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ENHANCED ANTI-FOULING BEHAVIOR AND PERFORMANCES OF NANO HYBRID PES-SiO_2 AND PES-ZnO MEMBRANES FOR PRODUCED WATER TREATMENT

Tutuk Djoko Kusworo[a]*, Ahmad Fauzi Ismail[b], Nita Aryanti[a], Widayat[a], Qudratun[c], Dani Puji Utomo[a]

[a]Department of Chemical Engineering, University of Diponegoro, Semarang, Indonesia
[b]Advance Membrane Technology Research Center, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[c]Nano Center Indonesia, South Tangerang, Indonesia

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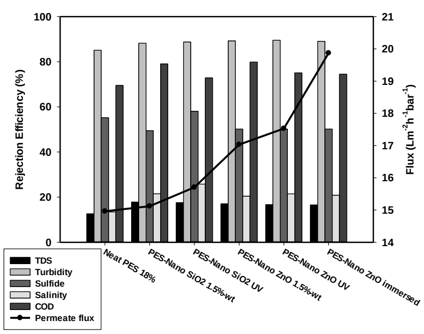
*Corresponding author
tdkusworo@che.undip.ac.id

Graphical abstract



Abstract

This research is implemented primarily to obtain the enhanced performance in terms of permeability, solute rejection and anti-fouling behavior of PES membrane towards produced water treatment by incorporating nano-SiO2 and nano-ZnO as nano inorganic filler. The fabricated membrane was modified through UV irradiation and immersion in Acetone-Ethanol mixture. The effect of several modification treatments is investigated in this study. Nano hybrid PES-SiO2 and PES-ZnO membrane were prepared using Loeb-Sourirajan methods (NIPS phase inversion). The casted membrane was exposed under UV lights for 2 min and followed by immersion in Acetone-Ethanol mixture for 24 h. The result of SEM and FTIR analysis confirmed that the nano particles incorporation change the membrane surface structure, while UV treatment and Ac-Et immersion significantly enhanced the hydrophilicity of membrane material. Nano hybrid membrane displayed high efficiency of oil removal up to >99%, the immersion in the Ac-Et increased the water permeability about 20% and caused slightly decrease in solute rejection. The modified nano hybrid membrane performed an anti-fouling behavior in produced water filtration process.

Keywords: Acetone, Ethanol, Nano-SiO2, Nano-ZnO, Polyethersulfone, Produced water, Ultraviolet

Abstrak

Tujuan utama kajian ini dilaksanakan adalah untuk meningkatkan prestasi membran PES dari segi kebolehtelapan, penyingkiran bahan boleh larut dan tingkah laku pengotoran membran PES ke arah rawatan air yang dihasilkan dari medan minyak dengan menggunakan nano-SiO_2 dan nano-ZnO sebagai pengisi tidak organik nano. Membran yang telah difabrikasi diubah suai melalui penyinaran UV dan rendaman didalam campuran Aseton-Etanol. Kesan beberapa rawatan pengubahsuaian telah dikaji. Membran hibrid nano PES-SiO_2 dan PES-ZnO telah disediakan menggunakan kaedah Loeb-Sourirajan (fasa berbalik NIPS). Membran yang telah dituang didedahkan di bawah lampu UV selama 2 minit diikuti dengan rendaman didalam campuran Aseton-Etanol (Ac-Et) selama 24 jam. Hasil analisis SEM dan FTIR mengesahkan bahawa kemasukan zarah nano telah mengubah struktur permukaan membran, sementara rawatan UV dan rendaman Ac-Et telah meningkatkan hidrofililik bahan membran dengan ketara. Membran hibrid nano mempamerkan kecekapan yang tinggi dalam penyingkiran minyak sehingga > 99%, rendaman dalam Ac-Et meningkatkan kebolehtelapan air kira-kira 20% dan menyebabkan sedikit penurunan didalam penyingkiran bahan boleh larut. Membran hibrid nano yang telah diubahsuai menunjukkan anti-pengotoran membran dalam proses penapisan rawatan air yang dihasilkan dari medan minyak.

Kata kunci: Aseton, Etanol, Nano-SiO_2, Nano-ZnO, Polietersulfona, rawatan air yang dihasilkan dari medan minyak, Ultraviolet

1.0 INTRODUCTION

In the recent years, membrane technology becomes a preference in the water treatment process in certain condition because it provides simplicity, sustainability and relatively low energy consumption [1]. The problem of current global water security is not only due to limited freshwater sources, but also its environmental impacts for its entire water lifecycle, from domestic, industrial, and agricultural disposal, river body, lake, sea, and recycling. For the huge demands for water, a sustainable water treatment technology and water resources are required [2, 3]. Produced water is a side product of oil and gas production. The produced water can be one of potential water resources which can be treated as clean water to fulfill the water demand around drilling area.

Produced water is the highest quantity of waste generated in oil and gas industries. The production of water generally reached three times greater than produced oil [4]. The production continues to increase with the maturity of oil and gas fields [5]. Produced water contains a high concentration of pollutants. In general, it contains 1.2 – 200 ppm of emulsified oil majority consisting of alkanes, aromatics, polynuclear aromatics, hydrocarbon compounds containing sulfur, nitrogen, oxygen and unknown hydrocarbon. Moreover, there are 1,000 – 15,000 ppm of total dissolved solid with predominant cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} as well as anions such as Cl^- and SO_4^{2-}. The produced water also contains 20 – 2,250 ppm of COD, and 5 – 4,200 ppm of total suspended solids [6, 7]. The management of produced water becomes the most challenging issues for the oil and gas industries and preventing the damage of human health and the environment. Produced water with complex physicochemical composition has problematic treatment. The conventional physicochemical methods were not effectively removed all the contamination components. In contrast, application of some chemical methods for produced water treatment generated sludge which is required further complex treatments [8]. In this case condition, membrane technology offered a better separation process without any chemicals addition and less harmful wastes [9]. The nanofiltration (NF) and reverse osmosis (RO) technologies were applied to reject the minerals content for high purity water production [10]. However, this study was focused on produced water treatment using nanofiltration having a size of 0.5 – 2 nm which effectively removes divalent ions or higher [11].

Polymeric membranes such as cellulose acetate, polyacrylonitrile, polyethersulfone, polyamide, polyvinylidene fluoride, and polysulfone were widely applied for water treatment [12-14]. The polyether sulfone was the mostly selected materials due to its excellent behavior such as tolerant of high temperatures, chemicals, and has high dimensional stability for membrane separation application in various conditions [15]. The problems that often occur in the membrane separation process is fouling that blocks the permeate water to pass through the membrane barrier. This blockage decreases the permeability and lowers the productivity [16]. This is a serious obstacle in the membrane separation process. To overcome the obstacle, the membrane should have high permeability, rejection, and anti-fouling performance. In the produced water treatment, oil droplet contained in produced water will be the potential foulant. Specific membrane characteristics should be addressed, and advances in membrane materials development are required.

Improvement of membrane properties was currently dominated by attempts to enhance permeability without reducing the rejection. Membrane separation properties depend on polymer concentration, additive, solvent, casting temperature, solvent evaporation rate, the thickness of the membrane, pre-treatment, and post-treatment during membrane fabrication [17]. The recent concept in advanced membrane material development is the development of inorganic incorporated membrane [18]. In this concept, the inorganic material is incorporated into the polymer matrix to combine the desired separation properties of the molecular sieve (inorganic filler) as well as to lower the cost of polymer material fabrication. The addition of inorganic material also provided an excellent performance of membrane stability in high-pressure operation, as reported by Zhang *et al*. [19]. Lin *et al*. [20] also indicated that the performance of nano-WS_2 embedded PES membrane was significantly enhanced the membrane performance. In addition, the nano-graphene oxide was used by Zhao *et al*. [21] to enhance water permeability, separation efficiency, and anti-oil-fouling. Furthermore, the utilization of nano-SiO_2 was employed by Miao *et al*. [22] to develop SPPO membrane performance. The consequences of incorporation inorganic material in membrane fabrication was the voids formation which reduced the solute rejection [23, 24]. Ismail *et al*. [24] also found that over embedding of nano-material leads on the formation of nano-particles domain agglomeration. Kusworo *et al*. [25] concluded that application of silicone rubber coating on the PES membrane surface was able to overcome the aforementioned problem. The membrane successfully removed the nano-gaps between PES polymer and incorporated nano-SiO_2.

Cross-linking of the polymeric membrane with low molecular polymer or polymer having specific characteristic has been identified enhancing the separation properties of the membrane [26]. However, it lowered the permeate flux. Konruang *et al*. [27] and Homayoonfal *et al*. [28] reported that UV irradiation on the membrane surface significantly enhanced the permeate flux. The effort to improve the pollutant rejection and anti-fouling properties of the membrane using thermal post-treatment has been conducted by Kusworo *et al*. [25], [29-30]. In this current research, the effect of treatments comprising a mixture of acetone and ethanol employed as an immersion solvent and combined with pre-treatment of UV irradiation on the membrane surface have been investigated. Based on the study of literature, there is no report on the investigation of nano hybrid membrane performance improvement by employing the combination of UV irradiation and Acetone-Ethanol (Ac-Et) immersion. The performance of modified membrane in terms of permeability, selectivity, and anti-fouling were compared with the existing unmodified PES membrane.

2.0 METHODOLOGY

2.1 Materials

Polyethersulfone (PES) powder was purchased from Solvay Advance Polymer USA. Nano-SiO_2 and nano-ZnO were prepared in Nano Center Indonesia with the average nanoparticles size is 50 nm. 1-methyl-2-pyrrolidone (NMP) was obtained from Sigma-Aldrich. Ultrapure distilled water for coagulation bath and preparing the stock solution of all reagents was produced in Mer-C (Membrane Research Centre) Diponegoro University. The produced water sample was supplied by PT. Pertamina Indonesia oil and gas company.

2.2 Preparation of Membrane Materials

Polyethersulfone (PES) was dried before being used as membrane material to avoid the interaction between water absorbed with the solvent. The PES powder was dried in an oven at 120°C for 24 h and then cooled under vacuum desiccator. Nano-SiO¬2¬ and nano-ZnO were dehydrated to remove water vapor and absorbed organics under vacuum oven at 150°C for 3 h before being used as nano-filler in membrane fabrication. The nano-powder was then cooled down in a vacuum and dry desiccator to prevent the re-adsorption of water vapor.

2.3 Fabrication of Nano Hybrid PES Membrane

Nano hybrid PES-SiO_2 and PES-ZnO membranes were fabricated using Loeb-Sourirajan methods (NIPS) from a prepared dope solution consisting of 18% PES. The dope solution was prepared by weighing nano-SiO_2 and nano-ZnO with the various amount (0 - 1.5 %-wt in total solid). An appropriate quantity of nano-particles were dispersed in NMP solvent at the constant stirred for 4 h to avoid particles aggregation. Then, the proper weight of PES was added to NMP-nanoSiO_2 and NMP-nanoZnO. The polymer solutions containing nano-SiO_2 and nano-ZnO were stirred at 32°C for 6 h to obtain a homogeneous dope solution as indicated by the turbidity of the dope solution. The dope solutions were kept overnight to remove air bubbles. The air bubbles should be removed to prevent micro-voids formation. The polymer solutions were cast using a manual membrane casting knife with the thickness was set in 150 μm. The casted film was pre-treated under UV light for 2 minutes and then immersed immediately in a coagulation bath containing ultra pure distilled water as non-solvent at a temperature of 30 ± 2°C. The membranes were drawn out from coagulation bath when the phase inversions are completely occurred and soaked in another distilled water bath for 24 hours to ensure the complete separation between polymer and solvent. Finally, the membranes were dried in a drying chamber at 40-50°C for overnight. The prepared membranes were ready to be post-treated to modify the membrane transport properties.

2.4 Nano-hybrid PES Membrane Post-treatment by Immersion in Acetone-Ethanol (Ac-Et)

In order to improve the performance of the fabricated membrane for produced water treatment, dried membranes were immersed in the mixture of Acetone-Ethanol solution at Ac-Et mass ratio of 1:3. The membrane immersion to the solvent was allowed for 24 h at ambient temperature (30 ± 2°C). Further, the membranes were shortly rinsed with distilled water. After the wetting process, the membranes were used to filter produced water to define the permeate water flux and rejection of solute. The performance of modified membrane was compared to the unmodified polyethersulfone (PES) membrane.

2.5 Nano hybrid PES Membranes Characterization

Fourier transform infra-red spectrophotometer (Shimadzu Series IR-prestige 21, Japan) was used to analyze the FT-IR spectra in the range of wavenumber 400 – 4000 cm^{-1}. The record of FT-IR spectra was interpreted to obtain the information of the specific functional group that may change along the treatment process. In addition, the spectra investigate the dominant specific functional group that plays a major role in transport properties. An appropriate sample of the membrane was ground with KBr and then placed in the sample holder, and the sample was analyzed.

The Scanning Electron Microscopy (SEM) (JEOL JSM-6510-LA, Japan) was used to determine the surface morphology of the membrane. The investigation of the surface morphology is necessary to consider the effect of the treatment on the structure of the membrane. The membrane samples were cleaned with filter paper, then fractured in liquid nitrogen and attached to the grid using carbon copper tape and sputtered with gold by means of sputter coater. The membranes surfaces were observed under 20,000x magnification. The images of membrane surface morphology were recorded in the computer for further analysis. The SEM analysis was performed in Integrated Laboratory in University of Diponegoro.

2.6 Nano Hybrid PES membranes Performance

Permeate water flux and solute rejection were determined using a cross-flow membrane cell (Figure 1) with effective membrane area of 12.57 cm^2. Preceding to flux measurements, the membranes were mounted in membrane cell and then were initially compacted at 4 bar gauge for 30 minutes using distilled water. After compaction process, the distilled water in the feed tank was replaced by original produced water sample. The permeability test was conducted at ambient temperature (30 $\pm$ 2°C) and constant pressure (4 bar gauge). The permeate water was drawn for every 30 minutes of operation time and then measured the volume to determine the flux at the time. The permeate water flux was defined by equation (1) [30]

$$J_{pw} = \frac{V_{pw}}{A \times t \times P} \quad (1)$$

Where J_{pw} is the permeate water flux ($Lm^{-2}h^{-1}bar^{-1}$). V_{pw} is the permeate water volume (L), A is the membrane area (m^{-2}), t is the time (h), and P is the operating pressure (bar).

The solute rejections were calculated by measuring the concentration of solute in the produced water feed and permeate water. This research investigated rejection parameters consisting of TDS, turbidity, sulfide, salinity, and COD. The main physico-chemical of original produced water sample were initially determined. The pre-filtered and permeate water characteristics were used to study the rejection performance of membranes. The rejection efficiency of the membrane was calculated by equation (2) [30].

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

Where %R is the rejection efficiency, C_f is the concentration of solute in feed, C_p is the concentration of solute in permeate water.
The antifouling characteristics of prepared nano hybrid membranes were evaluated using based on the profile of flux and rejection obtained from performance test. Furthermore, the SEM images of membrane surface after being used was observed to evaluate the foulant deposition on the membrane surface.

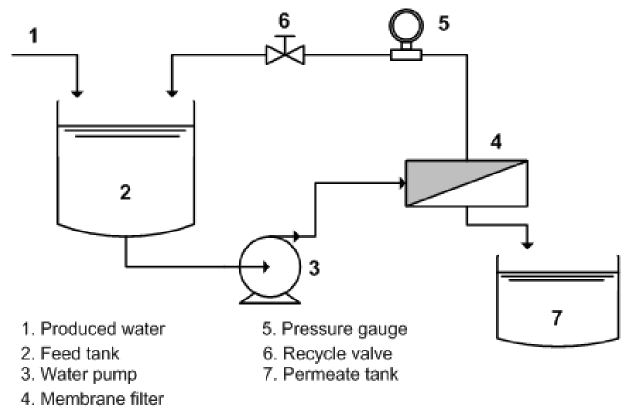


Figure 1 Schematic flow diagram of cross-flow membrane system

2.7 Original Produced Water Sample Characteristics

Original produced water sample was supplied from PT. Pertamina Jatibarang Indonesia. The produced water was used as feed water in membrane-based filtration system in batch mode. The produced samples were collected from three-phase separation tank, dehydration unit, and stabilization process of oil refinery activities. The produced water sample was characterized to obtain the information about the constituents containing in the produced water such as oil, mineral, suspended solid, organic and other contaminants content. The oil content was determined as total hydrocarbon in the sample using Gas chromatography. The mineral contents were analyzed as TDS and salinity content. The suspended solid were represented by turbidity analysis, and the organic content was measured as chemical oxygen demand (COD). Average concentrations of constituents in the feed are summarized in Table 1.

Table 1 Concentration of major constituent in the feed solution

Analyte	Unit	Concentration
TDS	mg/L	5800
Turbidity	NTU	7.80
Salinity	mg/L	5238
Sulfide	mg/L	67.20
COD	mg/L	150.82
Oil Content	mg/L	0.15

Based on Table 1, the concentrations of constituents such as oil content, mineral, and COD in produced water feed did not meet the specific requirement for disposal. Moreover, for clean water usage of produced water, the concentration of mineral can cause corrosion in the metal equipment. Hence, the proper treatment of the produced water feed is required.

3.0 RESULTS AND DISCUSSION

3.2 Nano Hybrid PES Membranes Characterization

FT-IR spectra were used to investigate the specific functional groups of the prepared membrane. The specific functional groups of the membrane are essential since they played a major role in transport properties of the membrane. According to the FT-IR spectra, as depicted in Figure 2, it verifies that the membrane was formed by the consistence of diaryl sulfone (Ar-SO_2-Ar) and diaryl ether (Ar-O-Ar) as PES backbone. This is due to the presence of medium to strong bands at 1151 and 1242 cm^{-1}, respectively. The typical aromatics (C-H) bond also appears as indicated by peaks at 837 and 867 cm^{-1}. The comparison of FT-IR spectra between the untreated nano hybrid PES-SiO_2 membrane with the treated nano hybrid PES-SiO_2 membranes (Ac-Et immersion and UV irradiation) shows an alteration in the structural-functional group. The new peaks are found at 2350 cm^{-1} for both treated membranes with UV irradiation and Ac-Et immersion. The intensity change also occurred in the treated membrane showed higher peak intensity at 1400, 1300, 1200, 1100, and 860 cm^{-1}. The highest intensity of those peaks was displayed by a membrane with Ac-Et immersion. This could be indicated that the treatments successfully changed the chemical structure of the membrane. At those peaks, the hydrophilic functional groups such as carbonyl, C-O, and hydroxide (OH) may exist. The acetone-ethanol in the mixture of immersion solvent results in hydrophilic enhancement, and this also showed by a membrane with UV irradiation treatment. This hydrophilic enhancement was expected to lead to the permeability and anti-fouling behavior enhancement.

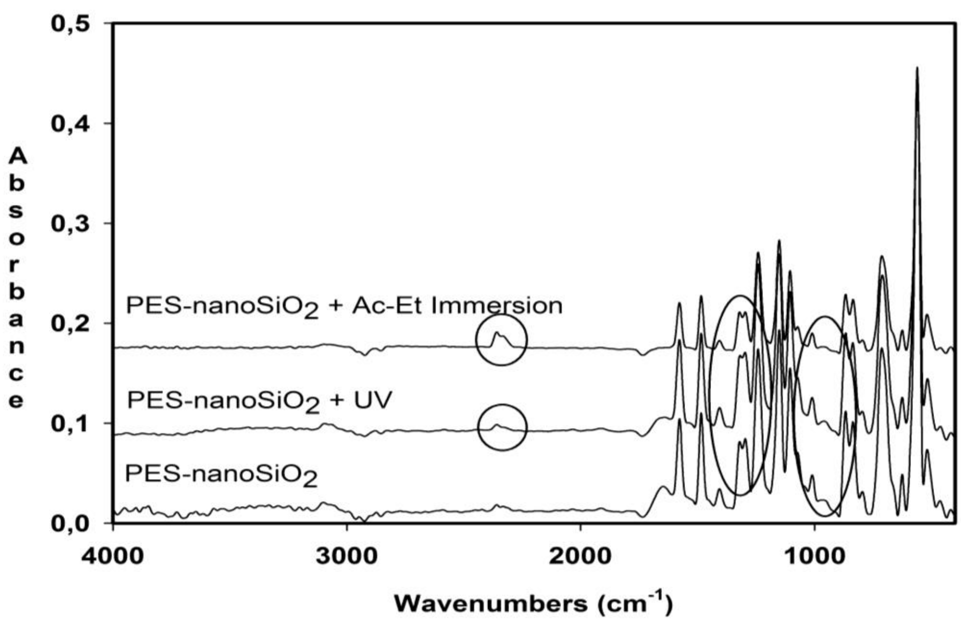


Figure 2 FT-IR spectra of nano-hybrid PES-SiO_2 membrane

The SEM analysis was performed to characterize the surface morphology of the nano hybrid PES-SiO_2 and PES-ZnO membranes. Figure 3 shows six SEM images of membrane surface at different treatment. The Figure 3.A presents the surface of nano hybrid PES-SiO_2 without any modification treatments. The membrane surface was dense and smooth, The nano-SiO_2 particles were observed spreading on the membrane surface. It indicates that nano-SiO_2 is well mixed homogenously. However, at the magnification of 20,000x, the pores of the membrane could not be observed confirming that the pores were in the nano-scale. The nano-gaps between nano-particles and the polymer was not found. It seems that nano-SiO_2 has a good interaction behavior with PES polymer and are attached each other. Figure 3.B displays the surface morphology of nano hybrid PES-ZnO. Compared to the images of nano hybrid-silica, the image of nano-ZnO formed an aggregation between nano-particles to form a nano domain on the membrane surface. It indicates that the cohesion between nano-ZnO particles is higher than the adhesion between nano particles and PES polymer matrix. The formation of nano domain induced the higher permeability but lowering the solute rejection due to the formation of nano-gaps among the nano particles in nano domain. This phenomenon could also be affected by the shape of nano particle itself. Nano-SiO_2 has mostly spherical shapes while nano-ZnO was a cube-like shape. The particle shapes were expected to provide an influence on nanoparticle distribution on the membrane surface.

The nano hybrid membrane with Ac-Et immersion and without immersion is displayed in Figure 3.C and 3D. Based on the Figure 3.C, the SEM image shows the surface morphology of nano hybrid PES-SiO_2 without immersion treatment in Ac-Et mixture. As mentioned in the previous discussion, nano hybrid PES-SiO_2 membrane has a smooth and dense surface, and the nano-SiO_2 particles are well distributed on the membrane surface. Figure. 2.D displays the SEM image of nano hybrid PES-SiO_2 membrane surface morphology with immersion in the mixture of Ac-Et (1:3) for 24 h. The image shows the membrane surface with an appearance of nanosilica particles aggregation. Furthermore, after immersing in the Ac-Et, it seems that the solvent attracted the outer surface of the membrane due to its high affinity for ethanol and membrane surface with the appearance of nanosilica embedded in the outer membrane layer. No pore was observed at this magnification, indicating that the immersion in the Ac-Et had no significant effects on the membrane pores structure.

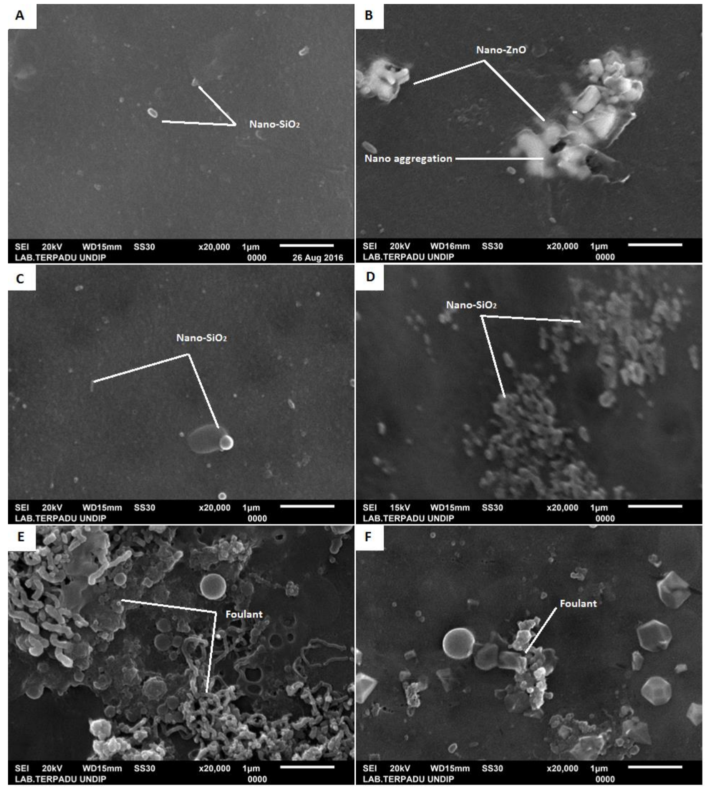


Figure 3 Surface morphology of Nano hybrid A) PES-SiO_2; B) PES-ZnO; C) without immersion in Ac-Et; D) immersed in Ac-Et; E) unirradiated under UV light; and F) Irradiated under UV light

Figure 3.E and 3.F show the SEM images of membrane surface morphology examining the effect of UV irradiation treatment. The observed membranes are the membranes that have been used in produced water filtration. This observation was performed to investigate the anti-fouling behavior of membrane after being irradiated under UV lights. Based on the Figure 3.E, the SEM image showing the surface of the membrane without UV treatment indicated high foulant deposition on the membrane surface. This could be due to the activity of oil droplet with PES matrix. The PES is originally slightly hydrophobic, and hence the oil droplet will easily adhere to the membrane surface to form foulant blockage. On the other hand, figure 3.F shows SEM image of membrane surface with UV irradiation. The figure confirms less foulant deposition on the membrane surface and indicates that the UV irradiation on the membrane surface enhances anti-fouling behavior.

3.3 Nano Hybrid Capability for Oil Removal

Produced water is a byproduct of oil and gas industry. One of the main parameters of the produced water is the content of oils and grease. Produced water generally contain a high concentration of oil, and for reuse purposes, the oil and grease in the produced water must be minimalized [31]. The oil and grease present in produced water can be either paraffin and aromatic hydrocarbons such as benzene, ethylbenzene, toluene, and xylene. Table 2 shows the results of the processing of produced water using PES membrane and modified PES membrane.

Table 2 Oil and Grease rejection

Membrane	Total Oil and Grease content (mg/L)		Oil and Grease rejection efficiency
	Feed produced water	Permeate water	
Pure PES membrane	0,150	0,10	33%
$PES\text{-}SiO_2$ membrane	0,150	0,00 (< LOD)	>99%

The polyether sulfone membrane can reject oils and grease in the produced water up to 33%. The polyethersulfone is a membrane material having slightly hydrophobic properties. Then, it would be difficult to be applied for separation of oil and grease from produced water. The improvement of hydrophilic properties of the membrane should be conducted to increase oil and grease rejection. In this study, embedded nano-SiO_2 in PES membrane gives much better rejection of oil and grease up to >99%. Good hydrophilic particles such as silica which were dispersed in membrane enhance the hydrophilic properties, tensile strength, and the anti-fouling ability of membrane [32]. In this study, the addition of nanosilica enhances the hydrophilic properties and the anti-fouling ability of the PES membrane to reject oil and grease effectively. By using a hydrophilic membrane, the adhesion of oil on the membrane surface could be decreased. This subsequently resulted in the reduction of membrane fouling and enhancement of water productivity [33].

3.4 Effects of Nano-SiO_2 Loading on Nano Hybrid PES Membrane Performance

The performance of nano hybrid PES-SiO_2 membrane can be evaluated according to the flux and rejection profile. In order to investigate the effect of nanosilica concentration on membrane performance, the membranes with various nanosilica loading ranging from 0.5 to 1.5 wt% were prepared. Membrane flux measurements were carried out using cross-flow filtration system for measuring the membrane permeate flow rate. The results of flux measurements profile of nano hybrid PES-SiO_2 membrane for produced water treatment are shown in Figure 4.

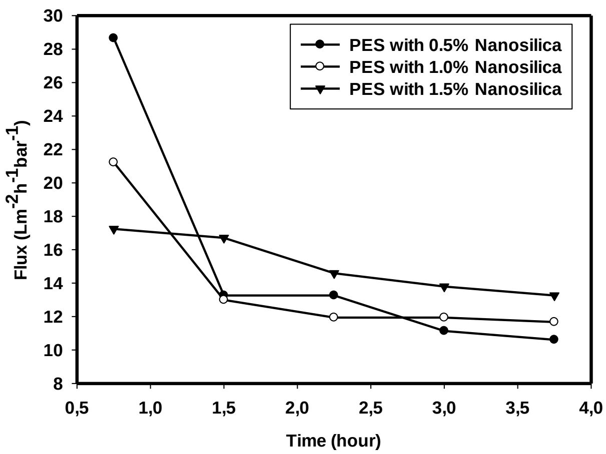


Figure 4 Permeate water flux of nano hybrid PES-SiO_2 membranes

Based on Figure 4, it can be seen that in the early minutes, the highest flux performance was achieved by PES membrane with 0.5 %-wt of nano-SiO_2 loading, (flux of 28.85 $Lh^{-1}m^{-2}bar^{-1}$). This is due to the initial conditions, the more number of pores present in the membrane with lowest nanoparticles loading. The silica particles occupy membrane pores thus blocking the water molecules to pass through the membrane pores. However, with the increase of operating time filtration, the permeate water flux of nano hybrid membrane with nano-SiO_2 concentration 0.5 and 1.0 %-wt decreased drastically to 12.15 and 14.86 $Lh^{-1}m^{-2}bar^{-1}$, respectively. On the contrary, the membranes with 1.5 %-wt nano-SiO_2 loading had stable flux at 14,87 $Lh^{-1}m^{-2}bar^{-1}$. This phenomenon occurs as a result of the deformation of the pores of the membrane. On the membrane with lower nano-SiO_2 loading, the pores of the membrane undergo to deform and compacted. In contrast, the nanosilica loaded membranes are dimensional stable due to the capability of nanosilica particle in holding the membrane structure and the addition of nanoparticle enhances structure stability of membrane [34]. Hence, the addition of nanosilica is able to maintain flux PES membrane, as confirmed by the previous study [35]. It was stated that water flux of the mixed matrix membranes significantly improved after the addition of both types of ZnO nanofillers due to a higher hydrophilicity and porosity of the prepared membranes. The similar result has been achieved by Ghandashtani *et al*. [34] which studied nanosilica embedded PES membrane. They found that high concentration of nanosilica can increase hidrophylicity of PES membrane but lower its porosity. The effects of nano-SiO_2 loading on the nano hybrid PES-SiO_2 membrane rejection was performed by analyzing TDS, turbidity, sulfide, salinity, and COD in the feed and permeate water. The results of rejection efficiency of nano hybrid PES-SiO_2 membrane with different concentrations of nanosilica loading is shown in Figure 5.

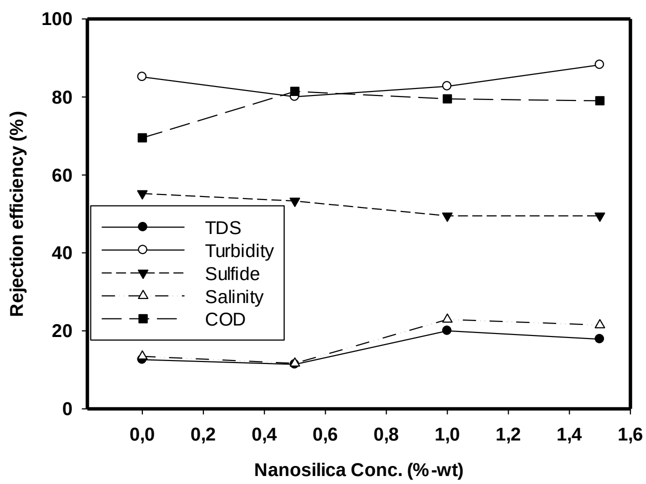


Figure 5 Rejection efficiency of nano hybrid PES-SiO_2 membranes with different nano-SiO_2 concentration

Based on Figure 5, it can be seen that the rejection of total dissolved solid increases due to the existence of nanoparticles which acts as a molecular sieve with excellent separation properties. On the other hand, the PES membrane without nano-SiO_2 loading has the lowest rejection performance, that is 12.31%. The highest TDS rejection performance achieved by nano hybrid membrane with a nano-SiO_2 concentration of 1.0 %-wt, with the rejection efficiency is 19.50% for TDS. Based on the rejection profile of turbidity, the neat PES membrane appeared to have stable rejection performance is stable at 85%, while the best performance was demonstrated by the rejection of nano hybrid membrane PES-SiO_2 membrane 1.5 %-wt with the rejection of turbidity reaches 93 %. According to Figure 5, it can be observed that the rejection of sulfide using neat PES membrane PES is 54% with the best performance of rejection was shown by pure PES membrane. In contrast, the lowest performance of rejection was demonstrated by the nano hybrid PES-SiO_2 membrane 1.5%-wt. It indicates that sulfides were significantly removed using more hydrophobic membrane instead of a hydrophilic membrane. The rejection of the produced water salinity by a nano hybrid membrane is higher than the neat PES membrane. Nano hybrid PES-SiO_2 membrane of 1.0 and 1.5% membrane capable of rejecting salinity up to 25 %. On the other hand, for nano hybrid PES-SiO_2 membrane of 0 and 0.5% rejected the salinity in the range of 15 %. COD represents the organic compounds contained in the produced water which can be chemically oxidized. The most of COD in the produced water is emulsified oils and glycols. Figure 5 shows that the neat PES membrane displays the lowest COD rejection performance, which is having rejection value about 70%. While for all the nano hybrid PES-SiO_2 membranes showed a similar rejection performance ranging from 78 to 82 %.

Based on the rejection performance as depicted in Figure 5, it demonstrates that the membranes with nanosilica loading provided better performance than the rejection of membrane without nanosilica loading. This such behavior is related to the interactions at the interface between the nano-fillers and the polymer matrix. These interactions are strong due to the formation of an amorphous layer of immobilized polymer molecules on the silica nanoparticles. This is attributed to the smaller particle size and the better uniformity of their dispersion inside the solution. According to the Figures 5, the percentage of rejections are different each other. For example, turbidity has the highest rejection level about 95% followed by COD rejection, the sulfide rejection, and the lower rejections are TDS and salinity. This has a relation with the similarity of separation mechanism in the membrane and conventional filtration where particles having a size larger than the pore size will be rejected. The turbidity of produced water is caused by insoluble compounds or suspended solid in water which has a particle size ranging from 2-30 μm [36]. The particle size of suspended solids is much larger than membrane pore size which is ranging from 2-100 nm, while TDS and salinity are minerals salt which has particle size lower than 100 nm.

3.5 Effects of UV Irradiation on Nano Hybrid PES Membrane Performance

To observe the effect of the combination of the nanosilica addition and UV modification, the membrane was fabricated with 1.5 wt% nanosilica loading and was exposed using UV light for 2, 4, and 6 minutes. Then the membrane is used to treat produced water to evaluate the flux and rejection. The profile of the modified nano-hybrid PES membrane is shown in Figure 6.

Figure 6 indicates that the flux decreased during filtration operation using a PES membrane. The highest flux was achieved by nano hybrid PES-SiO_2 membrane with UV irradiation for 6 minutes. The permeate water flux value at the initial of operation is 32.36 $Lh^{-1}m^{-2}bar^{-1}$ and decreased to 21.2 $Lh^{-1}m^{-2}bar^{-1}$. The lowest flux was achieved by a nano hybrid PES-SiO_2 membrane without UV irradiation treatment at flux in the range of 13-17 $Lh^{-1}m^{-2}bar^{-1}$. This phenomenon is caused by the effects of UV light exposed to the polymer membrane. The UV light-induced the polymer chains to restructure and grafting resulting on the denser polymer. The longer exposure of UV light on the membrane surface, it leads to the polymer chain degradation of polyethersulfone polymer. As the consequences, the membrane pores will be larger, and the UV treatment increases the hydrophilicity of PES membrane as well as increases the flux [28]. This result corresponds with previous research performed by Nor *et al.* (2016). It was reported that the nano-TiO_2 composite PVDF membrane under UV irradiation would increase the hydrophilicity of the membrane due to rich of hydroxyl group formation, this condition leads to higher flux ratio of the membrane. The similar result also has been reported by Konruang *et al*. [27] where PES membrane becomes more hydrophilic after exposing under UV lights.

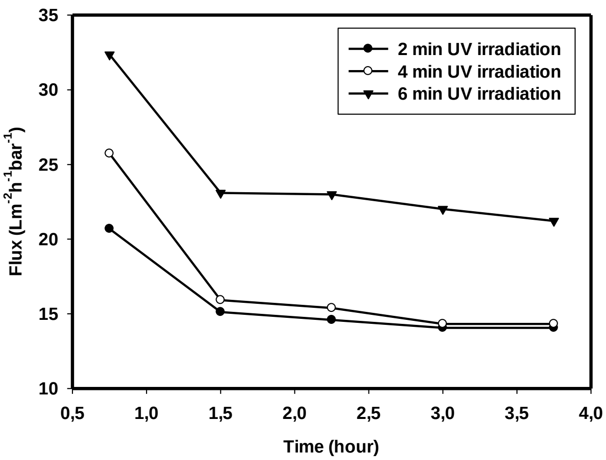


Figure 6 Permeate water flux of UV-irradiated nano hybrid PES-SiO_2 membranes

3.6 Performance Comparison of Nano Hybrid PES-SiO_2 and PES-ZnO Membranes

In this study, the performance of nano hybrid PES-SiO_2 and PES-ZnO in produced water treatment was compared. Figure 7 shows the water flux of both membranes depending on time operation. The flux decrease along with separation process time. The flux decrease was caused by foulant deposition on the membrane surface. In addition, this provides a hindrance for water molecules to pass through the membrane. The permeate water flux of nano hybrid PES-ZnO membrane was higher than PES-SiO_2 membrane. It corresponds to the surface structure morphology of membrane. As described in the Membrane Characterization section, the nano-ZnO formed an aggregation to form nano-domain on the membrane surface. This nano domain induced the high permeability due to a void fraction (nano-gaps) among the nano particles in the domain. By using the nano-ZnO, the water permeability increased to about 20 % compared with nano-SiO_2. Both of nano-ZnO and nano SiO_2 are hydrophilic particles, but the nano-ZnO has a stronger hydrophilic characteristic, and hence it could not perfectly attach to PES matrix due to the hydrophobicity of PES molecules.

The permeates from both membrane were evaluated, and the result showed that the pollutant rejection of PES-ZnO membrane was slightly lower than nano hybrid membrane PES-SiO_2 as illustrated in Figure 8. The water permeate of nano hybrid PES-ZnO is much higher with relatively constant rejection. Undoubtedly, PES-ZnO membranes are more favorable to be applied in produced water treatment. These promising results indicate that the nano hybrid membranes could be successfully implemented for salts rejection from saline water and for their use as a pretreatment in reverse osmosis desalination plants.

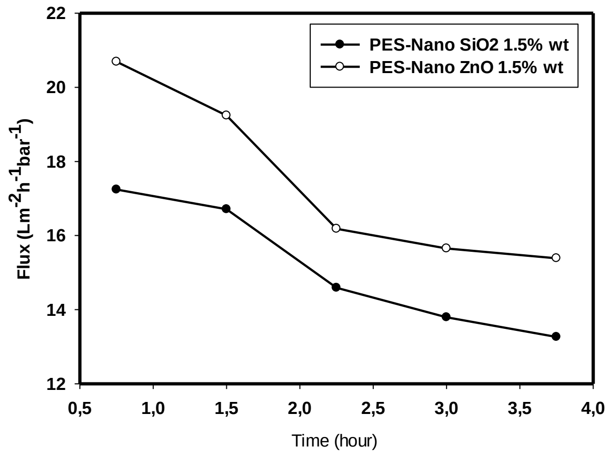


Figure 7 PES-SiO_2 and PES-ZnO membranes performance in terms of permeate water flux

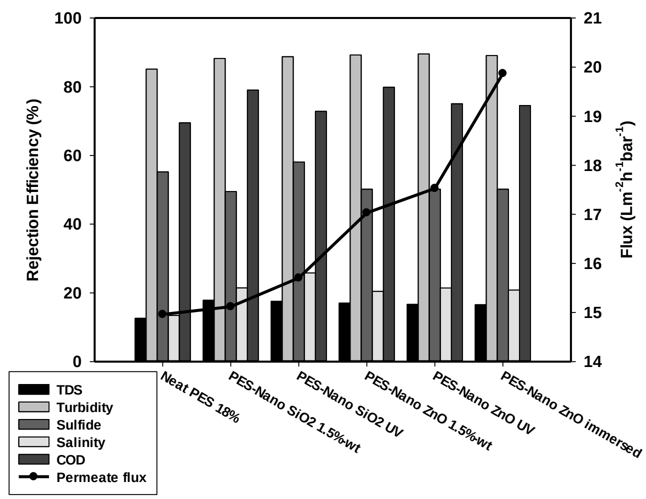


Figure 8 The performance of various membranes

3.7 Effects of Immersion in Ac-Et on Nano Hybrid PES Membrane Performance

Permeate water flux of the membranes was measured by filtering produced water as illustrated in Figure 1. The permeation fluxes for Nano hybrid PES-ZnO membrane according to various treatments are shown in Figure 9. It can be seen that the flux of all membrane decreases during the filtration process. In addition, the Figure 9 confirms that nano hybrid PES-ZnO membrane after being immersed in the mixture Ac-Et and without immersion in Ac-Et shows an enhancement performance. It displays higher fluxes for immersed nano hybrid membrane compared to the nano hybrid PES-ZnO membrane without immersion in the Ac-Et. This could be due to the membrane was wetted easily when the membrane was immersed into Ac-Et. The membrane wetting could lower the surface tension and enhance the hydrophilic properties of the membrane, resulting in higher membrane fluxes.

The increase of permeate water flux could be due to the effect of immersion membrane into Ac-Et 1:3 reduce the surface tension of the membrane. Acetone has a surface tension of 25.2 dyne/cm while Ethanol has a surface tension of 22.1 dyne/cm. the higher concentration of ethanol in the mixture lowering the total surface tension of the mixture. Kochan *et al*. [37] found that the immersion of PES into the organic solvent changed the surface tension of the membrane. Surface tension is a very important factor that plays a role in enhancing the permeate water flux. The lower surface tension indicates the lower resistance in the interface between feed water and membrane surface. Besides that, the UV irradiation induces the formation of the hydrophilic group. The hydrophilic membrane was known obtained higher permeate water flux [38].

The immersion of membrane material in the organic solvent has been reported to be able to give effects to membrane transport properties. This can be concluded that the concentration of ethanol contributed to the permeate water flux of the membrane. The presence of ethanol-induced the hydrophilic property of the membrane surface, leading to the permeate water enhancement. The similar phenomenon was reported by Tolwinska *et al*. [39]. They stated that alkyl alcohol strongly enhanced the permeate water flux of the membrane and the shorter alkyl chain gives a greater effect of hydrophilicity.

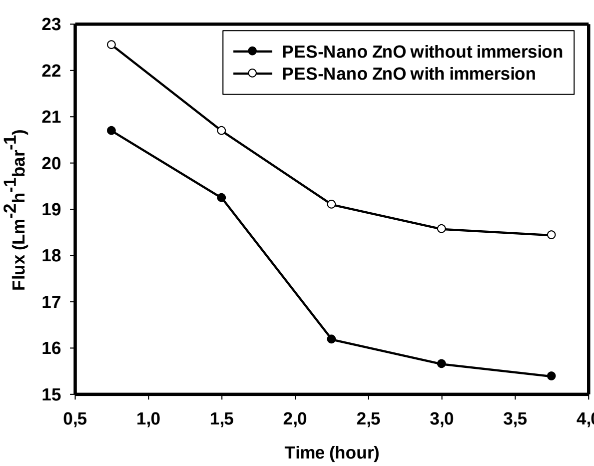


Figure 9 Flux profile of nano hybrid PES-ZnO with and without Ac-Et immersion

3.8 Stability and Fouling Analysis

Evaluation of nanofiltration for produced water treatment for 8 h was performed to evaluate the separation and anti fouling behavior of fabricated membrane. Figure 10 displayed the time dependency of the permeate water flux and rejection of nano hybrid PES-ZnO membrane with Ac-Et Immersion treatment. As shown in Figure 10, it can be seen that nano hybrid PES-ZnO membrane with immersion in the mixture of Ac-Et 1:3 for 24 h shows stable permeate water flux in. In addition, the figure presents the permeate water flux of all membrane decrease at an early period of filtration process and then approached a steady state condition after 2 h of the filtration process. This flux decrease is due to the membrane fouling by oil droplet and organic materials contained in the produced water which deposits on the membrane surface. Moreover, it is presented that even the membrane showing the decrease in flux, but the flux of modified nano hybrid membrane tends to reach constant fluxes until the end of the filtration process. This indicates that the modified nano hybrid membrane performed an anti-fouling behavior. This was supported by the previous researcher that the hydrophilic membrane has better anti fouling performance than the hydrophobic membrane. During the filtration process, the drastically increase of flux is not observed, indicating that the membrane excellent stability in membrane durability. This can be said that nano hybrid membrane with immersion in Acetone-Ethanol 1:3 for 24 h has an excellent stability performance in term of permeate water flux.

Another parameter concerning the membrane performance is rejection. The rejection defined as the capability of membrane materials to reject undesired pollutant present in the feed solution and allow only the desired component to pass through the membrane barrier. Figure 10 also displays the rejection rate for TDS by nano hybrid PES-ZnO membrane after being immersed in the mixture of Ac-Et for 24 h.

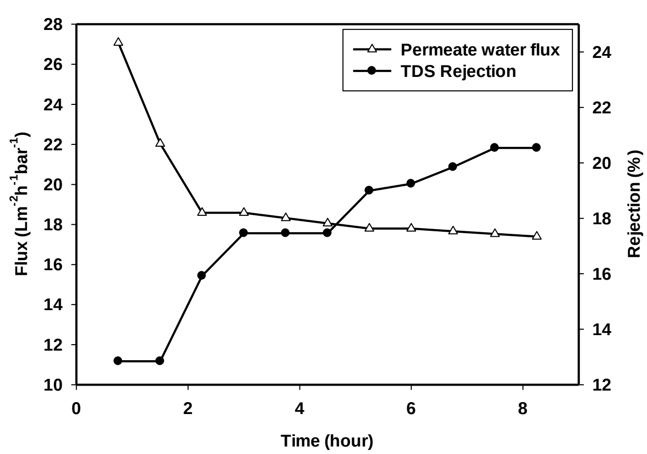


Figure 10 Stability performance of nano hybrid PES-ZnO membrane with Ac-Et immersion

As shown in figure 10, the TDS rejection of nano hybrid membrane PES-ZnO approach a steady state condition after 3 h filtration process. Ahmed *et al*. [40] reported that the addition of acetone to the PES molecule for membrane fabrication decreased the porosity in the sublayer and increased pore volume in the skin layer of membrane. The results proved that the combination treatment of UV irradiation and immersion in the Acetone-Ethanol on nano hybrid PES-ZnO membrane enhanced the permeate water flux up to 20% even the TDS rejection was slightly lower compared with nano hybrid PES-ZnO membrane without immersion in Ac-Et.

The permeate water flux and pollutant rejection are the most important parameter to determine the performance of the membrane. Permeate water flux is defined as the volumetric flow rate of pure water which is drawn in the downstream of membrane per unit area. High flux rate of a membrane is favorable, and many methods have been conducted to enhance the permeate water flux of membrane. Rejection also takes an important place in determining the performance of the membrane. Besides the permeability and solute rejection, the anti-fouling behavior of the membrane is an important characteristic for the favorable membrane.

According to the SEM image analysis in the previous discussion, it was showed that the membrane after being irradiated under UV lights and Ac-Et immersion has lower foulant deposition on the membrane surface. This behavior was due to the enhancement of hydrophilicity of the membrane. In summary, the nano hybrid PES-SiO_2 and PES ZnO inhibited the formation of foulant deposition on the membrane surface and showed an anti-fouling behavior.

4.0 CONCLUSION

The fabrication of nano hybrid PES-SiO_2 and PES-ZnO are feasible to be manufactured using NIPS method. The addition of nano-particles SiO_2 and ZnO to the PES matrix significantly enhanced the permeability, solute rejection and mechanical strength of the membranes. The modification treatments comprising UV irradiation and Ac-Et immersion improved the hydrophilicity of membranes material and the anti-fouling behavior of the membrane.

(i) The SEM images showed that SiO_2 nano particles have better distribution in PES membrane than the ZnO nanoparticles. UV irradiation and Ac-Et immersion of nano hybrid membrane reduced the foulant deposition on the membrane surface.
(ii) The FT-IR results presented that modification treatments changed the chemical structure of membrane to become more hydrophilic.
(iii) The nano-particles loading is the important factor that plays a role in the membrane separation properties. The higher concentration of nano particles increased the permeability, but the concentration above 1.5 % wt demonstrated an aggregation of the polymer. The distribution of nano particles was influenced by their shapes and intermolecular affinity.
(iv) UV irradiation on the membrane material induced the formation of the hydrophilic functional group and the longer irradiation time caused polymer photo-degradation.
(v) The immersion in the Ac-Et enhanced the hydrophilicity of membrane material and lowered the surface tension.

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