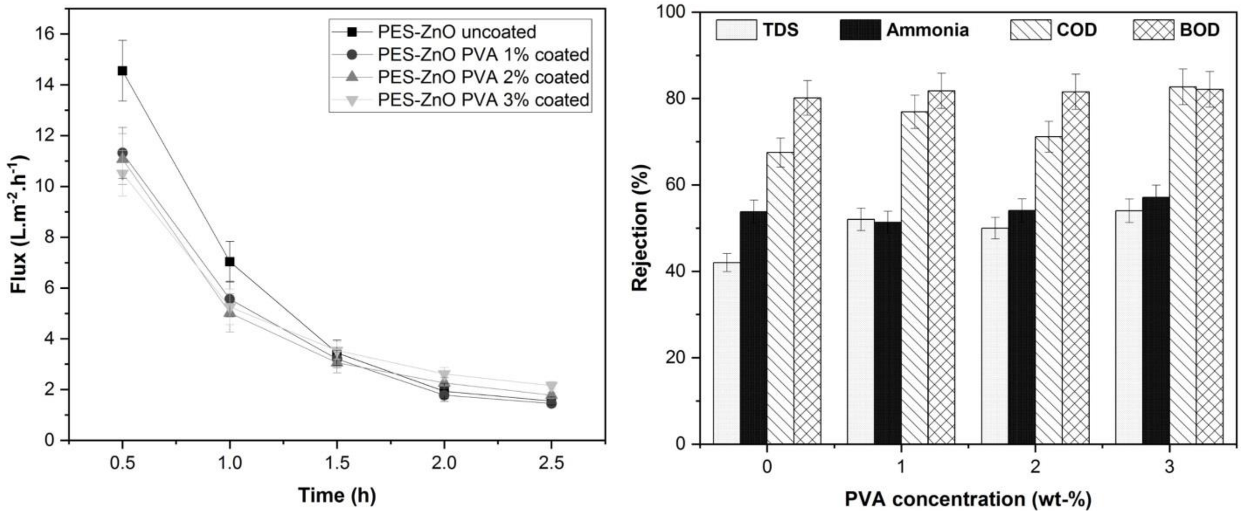

Fig. 8. Permeate water flux and pollutants rejection at various PVA concentration as nanohybrid membrane coating.

The concentrations of pollutants in permeate water obtained from membrane filtration using 3 wt.% PVA coated were 15.42 mg/L of BOD_5, 45.06 mg/L of COD, 95.87 mg/L of TDS, and 10.78 mg/L of $N\text{-}NH_3$. The pollutant concentrations in permeate met the quality standard of discharged wastewater from the rubber industry based on the Indonesian Ministry of Environment Regulation No. 51 [36]. The maximum levels of BOD_5, COD, TDS, and $N\text{-}NH_3$ based on the aforementioned standard were 150, 300, 150, and 10 $mg.L^{-1}$, respectively. The permeate water generally met the required standard except for $N\text{-}NH_3$, where the level was still slightly higher than standard, and efforts are still needed to reduce levels of ammonia so the treated water can meet the standards.

3.8. Analysis of membrane antifouling

The membrane fouling could be qualitatively evaluated through observation under SEM scanning and FT-IR analysis. SEM analysis result exhibits the visual appearance of foulant attachment on the membrane while FT-IR provides detailed information about foulant types which attached on the membrane through functional group analysis [27]. Then, a flux decline ratio is essential for evaluating the antifouling behavior of fabricated membranes [7]. Figures 2C and 2f showing the SEM membrane characterisation results indicate that foulant deposition on the PVA coated membrane was fewer than that of uncoated nanohybrid membrane. Quantitative evaluation was also performed using flux decreasing ration which is presented in Figure 9.

Further, a decreased membrane ratio occurs in each membrane during the filtration period. The flux ratio profile of 3-wt% PVA coated membrane declines and reaches a stable condition after 120 minutes of filtration time. Moreover, flux reduction ratio is only 8.2% using 3 wt.% PVA coated nanohybrid membrane, lower than that of the uncoated nanohybrid membrane (23.17%). The anti-fouling behavior of the modified membrane was significantly improved by the coating PVA polymer on the membrane surface. However, it is necessary to provide additional pretreatment such as ozonation or adsorption prior to membrane separation. The pretreatment is expected to decrease the level of organic contaminants so the membrane is not overburdened by foulant deposition.

Figure 10 is a PES-ZnO nanoparticles membrane with the addition of 3% PVA before filtration was used and after filtration has decreased foulant. From the Figure 10, a change in the peak around 3360 cm^{-1} was due to the vibration of O-H stretches. The wide strong band at 3700–2000 cm^{-1} indicates the presence of -OH groups in the membrane surface. Meanwhile, the membrane after filtration shows lower wide peak in hydroxyl vibration are that might be due to the interaction between foulants with -OH group. Likewise, the peak at 1720-1740 cm^{-1} is indicating the vibration of aldehyde carbonyl (-C-O-) from crosslinked PVA was shifted to around 1890 cm^{-1} in the membrane after filtration which may be caused by the interaction with foulants from rubber wastewater such as peptides and acids. The FTIR Spectrum also explained that no damage to the PES-ZnO nanoparticles membrane backbone. These results explain that the addition of 3% PVA produces a stable membrane.

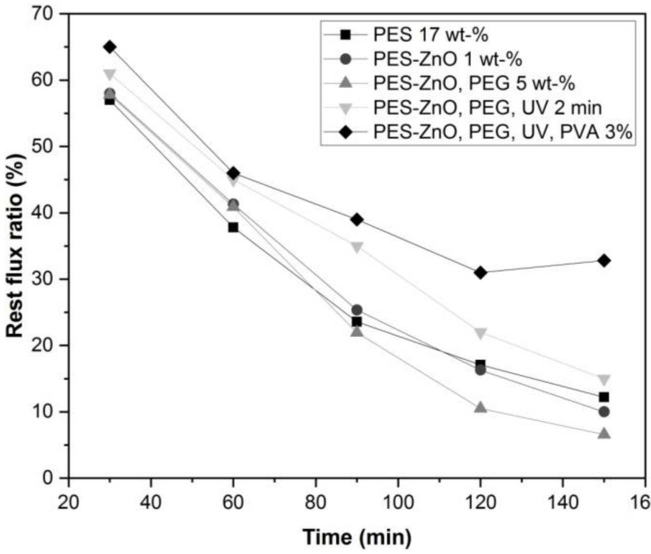

Fig. 9. The flux decline ratio profiles of tested fabricated membranes.

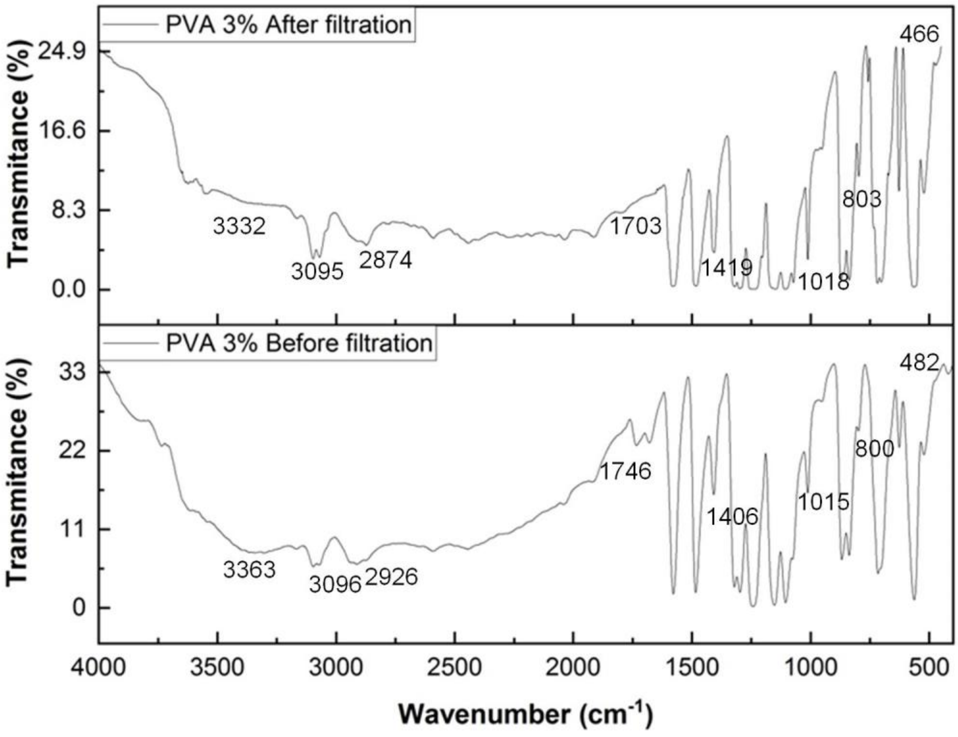

Fig. 10. FT-IR Spectrum addition of 3% PVA on PES-ZnO nanohybrid membranes.

4. Conclusions

Modification of PES-ZnO nanohybrid membranes through UV irradiation followed by PVA coating successfully improved membrane structure and anti-fouling properties. UV irradiation on pre-coagulated membrane increased the hydrophilic properties of the membrane through the generation of radicals on membrane surface sites and PVA coating provided hydrophilic property and positively charged surface which can reject positive charged pollutants. The combination of UV irradiation and PVA by coating provides a synergistic effect. UV irradiation on pre-coagulated membrane increased the membrane permeate flux while PVA coating increased the pollutant rejection with acceptable flux decrease. The longer UV irradiation time increased the flux value. The higher concentration of PVA will increase membrane rejection performance; however, the overall permeate flux slightly decreased. Therefore, the UV irradiation and PVA by coating can increase the permeate flux and pollutants rejection efficiency of PES-ZnO nanohybrid membranes. The anti-fouling property of the modified membrane based on this study was slightly improved; therefore, the proper pre-treatment was required prior to membrane separation in rubber wastewater treatment to prevent the overburdened membrane.

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