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Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

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Abstract

Oil exploration waste, also called produced water, contains hazardous pollutants, such as benzene; benzene, toluene, and xylene (BTX); naphthalene, phenanthrene, and dibenzothiophene (NDP); polyaromatic hydrocarbons (PAHs); and phenol. Produced water is characterized by high chemical oxygen demand (COD) and oil content, which exceed the standard limits of regulation. In this study, the combination of ultrafiltration (UF) and ozone pre-treatment and post-treatment were applied for treatment of produced water to minimize its environmental impact. Produced water and membrane were characterized, and their ultrafiltration performance for removal of oil content, benzene, toluene, xylene, and COD. Two commercial polyethersulfone membranes, with molecular-weight cut-off values of 10 and 20 kDa, were used. The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Separation performance was evaluated based on flux profile and removal of COD, oil and grease content, toluene, and xylene. The flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Significant finding was found where the combination of UF with ozone pre-treatment and post-treatment could significantly eliminate COD, oil content, toluene, and xylene. The rejection of these components was found higher than conventional process, which was in the range of 80% to 99%. In addition, almost oil and grease can be removed by using this combined system. Permeate quality of this system confirmed the acceptable level as water discharge.

Keywords

Ultrafiltration, Ozone, Produced Water, Benzene, Toluene, Xylene

1 Introduction

Oil explorations are the primary source of energy, and their corresponding activities generate a large volume of oilfield wastewater, also referred as produced water. For each barrel of oil, three barrels of produced water are generated [1]. In general, produced water is reused to enhance oil recovery or treated prior to discharge into the environment. Produced water comprises various organic and inorganic substances, which are potentially characterized as hazardous and toxic wastes. Produced water compound is categorized as organic substance, inorganic substance, and radionucleotide. Moreover, produced water contains important compounds, such as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids, and dissolved gases [2]. Oils consist of monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAH), and related heterocyclic aromatic compounds [3]. BTEX and phenols are dissolved in water. Residual chemicals, such as corrosion and scale inhibitors, emulsion breakers, and biocides, are also present in produced water [4].

Compounds in produced water are toxic and adversely affect the environment. Bakke et al. [5] published a review of the environmental impact of produced water and oil drilling in the offshore petroleum industry. Alkylphenols, naphthenic acids, and PAHs from produced water may disrupt reproductive functions and affect several chemicals, biochemical, and genetic biomarkers. As a consequence of the lethal effects of produced water contaminants, many countries have implemented a stringent regulatory standard for discharging produced water to alleviate their adverse environmental impacts. Produced water quality can be represented as oil content or concentration and chemical Oxygen Demand (COD). The concentrations of oil and COD in produced water are relatively high, reaching 565 and 1220 mg/L, respectively [1]. The government of the Republic of Indonesia through Regulation of the Minister of State for Environment No. 19 set standard limits for wastewater for oil and gas activities in 2010. The permitted oil concentration and COD are within 20–50 and 200 mg/L, respectively. Hence, treatment of produced water is a responsibility for oil and gas explorations.

Membrane technology has been applied to treat produced water and reviewed comprehensively [6]. Ultrafiltration membrane is also an appropriate method for produced water treatment. Ultrafiltration (UF) is a low-pressure driven membrane filtration process operating at 2–10 bar [7]. The pore size of an UF membrane ranges from 0.001 µm to 0.1

µm; as such, the membrane rejects compounds with molecular weight of 1000 to 100.000 Da [8]. Several researchers have examined the use of UF membranes for handling produced water [9-13].

However, studies on produced water treatment only investigated method performance through determination of general effluent parameters, such as COD, BOD, total dissolved solids, total suspended solids, oil content, and total organic carbon and analysis of anions and cations. Several studies have evaluated specific BTX content in produced water [14-16]. However, to the best of our knowledge, limited works have examined the performance of UF in BTX removal. The present study mainly aims to investigate the performance of ultrafiltration in treating produced water, specifically in filtering BTX pollutants. In detail, polyethersulfone (PES) was selected as membrane material for ultrafiltration due to its hydrophilic property. To enhance the ultrafiltration performance, this research combined ultrafiltration and ozone pre-treatment and post-treatment for removal of produced water compounds. Ozone was selected because it can break up large organic molecules. Ozone can break complex molecular organic compounds in crude oil, which is a component of produced water [17-18]. Ziabari et al. [19] studied the removal of hydrocarbons from aqueous solution by ozonation. In addition, Zha et al. [20] reported that ozone could oxidize compounds having a large molecular weight to generate smaller compounds. Ozone can also reduce fouling associated with microfiltration and ultrafiltration [21-24]. Hence, we confirm novelty of this research by implementing the combination of ultrafiltration and ozone to improve ultrafiltration performance for produced water treatment. The improvement was achieved not only in the term of permeate quality but also reduction of membrane fouling. Results provide novel significant findings in this research area.

2 Materials and Method

2.1 Membrane characterization

Two available commercial membranes made of PES (NADIR Filtration, Germany) were used to filter produced water. Membranes with molecular-weight cut-off of 10 and 20 kDa and were labeled as PES 1 and PES 2, respectively. Specific functional groups were identified using Fourier transform infrared spectroscopy (Shimadzu IR Prestige-21). Specific functional groups were examined based on their wavelength as a function of absorbance (Fig. 1).

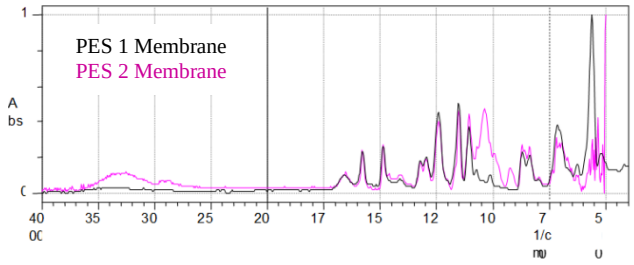


Fig. 1 FTIR results of PES 1 and PES 2 membranes

Similar peaks at 1577.77 and 1485.19 cm^{-1} are characteristics of PES membrane. Peaks at 1485,19 and 1577.77cm^{-1} indicate the presence of aromatic components (C=C stretching) in benzene, and peaks at 1240.23 and 1242,16 cm^{-1} represent ether aromatic compounds [25-26] (Saha et al. 2007, Belfer et al. 2000). In addition, peaks at 1151.5 and 1105.21 cm^{-1} exhibit SO_2 symmetrical stretching and are assigned to a sulfuric component. Peaks at 1656 and 1321 cm^{-1} are predicted as preservative PVP (poly-N-vinyl-2-pyrrolidone) because it is an additive polymer used for pore formation on PES and polysulfone membrane [26]. Moreover, a specific peak at 3500-3000 cm^{-1} is assigned to PES 2 membrane and indicates the existence of OH stretching radical. The PES 2 membrane was found to be more hydrophilic than the PES 1 membrane.

Table 2 summarizes the properties of UF membrane in relation to its pore size and water flux.

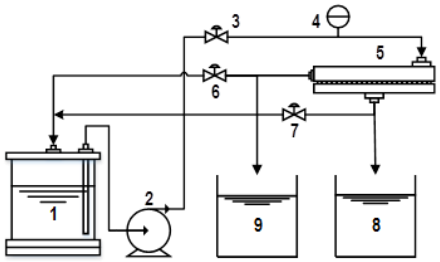
Table 1 Properties of UF membranes used in this work

Membrane	MWCO (Da)	Pure Water Flux ($L/m^2.hr$)
PES-1	10.000	11.25
PES-2	20.000	94.27

Table 1 shows that the pure water flux of the PES 2 membrane was higher than that of the PES 1 membrane. The pure water flux was mainly determined by membrane pore size and its surface hydrophilicity [27]. Given that the PES 2 membrane possessed a large pore size, it exhibited higher pure water flux. Membrane surface morphology was analyzed by scanning electron microscopy (FEI, Type Inspect-S50, Japan) at a specific magnification.

2.2 Ultrafiltration

Ultrafiltration experiments were conducted in a homemade laboratory-scale test cell. The apparatus consisted of a 500 mL feed tank, a pump, a pressure indicator, and a stainless steel membrane cell. Fig. 2 shows the schematic of the ultrafiltration cell.



1. Feed Tank
2. Feed Pump
3. Feed Valve
4. Pressure Gauge
5. UF Membrane Module
6. Retentate Recycle Valve
7. Permeate Recycle Valve
8. Permeate Tank
9. Retentate Tank

Fig. 2 Schematic of the ultrafiltration cell

All filtration runs were carried out at room temperature (29 ± 2°C). The membrane was compacted by filtering water through the membrane at a pressure of 2 bar for 0.5 h. For each experimental run, a new circular membrane sheet with an area of 13.85 cm2 was used for measurement of initial water flux (J0). Initial water flux (J0) was determined by measuring the volume of permeate water collected at a specific recording time. Filtrations were carried out using total recycle mode, where both permeate and retentate were recycled to the feed tank, to maintain the same concentration. Permeate flux (J) was determined by analytically weighting permeate collected at every 5 min intervals for 60 min. Membrane or permeate fluxes (J) were calculated by dividing the volume of permeate (Q) by the effective membrane area (A) and the sampling time (t), as defined in Eq. (1):

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

where:

J: flux (L/ m^2h), Q: volume (L), A: membrane area (m2), and t: time interval (h).

The ability of the membrane for removing specific pollutants from produced water was determined by % rejection (R). Membrane rejection was calculated by dividing the difference between the concentration of a specific pollutant in the feed (Cf) with the concentration of specific pollutants in permeate (Cp), as expressed in Eq. (2).

$$\%R = 1 - \frac{Cp}{Cf} \times 100\% \quad (2)$$

In this research, the term rejection and permeate and feed concentrations refers to rejection and concentrations of COD, total oil content, toluene, and xylene.

2.3 Ozonation

Ozonation pre-treatment and post-treatment were conducted by Ozonizer, a generator (Krisbow) and flow meter. In the pre-treatment process, ozone was purged into the produced water feed. For the post-treatment, ozone was added into the permeate. Ozone concentration was tested using HI38054 Ozone Test kit. The ozone flow rate was set as 2 L/min, the contact time was 5 min, and the corresponding ozone concentration was 0.3 mg/L.

2.4 Produced Water Quality Analysis

Produced water was collected from offshore facilities in Cepu region, Central Java, Indonesia. Water quality was assessed using the produced water in the feed and permeate. COD of the feed and permeate samples were determined by Test Tube Heater-COD Reactor (HANA HI 839800). Analysis on the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry. Table 2 shows the characteristics of produced water.

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	1872 mg/L
Oil and grease content	931.01 mg/L
Benzene	<0.8 mg/L
Toluene	2.62 mg/L
Xylene	3.11 mg/L
Fenol	<0.03 mg/L
Ammonia	0.22 mg/L
pH	8

According to Table 2, the mean levels of benzene, toluene, and xylene in the produced water sample were below 0.8, 2.62, and 3.11 mg/L, respectively. For comparison, produced water was also collected from the Bonsucesso treatment plant, State of Sergipe, Brazil and had average concentrations of 1397, 1263, and 312 μg/L for benzene, toluene, and xylene, respectively [15]. Similar results were also found in an oilfield wastewater platform in the Gulf of Mexico. Examination of oilfield wastewater in those area indicated that the concentrations of benzene, toluene, and xylene were 0.8–4.6, 1.0–3.5, and 0.2–0.7 mg/L, respectively [16]. In the Campos Basin, State of Rio de Janeiro, Brazil, the levels of benzene, toluene, and

xylene were 283–1855, 87.04–2224, and 67.35–5969 mol/L, respectively [14].

3 Results and Discussions

3.1 Membrane Flux Behaviour

Normalization of flux profiles (J/J0) as a function of time is presented in Fig. 3.

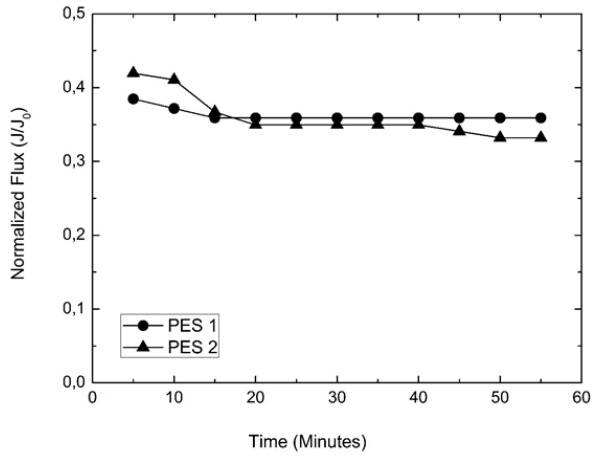


Fig. 3 Performance of membrane normalized fluxes as a function of time in treatment of produced water by using membranes with different pore sizes (TMP = 1 bar)

In general, the flux showed a declining trend during ultrafiltration. The reduction of membrane flux is a characteristic of membrane fouling, which can be generated by an increase in membrane resistance due to pore blocking, concentration polarization, and cake formation [22]. Fouling can be related to the accumulation of a substance (called foulant) on the membrane surface or inside the membrane pores. At the beginning of ultrafiltration, no foulant deposit was found on the membrane surface. As the time increased, foulants accumulated on the membrane surface and generated a cake/gel layer, leading to decreased flux value and normalized fluxes. In the ultrafiltration treatment of produced water, its components, such as oil and other organic compounds, are significant sources of fouling. Ashaghi et al. [28] and Maguire-Boyle and Barron [29] proposed that fouling during filtration of produced water could be due to biofouling, scaling, organic fouling, and colloidal fouling. Fouling could also be attributed to microbial contaminants (biofouling), salt precipitation resulting in scaling, organic fouling due to pore plugging or pore coating by hydrocarbon compounds, and clay and silica accumulation on the membrane surface (colloidal fouling). However, flux reduction was relatively steady along with time because of the compression of the cake/gel layer and its constant thickness.

The flux decline of the PES 2 membrane was more pronounced than that of the PES 1 membrane. The flux decline (final flux compared with the initial flux) values of PES 2 and 1 membranes were found to be 8.7% and 2.5%, respectively. The flux decline can be explained by membrane fouling caused by pore blocking or membrane adsorption due to contaminants in the produced water. The pore size of the PES 1 membrane was slightly smaller than that of the PES 2 membrane. Contaminants with size bigger than the membrane pores have a tendency to form a cake/gel layer on the membrane surface. By contrast, contaminants with size smaller than the membrane pores are likely to induce membrane pore blocking or adsorption. In the PES 2 membrane, contaminants most likely close the membrane pores strongly and accumulated on the membrane surface [30].

Two levels of transmembrane pressure (TMP) were applied to study its effect on membrane behavior in produced water treatment (Fig. 4).

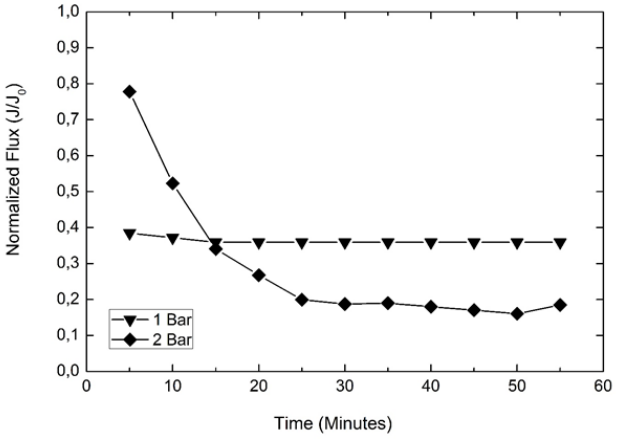


Fig. 4 Behavior of membrane normalized fluxes as a function of time in treatment of produced water under different trans membrane pressure levels (membrane : PES 1)

The initial normalized flux was high at high TMP but decreased at the end of the process. The flux decrease at TMP of 2 bar (59%) was higher than that at 1 bar (2.5%). As a general rule, the increase in TMP in ultrafiltration of oil exerts negative and positive influences on the permeate flux [31]. At high TMP, more oil droplets and solutes passed quickly through the membrane pores. However, more oil droplets contributed to oil droplet accumulation both on the membrane surface and in the pores. The

accumulation of oil droplets led to the formation of a cake layer on the membrane surface. The use of high TMP also resulted in the formation of a cake layer covering the membrane pores, thereby inducing membrane fouling [32].

Fig. 5 represents the effect of ozonation pre-treatment on ultrafiltration behavior.

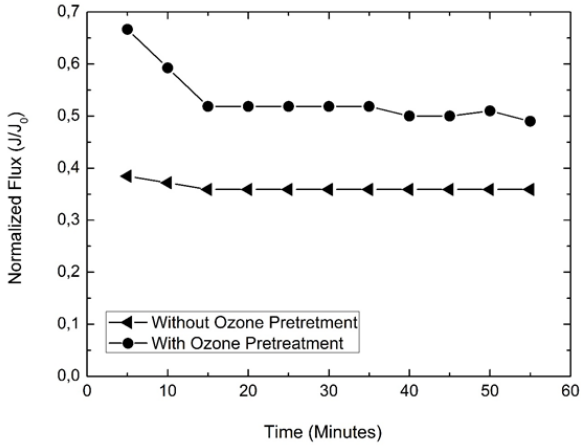


Fig. 5 Effect of ozonation pre-treatment on membrane normalized fluxes as a function of time for ultrafiltration of produced water (membrane: PES 1, TMP = 1 bar)

The normalized flux of the PES 1 membrane with ozone pre-treatment was higher than without ozone pre-treatment, but the flux decrease after ozone pre-treatment remained high. The flux decline of the membrane with ozone pre-treatment was about 18.5%, whereas the flux decrease of the membrane without ozone pre-treatment was only about 2.5%. Ozone can oxidize the majority of organic compounds (about 35%) in produced water into smaller intermediate products, which are then decompose into CO_2 and H_2O [18]. Ozonation of produced water could also generate new compounds, such as acids, amines, and aldehyde, which influence the fouling rate of membranes during filtration. Figure 6 reveals that ozone pre-treatment can diminish membrane fouling, as indicated by the superior normalized flux profile of the membrane subjected to UF with ozone pre-treatment over that that subjected to UF only. The flux decline was significant at the first stage of filtration but became steady thereafter. Pre-ozonation can also reduce dissolved organic carbon by mineralization of small organic molecules. The breaking of large molecules was found to be the dominant principle for fouling reduction [21]. This finding was supported by the images of the SEM membrane illustrated in Fig. 6.

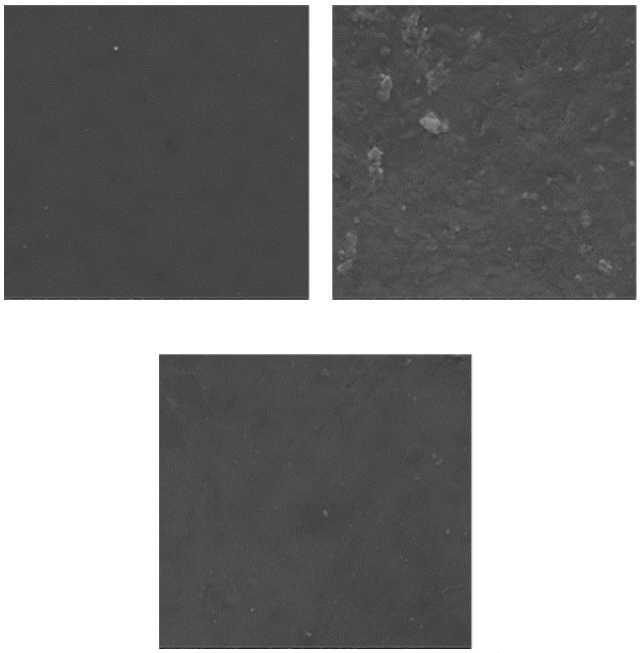


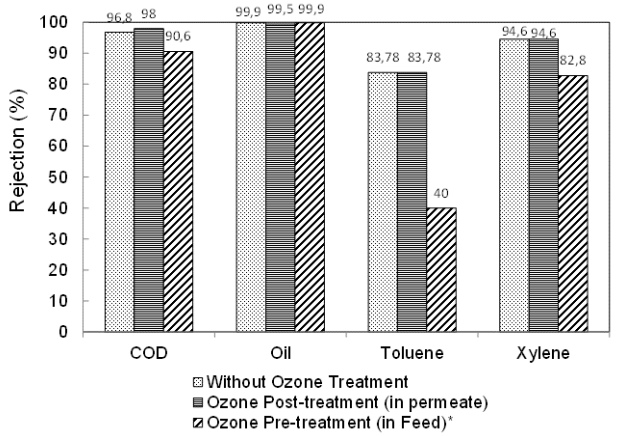
Fig. 6 SEM result of PES membranes (magnification of 20,000×): (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

Fig. 6 confirms the clean surface of the new membrane (Fig. 6.a) without any substances on its top. By contrast, Fig. 6.b shows some foulants deposited on the membrane surface when filtering produced water without pre-treatment. The foulant deposits formed a gel layer, with some small particles found above the gel layer. The foulants were almost certainly suspended solids and large-molecular-weight compounds, such as xylene, toluene, benzene, and phenol in the produced water; as such, the foulants blocked the membrane surface and then formed a gel layer. At a certain period, foulant particles accumulated and generated a thick gel layer, thereby promoting the deposition of the foulant on the gel surface. During the filtration of produced water feed with ozone pre-treatment (Figure 6.c), the membrane surface showed a better appearance. Some foulant deposits were observed, but their size was smaller than that in the deposits shown in Figure 6.b. Organic substances present in produced water are responsible for membrane fouling. Song et al. [33] also described that membrane fouling was produced by organic substances with a high molecular weight. Ozone may also oxidize organic compounds in produced water and effectively decrease the risk of fouling of the membrane. A similar result was also found by You et al. [24], who confirmed that the C=H bonds in the aromatic rings could be eliminated by

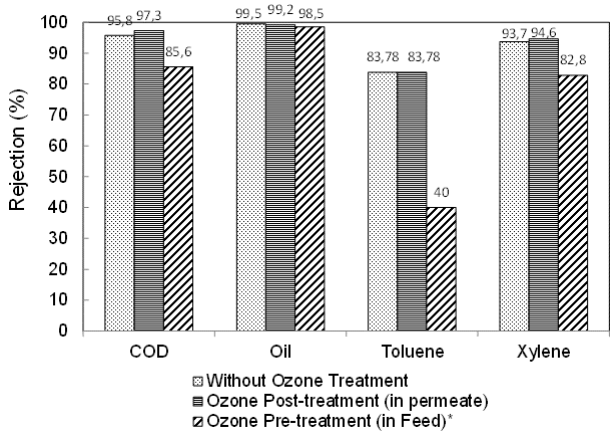
ozone and more C–H and C–H bonds could be produced in the alkanes. Moreover, ozone can destroy aromatic rings to form few alkanes with a linear chain.

3.2 Membrane Rejection

Membrane selectivity is determined by membrane rejection. The selectivity of a membrane is a measure of its ability to resist a substance or allow other substances [8]. Membrane selectivity depends on the interaction of its interface with substances, size of substances, and size of membrane pores on the surface. Substances with larger molecular weight than the size of the membrane pores will be retained on the surface as "retentate." By contrast, substances with a low molecular weight will pass through the membrane as a "permeate." Fig. 7 demonstrates the ability of ultrafiltration membrane to deal with produced water.



(a)



(b)

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2 * (Cf Toluene =C Toluene after feed ozonation = 0.10 mg/L).

The ultrafiltration membrane showed the significantly high rejection rates for COD, oil and grease, toluene, and xylene under various conditions, except for toluene during ozone pre-treatment. The low value of toluene rejection did not indicate its high concentration in the permeate because ozone pre-treatment could significantly reduce the toluene concentration. The rejection of the PES 1 membrane for COD and oil and grease concentration was considerably greater than that of the PES 2 membrane, which has bigger pore size. In membranes with a large pore size, oil that accumulated on the membrane surface will possibly permeate through large pores, resulting in slightly higher oil concentration in the permeate. Rejection or removal efficiency of this system to decrease oil and grease was considerably high (in the range of 98-99.9%) showing that almost all oil was removed. Physical treatment such as EPCON compact floatation unit reduced 50-70% dispersed oil [33]. Applying a copopymer could absorb up to 85% of oil in produced water [34]. On the other hand, utilizing biological treatment such as rotating disk, biological aerated filter was only able to reduce oil and grease to 74% [35].

Oil can be categorized as an organic compound; hence, the value of COD in the permeate was high, corresponding to low COD rejection. Implementation this system is able to reduce the COD in the range of 85.6-98%. This value of reduction is considerably high since the COD reduction by applying other method was low. Using electrochemical oxidation only removed up to 57% of initial COD concentration [36]. The sequence batch reactor SBR, with acclimated sewage sludge had COD removal efficiencies varied from 30% to 50% [37] and applying microwave (MW)-assisted CWAO (Catalytic Wet Air Oxidation) in produced water treatment showed more than 90% of COD was removed [38]. This combined system of ultrafiltation – Ozone was also confirmed superior than the immobilization of microorganism for produced water treatmen that was only removed 90% of initial COD at COD concentration of 2600 mg/L [39].

Table 2 presents the characteristics of ultrafiltration permeate and the standard regulation of on-shore produced water in Indonesia. According to the table, permeates both with UF only and Ozone combined-UF are in the range of acceptable level for water discharge. The result is significance since this method was able to reduce the oil and grease to the very low level (<0.03 - 8.18 mg/L) compared to the existing method. It is reported that the conventional method of produced water treatment reduced the oil and grease concentrations to 30-40 mg/L [35]. In addition, almost all of benzene, toluene, and xylene were removed during the ultrafiltration of produced water under various conditions. This result is superior compared to other method

of produced water treatment. It was reported that neutralized amine "tailored" zeolites were applied in produced water treatment, and only able to remove around 70 and 85% of BTEX from saline produced water [35]. In addition, this Ultrafiltration-Ozone combined system achived similar result with the commercialy available method such as Macro-porous polymer extraction (MPPE) technology, which the MPPE achieved 99% removal of BTEX [35].

Table 2 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Fenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

Produced water contains crude oil, which is a mixture of hydrocarbons, such as naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons (PAHs), and phenols. These hydrocarbons could not be dissolved but are dispersed in produced water. In this research, ultrafiltration membranes with molecular-weight cut-off (MWCO) values of 10.000 and 20.000 Da and pore sizes of 0,01 and 0,02 µm were used. The membranes rejected compounds with molecular weight within 10.000 and 20.000 Daltons. Produced water comprises organic compounds, such as benzene, toluene, and xylene (BTX), which have lower molecular weight than the molecular-weight cut-off. When applying the "membrane-sieving principle", the BTX components should pass through the membrane pores. However, the results showed the high rejection rates for toluene and xylene. BTX exists as dispersed oil and have size larger than that of the membrane pores; hence, BTX was rejected by the ultrafiltration membrane.

Ozonation pre-treatment significantly reduced the concentrations of toluene and xylene and COD. This method is accurate because ozone can degrade macromolecular matter into small organic matter [20] and change the composition and hydrophilicity of organic matter [40]. Šilhárová et al. [17] provided evidence that ozone treatment led to a low concentration of organic petroleum compound (BTEX). The removal efficiency of ozonation for xylene, toluene, and benzene reached 90%, 89%, and 86%, respectively. The removal efficiency was correlated with reaction kinetics of BTX and ozone. The reaction kinetic rates of ozone with benzene, toluene, and xylene were 4.75×10^{-2}, 7.30×10^{-2}, and 1.82×10^{-1} µg/m3.h, respectively.

COD is the oxygen required to degrade biodegradable and non-biodegradable organic compounds. As shown in Table 2, the concentration of COD was decreased by both ultrafiltration and ozone pre- or post-treatment. This finding verifies that the amount of organic compounds decreased when produced water was subjected to ultrafiltration combined with ozonation pre- or post-treatment.

4 Conclusion

The quality of produced water was examined based on oil and grease content as well as COD, which were found to be higher than standard limit of wastewater for oil and gas activities. Benzene, toluene, and xylene were also detected in the produced water. Two commercial Ultrafiltration PES membranes were used to treat the produced. Ultrafiltration was modified by combining it with feed ozonation (pre-treatment) and permeate ozonation (post-treatment). This experimental work demonstrated that ultrafiltration and its combination with ozone pre-treatment and post-treatment showed effective removal of COD, oil and grease, toluene, and xylene. It is also confirmed that almost oil and grase can be removed by using this combined system. Ultrafiltration with ozone pre-treatment led to higher flux profile than ultrafiltration only. This finding verifies that ozone pre-treatment did not only remove produced water pollutants but also diminished the fouling of the ultrafiltration membrane. In addition, it was confirmed that the quality of permeate satisfied the acceptable level to discharge.

Acknowledgement

NA thanks International Conference Grant (Letter Grant Number: 1361/E5.3/PB/2018) from Directorate of Research Strenghtening and Development, Ministry of Research, Technology and Higher Education, The Republic of Indonesia. The authors also acknowledge Ms Henny I. Safitri and Ms Fella R. Astuti for their assistance.

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Gmail

Nita Aryanti <nita.aryanti@gmail.com>

[CH] Submission Acknowledgement: 13491

1 message

Krisztina LÁSZLÓ <chemical@pp.bme.hu> 24 November 2018 at 14:04
To: Nita Aryanti <nita.aryanti@gmail.com>

Dear Nita Aryanti,

Thank you for submitting the manuscript, "Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment" to Periodica Polytechnica Chemical Engineering. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Manuscript URL: https://pp.bme.hu/ch/authorDashboard/submission/13491
Username: aryanti

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

Krisztina LÁSZLÓ

Periodica Polytechnica Chemical Engineering
https://pp.bme.hu/ch

Gmail Nita Aryanti <nita.aryanti@gmail.com>

[CH] Editor Decision: 13491

2 messages

Gábor Márk Tardy <tardygabor@gmail.com> 22 January 2019 at 23:08
To: Nita Aryanti <nita.aryanti@gmail.com>

Dear Nita Aryanti,

Based on the reviewers' commsnts (see below), we have reached a decision regarding your submission to Periodica Polytechnica Chemical Engineering, "Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment".

Our decision is to: **Resubmit for Review (Major revision)**

This means that we ask you to carefully consider the reviewer's remarks, modify the paper accordingly, and then upload a major revision for a new review cycle.

Please go to the **Review page** of your paper. Scrolling down you can find the **Revisions** section where you are supposed to press the **Upload File**. Please upload 1) the revised version of the paper; 2) the revised version of the paper with the changes tracked; 3) Please also prepare and upload a document that answers point-by-point to the reviewers' comments. Please do not use the Discussion section to upload your files.

Please upload the revised files no later than 19th of February.

Best regards

Gábor Márk Tardy
Budapest University of Technology and Economics
tardygabor@gmail.com

Reviewer #1
==========
This problem is relevant for journal scope. I suggest the acceptance after major revision. The concept and aim are clearly defined. The manuscript is well written, I could not find typing errors. The manuscript follows the formal regulations of journal.

Remarks

1. Please write some efficiency value (concrete flux and/or separation factor) where you mention other research work in the introduction part.

2. Please write more information about experimental apparatus: sizes, circulation rate etc. Inaccurate the mention of 29+/-2C as room temperature.

3. Please describe the analytical conditions (the spectrophotometry).

4. The calculation of separation factor is necessary for description of efficiency of membrane separation. Please calculate separation factors also in the case of chemical compounds.

5. Nothing is shown in Fig. 6. Reject it or repair its resolution.

6. What do the stars mean in Table 2? Stars must be explained in this table and the text too.

7. Please make the abbreviation list.

8. Please cite more papers from this journal at the last two years in the similar topic (water, wastewater, membrane) of this research.

Reviewer #2
==========
13491-Periodica Polytechnica Chemical Engineering review: Title: Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment
I have finished reviewing the manuscript submitted for publication in Periodica Polytechnica Chemical Engineering. The overall suggestion I have is that the paper is acceptable for publication after major revision. The manuscript contains new and valuable results and is worthy to be published. The manuscript “Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment” shows that the combination of UF with ozone pre-treatment and post-treatment could increase both the permeate flux and the membrane rejection values: the rejection of the tested components, using this combined system, was found higher than by conventional process.
The paper is written in quite good English.

My specific comments and questions are as follows:
1. In the abstract, there is one sentence, which appears twice:
Once in 6th line: „ The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only.”
Second time in 8th line: “The flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only.”
2. The x and y axis of Fig. 1 are not visible at all. Furthermore, the peaks unit, in the submission text, are not fitted to the numbers of the Figure 1.
3. In my opinion the contact angle results could be better characterisation of a polymer membrane, in hydrophilicity point of view, than FTIR values. What was the reason to change the FTIR? Moreover its results could not show big differences as well as ozone tolerance of the membrane material could be a better tested and selected feature. So the reconsideration and rewrite of this part is necessary!
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Periodica Polytechnica Chemical Engineering
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Submissions

Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

Nita Aryanti, Tutuk Djoko Kusworo,...

Submission Review Copyediting

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Round 1 Round 2

Round 1 Status

The submission must be resubmitted for another review round.

Notifications

[CH] Editor Decision: 13491	2019-01-22 04:08 PM
[CH] Editor Decision: 13491	2019-02-25 02:43 PM

Reviewer's Attachments

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[CH] Editor Decision: 13491

2019-01-22 04:08 PM

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RESPONSE TO REVIEWER
19 February 2019

Gabor Mark Tardy
Editor
Periodica Polytechnica Chemical Engineering

Dear Editor,

Thank you very much for reviewing our manuscript, “Performance of Ultrafiltration-Ozone Combined System for Produced Water Treatment”. We also highly appreciate the reviewers for their complimentary comments and suggestions. We have carried out the revision according to the reviewer’s suggestion.

Please kindly find the attached a point-by-point response to reviewer’s concerns. We also have upload the revised manuscript and the revised manuscript with the tracked changes. We hope that you find our responses satisfactory and that the manuscript is now acceptable for publication.

Sincerely,

Nita Aryanti, Ph.D
Department of Chemical Engineering
Universitas Diponegoro, Semarang, Indonesia
Email: nita.aryanti@che.undip.ac.id

Response to Reviewer #1:

We would like to express our gratitude to the reviewer for the careful and thorough reading of this manuscript. Also for the thoughtful comments and constructive suggestions, which help to improve the quality of this manuscript. The following are our point-by-point responses (the reviewer's comments are in ***italics,*** we also quotes the revised part in quotation mark, "…").

1.) *Please write some efficiency value (concrete flux and/or separation factor) where you mention other research work in the introduction part.*
Response: We have write the efficiency value (rejection value) in the introduction part as your suggestion (Page 2, column 1, line 2-8). We added,

"Previous study showed that UF treatment was able to reject 87.82% of COD, 98.7% of oil, 90.5% of TOC from produced water by using 20 kDa UF membrane [12]. The treatment of oil-field produced water using UF ceramic membrane also presented a good removal of oil content with 99.15% of oil rejection [11].."

2.) *Please write more information about experimental apparatus: sizes, circulation rate, etc. Inaccurate the mention of 29 +/- 2 ^oC as room temperature.*
Response: We have added the experimental apparatus information in the methods section (page 3, column 1, line 17-24). We added,

"The apparatus consisted of a 500 mL feed tank, a pump (Kemflow, with nominal flow rate of 1.0 L/min, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar), a pressure gauge (JAKO, maximum pressure of 10.34 bar), and a stainless steel membrane cell. The pressure and flow rate were controlled using feed valve (Needle Valve, 1/4" FNPT x 1/4" FNPT, maximum pressure of 5000 psi, materials SS 316)."

The correct temperature in our laboratory was 25 *+/- 2 ^oC* and this has been corrected. The average outside temperature in Semarang, Indonesia was in the range of 27-35 ^oC and inside the laboratory the temperature showed temperature of 25 ± 2 °C.

3.) *Please describe the analytical conditions (the spectrophotometry).*
Response: We have described the analytical condition in more detailed manner. The spectrophotometric methods were also completed based on the previous study. (page 4, column 1, line 1-5). We rewrite it as follows,

"Water quality was assessed using the produced water in the feed and permeate. The COD in the feed and permeate samples were determined by Test Tube Heater-COD Reactor (HANA HI 839800) for 2 hours at the temperature of 150 ^oC. Analysis on the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry (Perkin Elmer Lambda 20). The spectrophotometric analysis was performed based on the methods explained by Zadorojny, et al. (1973). The same methods was adapted by Indonesian standard analysis (SNI 06-6989.30-2005)"

4.) *The calculation of separation factor is necessary for description of efficiency of membrane separation. Please calculate separation factors also in the case of chemical compounds.*
Response: From our best knowledge, the separation factor was used for gas separation or the process using gas phase as the feed. However, there is no gas phase included in the separation process, except for analysis such as GCMS. To describe the efficiency and the performance of

membrane separation, we used the percent of rejection and the flux profile. Considering that the feed, retentate, and permeate are all in liquid phase.

5.) *Nothing is shown in Fig 6. Reject it or repairs its resolution.*
Response: We have repairs the image as best as we can. We hope the new image can show the described explanation. (Fig.5 page , column 2). The repaired pictures are as follows,

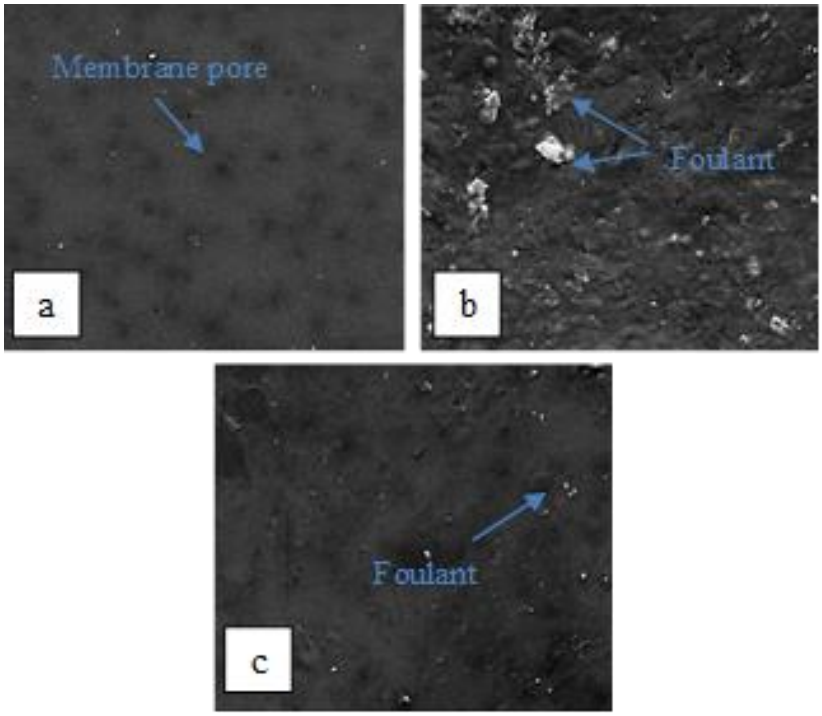

Fig. 6 SEM result of PES membranes (magnification of 20,000×): (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

6.) *What do the stars mean in Table 2? Stars must be explained in this table and the next too.*
Response: The explanation of star signs are written bellow the table 2, here is the additional explanation,

" Table 2 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Fenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

* Permeate characteristic of the parameter was not tested because its value is below the standard limit
** Average value of PES 1 and PES 2 membrane, 1 atm
*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia ”

7.) Please make the abbreviation list

Response: We have made the abbreviation list and placed it in the end of the manuscript (before acknowledgement). We cannot find the rules about how to do the abbreviation in the author guidelines, hence we explained the abbreviation both in the text, abbreviation list. The abbreviation list was arranged in alphabetical order. The abbreviation list is as follows,

Abbreviation list

A	Membrane area (m^2)
BTX	Benzene, toluene, and xylene
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
C_f	Concentration of a specific pollutant in the feed
C_p	Concentration of specific pollutants in permeate
J	Flux (L/ m^2h)
J/J_0	Normalization of flux profiles
J_0	Initial water flux
MWCO	Molecular weight cut off
PAH	Polyaromatic hydrocarbons
PES	Polyethersulfone
Q	Volume (L)
R	Rejection (%)
SEM	Scanning electron microscopy
t	Time interval (h)
TMP	Trans-membrane Pressure (bar)
UF	Ultrafiltration
UV-Vis	Ultraviolet visible spectrophotometer

8.) Please cite more papers from this journal at the last two years in the similar topic (water, wastewater, membrane) of this research.

Response: We cite more papers from Periodica Polytechnica Chemical Engineering at the last two years in the similar topic. The added citations are as follows,

[2] Nasiri, M. and Jafari, I. “Produced Water from Oil-Gas Plants: A Short Review on Challenges and Opportunities”, Periodica Polytechnica Chemical Engineering, 61(2), pp. 73-81, 2017. https://doi.org/10.3311/PPch.8786.

[3] Rezakazemi, M., Maghami, M. and Mohammadi, T. “High Loaded Synthetic Hazardous Wastewater Treatment Using Lab-Scale Submerged Ceramic Membrane Bioreactor”, Periodica Polytechnica Chemical Engineering, 62(3), pp. 299-304, 2018. https://doi.org/10.3311/PPch.11459

Response to Reviewer #2:

We would like to express our gratitude to the reviewer for the careful and thorough reading of this manuscript. Also for the thoughtful comments and constructive suggestions, which help to improve the quality of this manuscript. The following are our point-by-point responses (the reviewer's comments are in ***italics***).

1.) *In the abstract, there is one sentence, which appears twice: Once in 6th line: " The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only." Second time in 8th line: "The flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only."*

Responses: We have delete the second sentences in the 8th line "The flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only." (Page 1, Abstract section, line 6)

2.) *The x and y axis of Fig. 1 are not visible at all. Furthermore, the peaks unit, in the submission text, are not fitted to the numbers of the Figure 1.*

Responses: We have repaired the x and y axis of Figure 1, we also provide bigger figure then the previous image to give a better vision. (Page 2). The repaired figure is as follows,

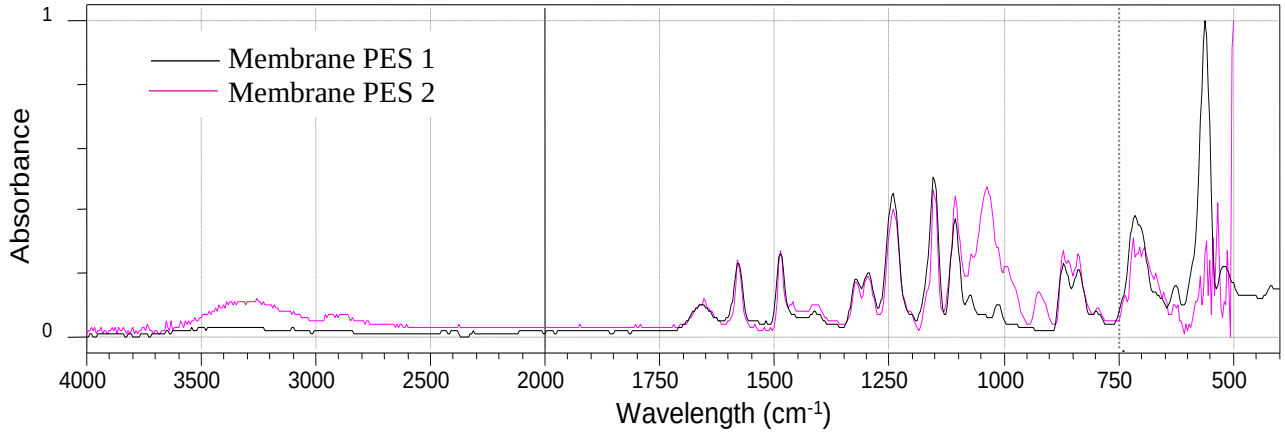

Fig. 1 FTIR results of PES 1 and PES 2 membranes

3.) *In my opinion the contact angle results could be better characterisation of a polymer membrane, in hydrophilicity point of view, than FTIR values. What was the reason to change the FTIR? Moreover its results could not show big differences as well as ozone tolerance of the membrane material could be a better tested and selected feature. So the reconsideration and rewrite of this part is necessary!*

Responses:

We evaluated the specific functional groups of the PES membrane since the membranes were a gift from the NADIR filtration. We only received information of the MWCO and did not have information about the membrane characteristic. Then by determining by FTIR it was predicted that we could identified the specific functional groups of the membranes. It was probably the membrane was fabricated by using different additives or other analysis. Yes, the term hydrophilicity is actually characterized by the contact angle. Since there was no information of the contact angle data from the manufature then we measured the contact angle as you suggested by using Optical Contact Angle

Meter (DataPhysics, OCA 15LJ). The contact angle for PES 1 and PES 2 are 70.7° and 50.1°, respectively.

4.) *From Fig. 3 and Fig. 4 the meaning of the J0 is not clear. In the submission J0 is defined as the clean membrane water flux (page 3, line 6), but from the figures it seems to be the first value of the measured tested water flux. It has to be more specified in the explanation of the figures. I suppose that this is the raw membrane water flux, since the first Normalized Flux (J/J0) values are far away from 1.*

Responses: In this study, J_0 is defined as the clean membrane water flux, correspond to our explanation in the methods section. We added some explanation in the methods section (page 3, column 2, line 2) as your recommendation.

'' Initial water flux (J_0) was determined by filtering pure water using a new clean membrane, then measuring the volume of water permeate collected at a specific recording time."

5.) *In Fig. 6 the identification of a, b and c parts is missing. It cannot be guess because nothing is visible from the pictures! It has to be replaced!*

Respones: We have repairs the image as best as we can. We hope the new image can show the described explanation. (Fig.6 page , column , line). The repaired pictures are as follows,

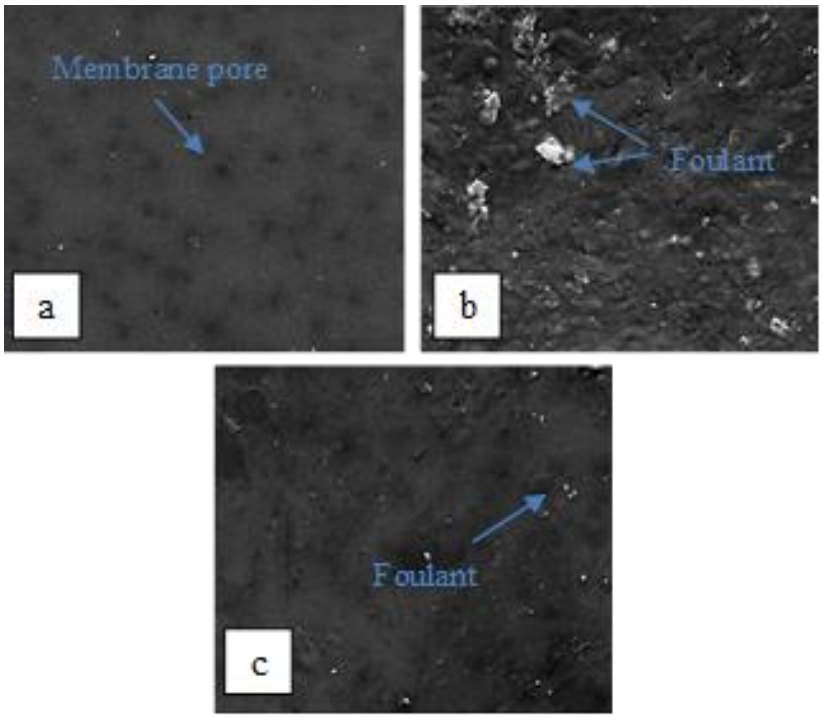

Fig. 6 SEM result of PES membranes (magnification of 20,000×): (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

6.) *Both gel layer (page 4, line 11; page 4, line 35; page 5, line 28, 29, 33, 35, and 36) and cake layer (page 4, line 5, 11, 24, and 35; page 5, line 1 and 3) are mentioned during the submission, however they have different meaning! It should be defined them and use the proper one!*
Responses:

We use term 'cake' layer and we added information after Figure 4 as follow.

"It is predicted that initially a gel layer is formed due to some solutes congeal on the membrane surface. A steady state of flux is obtained with assumption that the concentration does not increase. However, with the increase of pressure, the gel layer is transformed into cake layer. In cake layer, the fouling increases continuously and result in complete blocking with no flux".

According to Figure 4, the flux tend to decrese with the increae of pressure, so it is presumably the cake layer is occured. Then we use term 'cake layer' in disscusion. We do hope that it is acceptable.

7.) *In '3.2 Membrane Rejection' section the first 10 sentences are so basic in membrane science as well as they are not related to the results, so it should be rewrite or clear from the submission.*
Responses: We rewrite the first paragraph of "3.2 Membrane Rejection" section. The sentences that not related to the results is deleted. (page 6, column 1, line 32)
"The selectivity of a membrane is a measure of its ability to resist a substance or allow other substances [8]. Membrane selectivity depends on the interaction of its interface with substances, size of substances, and size of membrane pores on the surface. Substances with larger molecular weight than the size of the membrane pores will be retained on the surface as "retentate." By contrast, substances with a low molecular weight will pass through the membrane as a permeate." → this sentences is deleted.

8.) *In '3.2 Membrane Rejection' section the following sentence is written: "The rejection of the PES 1 membrane was considerably greater than PES 2." I think it is not so obvious from the Figure 7. From this Figure, it is not possible to say this is significant or not.*
Responses: Thank you for your correction, the difference is not significant, we made a revision to the sentences, the following is the revised sentences, (page 7, column 1, line 2)

"The rejection of the PES 1 membrane for COD and oil and grease concentration was slightly greater than that of the PES 2 membrane, which has bigger pore size."

There was only one measurement? Standard errors are not indicated in the figure.
Responses: The measurement was triplicate for each variable. We have added the standard errors bar. (Fig. 7, page 6) The revised figures are as follows,

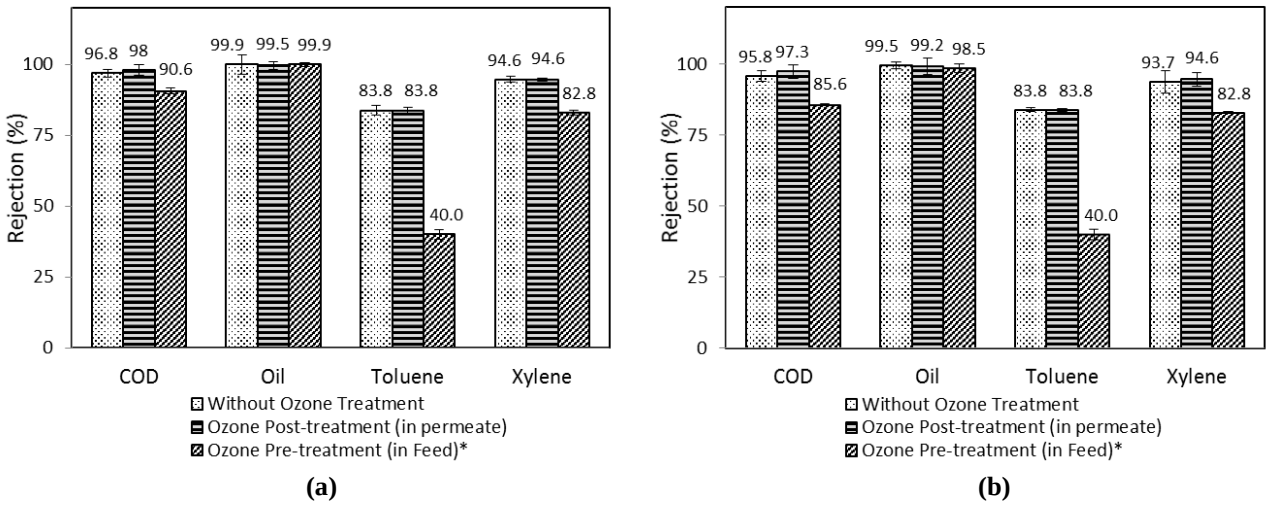

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2 * (C_f Toluene =C Toluene after feed ozonation = 0.10 mg/L)

From these results it seems to be that it would be better idea to test another pore size membrane also with much higher or lower MWCO, so with bigger cut-off range! And in the future: Carry out MF tests could be reasonable too.

Responses:

Thank you for your suggestions. It is definitely correct that the use of another pore size will provide better range. But we apologize that we can not add this information in this manuscript since we do not have similar produce water as we used in this manuscript. At that time, we had contract for research collaboration with the company and they could provide the produced water. However, the contract finished on January 2018 and we do not have access to request produced water sample from the same company.

9.) *It would be good idea to put the Feed results into the Table 3.*

Responses: "**Table 2** Characteristics of produced water used in this study" explain about the raw feed composition, that is why we placed it in the "Material and Methods" section. (Page 4, column 1).

We have also completed "**Table 3.** Comparison of the quality of feed and permeate" with the star signs information. Table 3 has explained about the comparison of feed treated by ozonation, UF permeate, UF permeate enhanced with ozonation, and the standard limits. Table 2 and Table 3 are as follows,

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	**1872 mg/L**
Oil and grease content	**931.01 mg/L**
Benzene	**<0.8 mg/L**
Toluene	**2.62 mg/L**
Xylene	**3.11 mg/L**

Phenol	**<0.03 mg/L**
Ammonia	**0.22 mg/L**
pH	**8**

Table 3 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	**Permeate****	**Permeate with ozonation****	**Standard Limits*****
COD	**790 mg/L**	**64.2 mg/L**	**56.9 mg/L**	**200 mg/L**
Oil and Grease	**351.61 mg/L**	**8.18 mg/L**	**< 0.03**	**25 mg/L**
Benzene	**<0.08 mg/L**	**n.a.***	**n.a.***	**n.a.**
Toluene	**0.10 mg/L**	**0.37 mg/L**	**< 0.06**	**n.a.**
Xylene	**1.67**	**<0.05 mg/L**	**<0.05 mg/L**	**n.a.**
Phenol	**n.a.***	**n.a.***	**n.a.***	**2 mg/L**
Ammonia	**n.a.***	**n.a.***	**n.a.***	**5 mg/L**
pH	**n.a***	**n.a***	**n.a***	**6-9**

* Permeate characteristic of the parameter was not tested because its value is below the standard limit
** Average value of PES 1 and PES 2 membrane, 1 atm
*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia

10.) *There are some annoying mistakes such as different written words: bar or Bar; transmembrane pressure or trans membrane pressure; oxygen demand or Oxygen Demand; Or such as index mistakes: m2 instead of m2, J/J0 instead of J/J0 or J0 instead of J0, or Cf instead of Cf, Cp instead of Cp... Please standardized them!*

Responses: Thank you very much for your detailed correction, we have standardized all of the mistakes.

Revision of manuscript with edited part
19 February 2019

Periodica Polytechnica Chemical Engineering

Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

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Abstract

Oil exploration waste, also called produced water, contains hazardous pollutants, such as benzene; benzene, toluene, and xylene (BTX); naphthalene, phenanthrene, and dibenzothiophene (NDP); polyaromatic hydrocarbons (PAHs); and phenol. Produced water is characterized by high chemical oxygen demand (COD) and oil content, which exceed the standard limits of regulation. In this study, the combination of ultrafiltration (UF) and ozone pre-treatment and post-treatment were applied for treatment of produced water to minimize its environmental impact. Produced water and membrane were characterized, and their ultrafiltration performance for removal of oil content, benzene, toluene, xylene, and COD. Two commercial polyethersulfone membranes, with molecular-weight cut-off values of 10 and 20 kDa, were used. The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Separation performance was evaluated based on flux profile and removal of COD, oil and grease content, toluene, and xylene. Significant finding was found where the combination of UF with ozone pre-treatment and post-treatment could significantly eliminate COD, oil content, toluene, and xylene. The rejection of these components was found higher than conventional process, which was in the range of 80% to 99%. In addition, almost oil and grease can be removed by using this combined system. Permeate quality of this system confirmed the acceptable level as water discharge.

Keywords

Ultrafiltration, Ozone, Produced Water, Benzene, Toluene, Xylene

Commented [A1]: Reviewer #2
We delete the second sentences in the 8th line "The flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only." Following the recomendation from reviewer.

1 Introduction

Oil explorations are the primary source of energy, and their corresponding activities generate a large volume of oilfield wastewater, also referred as produced water. For each barrel of oil, three barrels of produced water are generated [1]. In general, produced water is reused to enhance oil recovery or treated prior to discharge into the environment. Produced water comprises various organic and inorganic substances, which are potentially characterized as hazardous and toxic wastes. Produced water compound is categorized as organic substance, inorganic substance, and radionucleotide. Moreover, produced water contains some important compounds, such as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids, and dissolved gases [2]. Oils consist of monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAH), and related heterocyclic aromatic compounds [3]. BTEX and phenols are dissolved in water. Residual chemicals, such as corrosion and scale inhibitors, emulsion breakers, and biocides, are also present in produced water [4].

Compounds in produced water are toxic and adversely affect the environment. Bakke et al. [5] published a review of the environmental impact of produced water and oil drilling in the offshore petroleum industry. Alkylphenols, naphthenic acids, and PAHs from produced water may disrupt reproductive functions and affect several chemicals, biochemical, and genetic biomarkers. As a consequence of the lethal effects of produced water contaminants, many countries have implemented a stringent regulatory standard for discharging produced water to alleviate their adverse environmental impacts. Produced water quality can be represented as oil content or concentration and chemical oxygen demand (COD). The concentrations of oil and COD in produced water are relatively high, reaching 565 and 1220 mg/L, respectively [1]. The government of the Republic of Indonesia through Regulation of the Minister of State for Environment No. 19 set standard limits for wastewater for oil and gas activities in 2010. The permitted oil concentration and COD are within 20–50 and 200 mg/L, respectively. Hence, treatment of produced water is a responsibility for oil and gas explorations.

Commented [A2]: Reviewer #1
8.) We cite more papers from Periodica Polytechnica Chemical Engineering at the last two years in the similar topic.

Membrane technology has been applied to treat produced water and reviewed comprehensively [6,7]. Ultrafiltration membrane is also an appropriate method for produced water treatment. Ultrafiltration (UF) is a low-pressure driven membrane filtration process operating at 2–10 bar [8]. The pore size of an UF membrane ranges from 0.001 µm to 0.1

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8.) We cite more papers from Periodica Polytechnica Chemical Engineering at the last two years in the similar topic.

μm; as such, the membrane rejects compounds with molecular weight of 1000 to 100.000 Da [9].

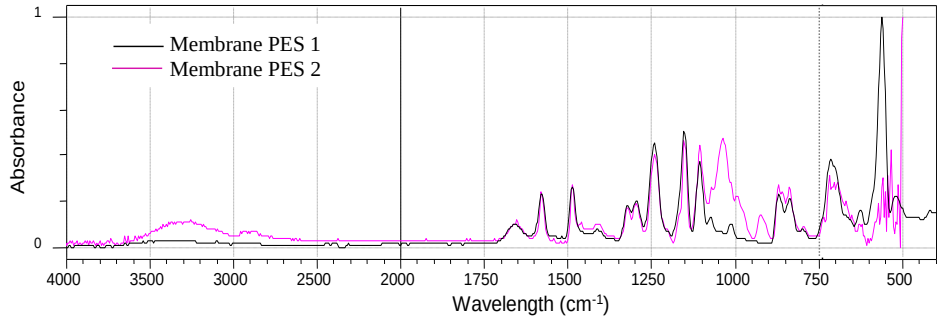


Fig. 1 FTIR results of PES 1 and PES 2 membranes

Commented [A4]: Reviewer #2
2.) We have repaired the x and y axis of Figure 1, we also makes the figure bigger to gives a better vision.

Several researchers have examined the use of UF membranes for handling produced water [10-14]. The previous study showed that UF treatment was able to reject 87.82% of COD, 98.7% of oil, 90.5% of Total Organic Compound (TOC) from produced water by using 20 kDa UF membrane [12]. The treatment of oil-field produced water using UF ceramic membrane also presented a good removal of oil content with 99.15% of oil rejection [11].

However, studies on produced water treatment only investigated method performance through determination of general effluent parameters, such as COD, BOD, total dissolved solids, total suspended solids, oil content, and total organic carbon and analysis of anions and cations. Several studies have evaluated specific BTX content in produced water [15-17]. However, to the best of our knowledge, limited works have examined the performance of UF in BTX removal. The present study mainly aims to investigate the performance of ultrafiltration in treating produced water, specifically in filtering BTX pollutants. In detail, Polyethersulfone (PES) was selected as membrane material for ultrafiltration due to its hydrophilic property. To enhance the ultrafiltration performance, this research combined ultrafiltration and ozone pre-treatment and post-treatment for removal of produced water compounds. Ozone was selected because it can break up large organic molecules. Ozone can break complex molecular organic compounds in crude oil, which is a component of produced water [18-19]. Ziabari et al. [20] studied the removal of hydrocarbons from aqueous solution by ozonation. In addition, Zha et al. [21] reported that ozone could oxidize compounds having a large molecular weight to generate smaller compounds. Ozone can also reduce fouling associated with microfiltration and ultrafiltration [22-25]. Hence, we confirm the novelty of this research by implementing the combination of ultrafiltration and ozone to improve ultrafiltration performance for produced water treatment. The improvement was achieved not only in the term of permeate quality but also reduction of membrane fouling. Results provide novel significant findings in this research area.

2 Materials and Method

2.1 Membrane characterization

Two available commercial membranes made of PES (NADIR Filtration, Germany) were used to filter produced water. Membranes with molecular-weight cut-off of 10 and 20 kDa and were labelled as PES 1 and PES 2, respectively. Specific functional groups were identified using Fourier transform infrared spectroscopy (Shimadzu IR Prestige-21). Specific functional groups were examined based on their wavelength as a function of absorbance (Fig. 1).

Similar peaks at 1577.77 and 1485.19 cm^{-1} are characteristics of PES membrane. Peaks at 1485,19 and 1577.77cm^{-1} indicate the presence of aromatic components (C=C stretching) in benzene, and peaks at 1240.23 and 1242,16 cm^{-1} represent ether aromatic compounds [26-27]. In addition, peaks at 1151.5 and 1105.21 cm^{-1} exhibit SO_2 symmetrical stretching and are assigned to a sulfuric component. Peaks at 1656 and 1321 cm^{-1} are predicted as preservative PVP (poly-N-vinyl-2-pyrrolidone) because it is an additive polymer used for pore formation on PES and polysulfone membrane [27]. Moreover, a specific peak at

3500-3000 cm^{-1} is assigned to PES 2 membrane and indicates the existence of OH stretching radical. The PES 2 membrane was predicted to be more hydrophilic than the PES 1 membrane. To confirm this finding, the contact angle of the membrane was measured by using Optical Contact Angle Meter (DataPhysics, OCA 15LJ). The contact angle of the PES 1 and PES 2 membrane were 70.7° and 50.1°, respectively.

Table 1 summarizes the properties of UF membrane in relation to its pore size and water flux.

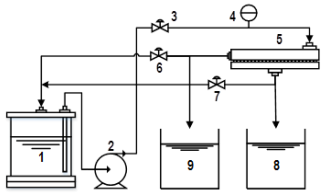
Table 1 Properties of UF membranes used in this work

Membrane	MWCO (Da)	Pure Water Flux ($L/m^2.hr$)
PES-1	10.000	11.25
PES-2	20.000	94.27

Table 1 shows that the pure water flux of the PES 2 membrane was higher than that of the PES 1 membrane. The pure water flux was mainly determined by membrane pore size and its surface hydrophilicity [28]. Given that the PES 2 membrane possessed a large pore size, it exhibited higher pure water flux. Membrane surface morphology was analyzed by scanning electron microscopy (FEI, Type Inspect-S50, Japan) at a specific magnification.

2.2 Ultrafiltration

Ultrafiltration experiments were conducted in a homemade laboratory-scale test cell. The apparatus consisted of a 500 mL feed tank, a pump (Kemflow, with nominal flow rate of 1.0 L/min, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar), a pressure gauge (JAKO, maximum pressure of 10.34 bar), and a stainless steel membrane cell. The pressure and flow rate were controlled using feed valve (Needle Valve, 1/4" FNPT x 1/4" FNPT, maximum pressure of 5000 psi, materials SS 316). Fig. 2 shows the schematic of the ultrafiltration cell.



1. Feed Tank
2. Feed Pump
3. Feed Valve
4. Pressure Gauge
5. UF Membrane Module
6. Retentate Recycle Valve
7. Permeate Recycle Valve
8. Permeate Tank
9. Retentate Tank

Fig. 2 Schematic of the ultrafiltration cell

All filtration runs were carried out at room temperature (25 ± 2°C). The membrane was compacted by filtering water through the membrane at a pressure of 2 bar for 0.5 h. For each experimental run, a new circular membrane sheet with an area of 13.85 cm^2 was used for measurement of initial water flux (J_0). Initial water flux (J_0) was determined by filtering pure water using a new clean membrane, then measuring the volume of water permeate collected at a specific recording time. Filtrations were carried out using total recycle mode, where both permeate, and retentate were recycled to the feed tank, to maintain the same concentration. Permeate flux (J) was determined by analytically weighting permeate collected at every 5 min intervals for 60 min. Membrane or permeate fluxes (J) were calculated by dividing the volume of permeate (Q) by the effective membrane area (A) and the sampling time (t), as defined in Eq. (1):

$$J = \frac{1}{A \cdot t} Q \quad (1)$$

where:

J: flux (L/m^2h), Q: volume (L), A: membrane area (m^2), and t: time interval (h).

The ability of the membrane for removing specific pollutants from produced water was determined by % rejection (%R). Membrane rejection was calculated by dividing the difference between the concentration of a specific pollutant in the feed (C_f) with the concentration of specific pollutants in permeate (C_p), as expressed in Eq. (2).

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

In this research, the term rejection and permeate and feed concentrations refers to rejection and concentrations of COD, total oil content, toluene, and xylene.

2.3 Ozonation

Ozonation pre-treatment and post-treatment were conducted by Ozonizer, a generator (Krisbow) and flow meter. In the pre-treatment process, ozone was purged into the produced water feed. For the post-treatment, ozone was added into the permeate. Ozone concentration was tested using HI38054 Ozone Test kit. The ozone flow rate was set as 2 L/min, the contact time was 5 min, and the corresponding ozone concentration was 0.3 mg/L.

2.4 Produced Water Quality Analysis

Produced water was collected from offshore facilities in Cepu region, Central Java, Indonesia. Water quality was assessed using the produced water in the feed and permeate. COD of the feed and permeate samples were determined by

Commented [A6]: Reviewer #1
2.) We made correction on the Temperature. The average outside temperature in Semarang, Indonesia was between 29-35 °C, that is the reason we write the temperature as 29 ± 2 °C

Commented [A7]: Reviewer #2
4.) In this study, J0 is defined as the clean membrane water flux, correspond to our explanation in the methods section. We added some explanation in the methods section as the reviewer's recommendation.

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4.) From our best knowledge, the separation factor was used for gas separation or the process using gas phase as the feed. However, there is no gas phase included in the separation process, except for analysis such as GCMS. To describe the efficiency and the performance of membrane separation, we used the percent of rejection and the flux profile. Considering that the feed, retentate, and permeate are all in liquid phase.

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2.) We have added the experimental apparatus information in the methods section

Water quality was assessed using the produced water in the feed and permeate. The COD in the feed and permeate samples were determined by Test Tube Heater-COD Reactor (HANA HI 839800) for 2 hours at the temperature of 150°C. Analysis of the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry (Perkin Elmer Lambda 20). The spectrophotometric analysis was performed based on the methods explained by Zadorojny et al. [29]. The similar method was adopted by Indonesian standard analysis (SNI 06-6989.30-2005). Table 2 shows the characteristics of produced water.

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	1872 mg/L
Oil and grease content	931.01 mg/L
Benzene	<0.8 mg/L
Toluene	2.62 mg/L
Xylene	3.11 mg/L
Phenol	<0.03 mg/L
Ammonia	0.22 mg/L
pH	8

According to Table 2, the mean levels of benzene, toluene, and xylene in the produced water sample were below 0.8, 2.62, and 3.11 mg/L, respectively. For comparison, produced water was also collected from the Bonsucesso treatment plant, State of Sergipe, Brazil and had average concentrations of 1397, 1263, and 312 µg/L for benzene, toluene, and xylene, respectively [17]. Similar results were also found in an oilfield wastewater platform in the Gulf of Mexico. Examination of oilfield wastewater in that area indicated that the concentrations of benzene, toluene, and xylene were 0.8–4.6, 1.0–3.5, and 0.2–0.7 mg/L, respectively [18]. In the Campos Basin, State of Rio de Janeiro, Brazil, the levels of benzene, toluene, and xylene were 283–1855, 87.04–2224, and 67.35–5969 mol/L, respectively [16].

3 Results and Discussions

3.1 Membrane Flux Behaviour

Normalization of flux profiles (J/J_0) as a function of time is presented in Fig. 3. In general, the flux showed a declining trend during ultrafiltration. The reduction of membrane flux is a characteristic of membrane fouling, which can be generated by an increase in membrane resistance due to pore blocking, concentration polarization, and cake formation [24]. Fouling can be related to the accumulation of a substance (called foulant) on the membrane surface or inside the membrane pores. At the beginning of ultrafiltration, no foulant deposit was found on the membrane surface. As time increased, foulants accumulated on the membrane surface and generated a cake layer, leading to decreased flux value and normalized fluxes.

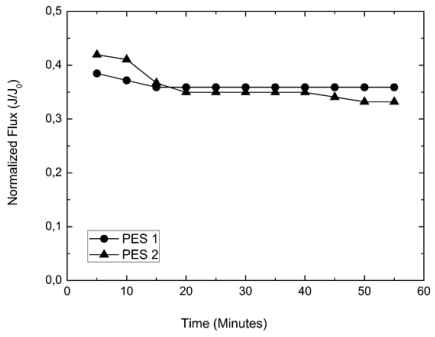


Fig. 3 Performance of membrane normalized fluxes as a function of time in treatment of produced water by using membranes with different pore sizes (TMP = 1 bar)

In the ultrafiltration treatment of produced water, its components, such as oil and other organic compounds, are significant sources of fouling. Ashaghi et al. [30] and Maguire-Boyle and Barron [31] proposed that fouling during filtration of produced water could be due to biofouling, scaling, organic fouling, and colloidal fouling. Fouling could also be attributed to microbial contaminants (biofouling), salt precipitation resulting in scaling, organic fouling due to pore plugging or pore coating by hydrocarbon compounds, and clay and silica accumulation on the membrane surface (colloidal fouling). However, flux reduction was relatively steady along with time because of the compression of the cake layer and its constant thickness.

The flux decline of the PES 2 membrane was more pronounced than that of the PES 1 membrane. The flux decline (final flux compared with the initial flux) values of PES 2 and 1 membranes were found to be 8.7% and 2.5%, respectively. The flux decline can be explained by membrane fouling caused by pore blocking or membrane adsorption due to contaminants in the produced water. The pore size of the PES 1 membrane was slightly smaller than that of the PES 2 membrane. Contaminants with size bigger than the membrane pores have a tendency to form a cake

layer on the membrane surface. By contrast, contaminants with size smaller than the membrane pores are likely to induce membrane pore blocking or adsorption. In the PES 2 membrane, contaminants most likely close the membrane pores strongly and accumulated on the membrane surface [32].

Two levels of trans membrane pressure (TMP) were applied to study its effect on membrane behaviour in produced water treatment (Fig. 4).

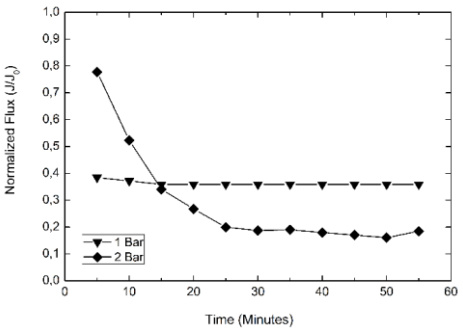


Fig. 4 Behavior of membrane normalized fluxes as a function of time in treatment of produced water under different trans membrane pressure levels (membrane : PES 1)

The initial normalized flux was high at high TMP but decreased at the end of the process. The flux decrease at TMP of 2 bar (59%) was higher than that at 1 bar (2.5%). As a general rule, the increase in TMP in ultrafiltration of oil exerts negative and positive influences on the permeate flux [33]. At high TMP, more oil droplets and solutes passed quickly through the membrane pores. However, more oil droplets contributed to oil droplet accumulation both on the membrane surface and in the pores. The accumulation of oil droplets led to the formation of a cake layer on the membrane surface. It is predicted that initially a gel layer is formed due to some solutes congeal on the membrane surface. A steady state of flux is obtained with assumption that the concentration does not increase. However, with the increase of pressure, the gel layer is transformed into cake layer. In cake layer, the fouling increases continuously and result in complete blocking with no flux. The use of high TMP also resulted in the formation of a cake layer covering the membrane pores, thereby inducing membrane fouling [34].

Fig. 5 represents the effect of ozonation pre-treatment on ultrafiltration behaviour.

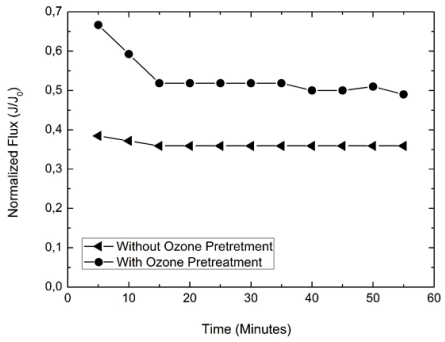


Fig. 5 Effect of ozonation pre-treatment on membrane normalized fluxes as a function of time for ultrafiltration of produced water (membrane: PES 1, TMP = 1 bar)

The normalized flux of the PES 1 membrane with ozone pre-treatment was higher than without ozone pre-treatment, but the flux decrease after ozone pre-treatment remained high. The flux decline of the membrane with ozone pre-treatment was about 18.5%, whereas the flux decrease of the membrane without ozone pre-treatment was only about 2.5%. Ozone can oxidize the majority of organic compounds (about 35%) in produced water into smaller intermediate products, which are then decomposed into CO_2 and H_2O [20]. Ozonation of produced water could also generate new compounds, such as acids, amines, and aldehyde, which influence the fouling rate of membranes during filtration. Figure 6 reveals that ozone pre-treatment can diminish membrane fouling, as indicated by the superior normalized flux profile of the membrane subjected to UF with ozone pre-treatment over that subjected to UF only. The flux decline was significant in the first stage of filtration but became steady thereafter. Pre-ozonation can also reduce dissolved organic carbon by mineralization of small organic molecules. The breaking of large molecules was found to be the dominant principle for fouling reduction [23]. This finding was supported by the images of the SEM membrane illustrated in Fig. 6.

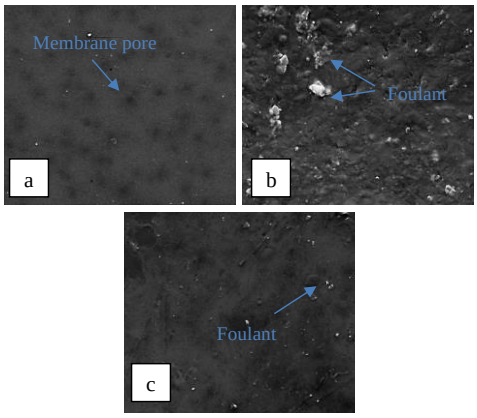
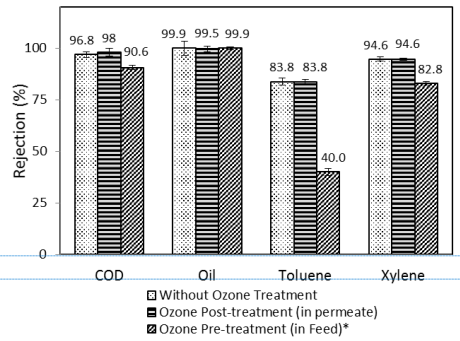


Fig. 6 SEM result of PES membranes (magnification of 20,000×): (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

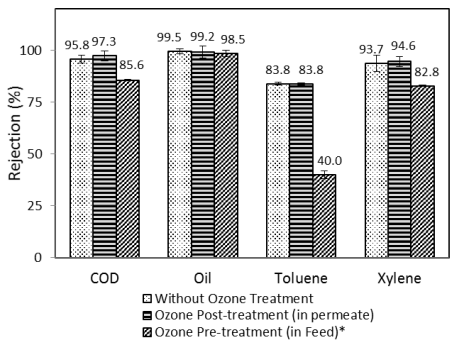
Fig. 6 confirms the clean surface of the new membrane (Fig. 6.a) without any substances on its top. By contrast, Fig. 6.b shows some foulants deposited on the membrane surface when filtering produced water without pre-treatment. The foulant deposits formed a cake layer, with some small particles found above the cake layer. The foulants were almost certainly suspended solids and large-molecular-weight compounds, such as xylene, toluene, benzene, and phenol in the produced water; as such, the foulants blocked the membrane surface and then formed a cake layer. At a certain period, foulant particles accumulated and generated a thick cake layer, thereby promoting the deposition of the foulant on the cake surface. During the filtration of produced water feed with ozone pre-treatment (Figure 6.c), the membrane surface showed a better appearance. Some foulant deposits were observed, but their size was smaller than that in the deposits shown in Figure 6.b. Organic substances present in produced water are responsible for membrane fouling. Song et al. [35] also described that membrane fouling was produced by organic substances with a high molecular weight. Ozone may also oxidize organic compounds in produced water and effectively decrease the risk of fouling of the membrane. A similar result was also found by You et al. [26], who confirmed that the C=H bonds in the aromatic rings could be eliminated by ozone and more C–H and C–H bonds could be produced in the alkanes. Moreover, ozone can destroy aromatic rings to form few alkanes with a linear chain.

3.2 Membrane Rejection

In the ultrafiltration membrane, membrane selectivity is determined by membrane rejection. The ability of the PES membrane to selectively resist COD, oil, toluene and xylene in the produced water was shown in Fig. 7.



(a)



(b)

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2 * (C_t Toluene =C Toluene after feed ozonation = 0.10 mg/L).

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8.) The measurement was triplicate for each variable. We have added the standard errors bar in each figures.

The ultrafiltration membrane showed significantly high rejection rates for COD, oil and grease, toluene, and xylene under various conditions, except for toluene during ozone pre-treatment. The low value of toluene rejection did not indicate its high concentration in the permeate because ozone pre-treatment could significantly reduce the toluene concentration. The rejection of the PES 1 membrane for COD and oil and grease concentration was slightly greater than that of the PES 2 membrane, which has bigger pore size. In membranes with a large pore size, oil that accumulated on the membrane surface will possibly permeate through large pores, resulting in slightly higher oil concentration in the permeate. Rejection or removal efficiency of this system to decrease oil and grease was considerably high (in the range of 98-99.9%) showing that almost all oil was removed. Physical treatment such as EPCON compact floatation unit reduced 50-70% dispersed oil [34]. Applying a copolymer could absorb up to 85% of oil in produced water [36]. On the other hand, utilizing biological treatment such as rotating disk, aerated biological filter was only able to reduce oil and grease to 74% [37].

Oil can be categorized as an organic compound; hence, the value of COD in the permeate was high, corresponding to low COD rejection. Implementation of this system is able to reduce the COD in the range of 85.6-98%. This value of reduction is considerably high since the COD reduction by applying another method was low. Using electrochemical oxidation only removed up to 57% of initial COD concentration [38]. The sequence batch reactor SBR, with acclimated sewage sludge, had COD removal efficiencies varied from 30% to 50% [39] and applying microwave (MW)-assisted CWAO (Catalytic Wet Air Oxidation) in produced water treatment showed more than 90% of COD was removed [40]. This combined system of ultrafiltration – Ozone was also confirmed superior to the immobilization of microorganism for produced water treatment that was only removed 90% of initial COD at COD concentration of 2600 mg/L [41].

Table 3 presents the characteristics of ultrafiltration permeate and the standard regulation of on-shore produced water in Indonesia. According to the table, permeates both with UF only and Ozone combined-UF are in the range of acceptable level for water discharge. The result is significant since this method was able to reduce the oil and grease to a very low level (<0.03 - 8.18 mg/L) compared to the existing method. It is reported that the conventional method of produced water treatment reduced the oil and grease concentrations to 30-40 mg/L [37]. In addition, almost all of benzene, toluene, and xylene were removed during the ultrafiltration of produced water under various conditions.

Table 3 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Phenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

* Permeate characteristic of the parameter was not tested because its value is below the standard limit
** Average value of PES 1 and PES 2 membrane, 1 atm
*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia

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9.) We have completed **Table 3.** with the star signs information. Table 3 has explained about the comparison of feed treated by ozonation, UF permeate, UF permeate enhanced with ozonation, and the standard limits.

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6.) The explanation of star signs were written bellow the table 2

This result is superior compared to other methods of produced water treatment. It was reported that neutralized amine "tailored" zeolites were applied in produced water treatment, and only able to remove around 70 and 85% of BTEX from saline produced water [37]. In addition, this Ultrafiltration-Ozone combined system achieved similar result with the commercially available method such as Macro-porous Polymer Extraction (MPPE) technology, which the MPPE achieved 99% removal of BTEX [37].

Produced water contains crude oil, which is a mixture of hydrocarbons, such as naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons (PAHs), and phenols. These hydrocarbons could not be dissolved but are dispersed in produced water. In this research, ultrafiltration membranes with molecular-weight cut-off (MWCO) values of 10.000 and 20.000 Da and pore sizes of 0,01 and 0,02 µm were used. The membranes rejected compounds with molecular weight within 10.000 and 20.000 Daltons.

Produced water comprises organic compounds, such as benzene, toluene, and xylene (BTX), which have lower molecular weight than the molecular weight cut-off. When applying the "membrane-sieving principle", the BTX components should pass through the membrane pores. However, the results showed high rejection rates for toluene and xylene. BTX exists as dispersed oil and has size larger than that of the membrane pores; hence, BTX was rejected by the ultrafiltration membrane.

Ozonation pre-treatment significantly reduced the concentrations of toluene and xylene and COD. This method is accurate because ozone can degrade macromolecular matter into small organic matter [20] and change the composition and hydrophilicity of organic matter [42]. Šilhárová et al. [19] provided evidence that ozone treatment led to a low concentration of organic petroleum compound (BTEX). The removal efficiency of ozonation for xylene, toluene, and benzene reached 90%, 89%, and 86%, respectively. The removal efficiency was correlated with reaction kinetics of BTX and ozone. The reaction kinetic rates of ozone with benzene, toluene, and xylene were 4.75×10^{-2}, 7.30×10^{-2}, and 1.82×10^{-1} $\mu g/m^3.h$, respectively.

COD is the oxygen required to degrade biodegradable and non-biodegradable organic compounds. As shown in Table 3, the concentration of COD was decreased by both ultrafiltration and ozone pre- or post-treatment. This finding verifies that the amount of organic compounds decreased when produced water was subjected to ultrafiltration combined with ozonation pre- or post-treatment.

4 Conclusion

The quality of produced water was examined based on oil and grease content as well as COD, which were found to be higher than the standard limit of wastewater for oil and gas activities. Benzene, toluene, and xylene were also detected in the produced water. Two commercial Ultrafiltration PES membranes were used to treat the produced. Ultrafiltration was modified by combining it with feed ozonation (pre-treatment) and permeate ozonation (post-treatment). This experimental work demonstrated that ultrafiltration and its combination with ozone pre-treatment and post-treatment showed effective removal of COD, oil and grease, toluene, and xylene. It is also confirmed that almost oil and grease can be removed by using this combined system. Ultrafiltration with ozone pre-treatment led to higher flux profile than ultrafiltration only. This finding verifies that ozone pre-treatment did not only remove produced water pollutants but also diminished the fouling of the ultrafiltration membrane. In addition, it was confirmed that the quality of permeate satisfied the acceptable level to discharge.

Abbreviation list

A	Membrane area (m^2)
BTX	Benzene, toluene, and xylene
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
C_f	Concentration of a specific pollutant in the feed
C_p	Concentration of specific pollutants in permeate
J	Flux (L/ m^2h)
J/J_0	Normalization of flux profiles
J_0	Initial water flux
MWCO	Molecular weight cut off
PAH	Polyaromatic hydrocarbons
PES	Polyethersulfone
Q	Volume (L)
R	Rejection (%)
SEM	Scanning electron microscopy
t	Time interval (h)
TMP	Transmembrane pressure (bar)
TOC	Total organic compound
UF	Ultrafiltration
UV-Vis	Ultraviolet, visible spectrophotometer

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7.) We have made the abbreviation list and placed it in the end of the manuscript (before acknowledgement). We cannot find the rules about how to do the abbreviation in the author guidelines, hence we explained the abbreviation both in the text, abbreviation list. The abbreviation list was arranged in alphabetical order.

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10.) Thank you very much for your detailed correction, we have standardized all of the mistakes.

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Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

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Abstract

Oil exploration waste, also called produced water, contains hazardous pollutants, such as benzene; benzene, toluene, and xylene (BTX); naphthalene, phenanthrene, and dibenzothiophene (NDP); polyaromatic hydrocarbons (PAHs); and phenol. Produced water is characterized by high chemical oxygen demand (COD) and oil content, which exceed the standard limits of regulation. In this study, the combination of ultrafiltration (UF) and ozone pre-treatment and post-treatment were applied for treatment of produced water to minimize its environmental impact. Produced water and membrane were characterized, and their ultrafiltration performance for removal of oil content, benzene, toluene, xylene, and COD. Two commercial Polyethersulfone membranes, with molecular-weight cut-off values of 10 and 20 kDa, were used. The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Separation performance was evaluated based on flux profile and removal of COD, oil and grease content, toluene, and xylene. Significant finding was found where the combination of UF with ozone pre-treatment and post-treatment could significantly eliminate COD, oil content, toluene, and xylene. The rejection of these components was found higher than conventional process, which was in the range of 80% to 99%. In addition, almost oil and grease can be removed by using this combined system. Permeate quality of this system confirmed the acceptable level as water discharge.

Keywords

Ultrafiltration, Ozone, Produced Water, Benzene, Toluene, Xylene

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1 Introduction

Oil explorations are the primary source of energy, and their corresponding activities generate a large volume of oilfield wastewater, also referred as produced water. For each barrel of oil, three barrels of produced water are generated [1]. In general, produced water is reused to enhance oil recovery or treated prior to discharge into the environment. Produced water comprises various organic and inorganic substances, which are potentially characterized as hazardous and toxic wastes. Produced water compound is categorized as organic substance, inorganic substance, and radionucleotide. Moreover, produced water contains some important compounds, such as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids, and dissolved gases [2]. Oils consist of monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAH), and related heterocyclic aromatic compounds [3]. BTEX and phenols are dissolved in water. Residual chemicals, such as corrosion and scale inhibitors, emulsion breakers, and biocides, are also present in produced water [4].

Compounds in produced water are toxic and adversely affect the environment. Bakke et al. [5] published a review of the environmental impact of produced water and oil drilling in the offshore petroleum industry. Alkylphenols, naphthenic acids, and PAHs from produced water may disrupt reproductive functions and affect several chemicals, biochemical, and genetic biomarkers. As a consequence of the lethal effects of produced water contaminants, many countries have implemented a stringent regulatory standard for discharging produced water to alleviate their adverse environmental impacts. Produced water quality can be represented as oil content or concentration and chemical oxygen demand (COD). The concentrations of oil and COD in produced water are relatively high, reaching 565 and 1220 mg/L, respectively [1]. The government of the Republic of Indonesia through Regulation of the Minister of State for Environment No. 19 set standard limits for wastewater for oil and gas activities in 2010. The permitted oil concentration and COD are within 20–50 and 200 mg/L, respectively. Hence,

treatment of produced water is a responsibility for oil and gas explorations.

Membrane technology has been applied to treat produced water and reviewed comprehensively [6, 7]. Ultrafiltration membrane is also an appropriate method for produced water treatment. Ultrafiltration (UF) is a low-pressure driven membrane filtration process operating at 2–10 bar [8]. The pore size of an UF membrane ranges from 0.001 μm to 0.1 μm; as such, the membrane rejects compounds with molecular weight of 1000 to 100.000 Da [9].

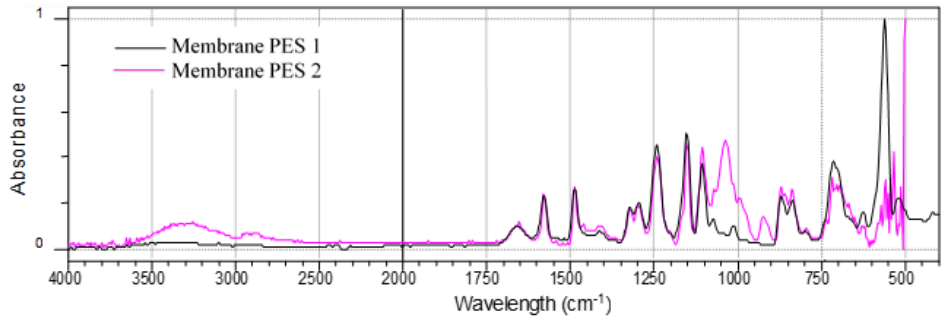

Fig. 1 FTIR results of PES 1 and PES 2 membranes

Several researchers have examined the use of UF membranes for handling produced water [10-14]. The previous study showed that UF treatment was able to reject 87.82 % of COD, 98.7 % of oil, 90.5 % of Total Organic Compound (TOC) from produced water by using 20 kDa UF membrane [12]. The treatment of oil-field produced water using UF ceramic membrane also presented a good removal of oil content with 99.15% of oil rejection [11].

However, studies on produced water treatment only investigated method performance through determination of general effluent parameters, such as COD, BOD, total dissolved solids, total suspended solids, oil content, and total organic carbon and analysis of anions and cations. Several studies have evaluated specific BTX content in produced water [15-17]. However, to the best of our knowledge, limited works have examined the performance of UF in BTX removal. The present study mainly aims to investigate the performance of ultrafiltration in treating produced water, specifically in filtering BTX pollutants. In detail, Polyethersulfone (PES) was selected as membrane material for ultrafiltration due to its hydrophilic property. To enhance the ultrafiltration performance, this research combined ultrafiltration and ozone pre-treatment and post-treatment for removal of produced water compounds. Ozone was selected because it can break up large organic molecules. Ozone can break complex molecular organic compounds in crude oil, which is a component of produced water [18-19]. Ziabari et al. [20] studied the removal of hydrocarbons from aqueous solution by ozonation. In addition, Zha et al. [21] reported that ozone could oxidize compounds having a large molecular weight to generate smaller compounds. Ozone can also reduce fouling associated with microfiltration and ultrafiltration [22-25]. Hence, we confirm the novelty of this research by implementing the combination of ultrafiltration and ozone to improve ultrafiltration performance for produced water treatment. The improvement was achieved not only in the term of permeate quality but also reduction of membrane fouling. Results provide novel significant findings in this research area.

2 Materials and Method

2.1 Membrane characterization

Two available commercial membranes made of PES (NADIR Filtration, Germany) were used to filter produced water. Membranes with molecular-weight cut-off of 10 and 20 kDa and were labelled as PES 1 and PES 2, respectively. Specific functional groups were identified using Fourier transform infrared spectroscopy (Shimadzu IR Prestige-21). Specific functional groups were examined

based on their wavelength as a function of absorbance (Fig. 1).

Similar peaks at 1577.77 and 1485.19 cm^{-1} are characteristics of PES membrane. Peaks at 1485.19 and 1577.77cm^{-1} indicate the presence of aromatic components (C=C stretching) in benzene, and peaks at 1240.23 and 1242.16 cm^{-1} represent ether aromatic compounds [26-27]. In addition, peaks at 1151.5 and 1105.21 cm^{-1} exhibit SO_2 symmetrical stretching and are assigned to a sulfuric component. Peaks at 1656 and 1321 cm^{-1} are predicted as preservative PVP (poly-N-vinyl-2-pyrrolidone) because it is an additive polymer used for pore formation on PES and polysulfone membrane [27]. Moreover, a specific peak at 3500-3000 cm^{-1} is assigned to PES 2 membrane and indicates the existence of OH stretching radical. The PES 2 membrane was predicted to be more hydrophilic than the PES 1 membrane. To confirm this finding, the contact angle of the membrane was measured by using Optical Contact Angle Meter (DataPhysics, OCA 15LJ). The contact angle of the PES 1 and PES 2 membrane were 70.7° and 50.1°, respectively.

Table 1 summarizes the properties of UF membrane in relation to its pore size and water flux.

Table 1 Properties of UF membranes used in this work

Membrane	MWCO (Da)	Pure Water Flux ($L/m^2.hr$)
PES-1	10.000	11.25
PES-2	20.000	94.27

Table 1 shows that the pure water flux of the PES 2 membrane was higher than that of the PES 1 membrane. The pure water flux was mainly determined by membrane pore size and its surface hydrophilicity [28]. Given that the PES 2 membrane possessed a large pore size, it exhibited higher pure water flux. Membrane surface morphology was analyzed by scanning electron microscopy (FEI, Type Inspect-S50, Japan) at a specific magnification.

2.2 Ultrafiltration

Ultrafiltration experiments were conducted in a homemade laboratory-scale test cell. The apparatus consisted of a 500 mL feed tank, a pump (Kemflow, with nominal flow rate of 1.0 L/min, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar), a pressure gauge (JAKO, maximum pressure of 10.34 bar), and a stainless steel membrane cell. The pressure and flow rate were controlled using feed valve (Needle Valve, 1/4" FNPT x 1/4" FNPT, maximum pressure of 5000 psi, materials SS 316). Fig. 2 shows the schematic of the ultrafiltration cell.

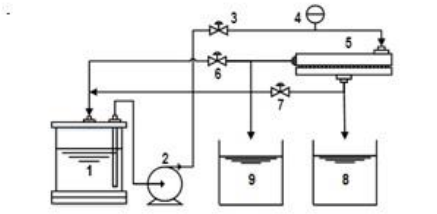

Fig. 2 Schematic of the ultrafiltration cell

All filtration runs were carried out at room temperature (25 ± 2°C). The membrane was compacted by filtering water through the membrane at a pressure of 2 bar for 0.5 h. For each experimental run, a new circular membrane sheet with an area of 13.85 cm^2 was used for measurement of initial water flux (J_0). Initial water flux (J_0) was determined by filtering pure water using a new clean membrane, then measuring the volume of water permeate collected at a specific recording time. Filtrations were carried out using total recycle mode, where both permeate, and retentate were recycled to the feed tank, to maintain the same concentration. Permeate flux (J) was determined by analytically weighting permeate collected at every 5 min intervals for 60 min. Membrane or permeate fluxes (J) were calculated by dividing the volume of permeate (Q) by the effective membrane area (A) and the sampling time (t), as defined in Eq. (1):

$$J = \frac{1}{A \cdot t} Q \quad (1)$$

where:

J: flux (L/ m^2h), Q: volume (L), A: membrane area (m^2), and t: time interval (h).

The ability of the membrane for removing specific pollutants from produced water was determined by % rejection (%R). Membrane rejection was calculated by dividing the difference between the concentration of a specific pollutant in the feed (C_f) with the concentration of specific pollutants in permeate (C_p), as expressed in Eq. (2).

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

In this research, the term rejection and permeate and feed concentrations refers to rejection and concentrations of COD, total oil content, toluene, and xylene.

2.3 Ozonation

Ozonation pre-treatment and post-treatment were conducted by Ozonizer, a generator (Krisbow) and flow meter. In the pre-treatment process, ozone was purged into the produced water feed. For the post-treatment, ozone was added into the permeate. Ozone concentration was tested using HI38054 Ozone Test kit. The ozone flow rate was set as 2 L/min, the contact time was 5 min, and the corresponding ozone concentration was 0.3 mg/L.

2.4 Produced Water Quality Analysis

Produced water was collected from offshore facilities in Cepu region, Central Java, Indonesia. Water quality was assessed using the produced water in the feed and permeate. COD of the feed and permeate samples were determined by Water quality was assessed using the produced water in the feed and permeate. The COD in the feed and permeate samples were determined by Test Tube Heater-COD Reactor (HANA HI 839800) for 2 hours at the temperature of 150°C. Analysis of the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry (Perkin Elmer Lambda 20). The spectrophotometric analysis was performed based on the methods explained by Zadorojny et al. [29]. The similar method was adopted by Indonesian standard analysis (SNI 06-6989.30-2005). Table 2 shows the characteristics of produced water.

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	1872 mg/L
Oil and grease content	931.01 mg/L
Benzene	<0.8 mg/L
Toluene	2.62 mg/L
Xylene	3.11 mg/L
Phenol	<0.03 mg/L
Ammonia	0.22 mg/L
pH	8

According to Table 2, the mean levels of benzene, toluene, and xylene in the produced water sample were below 0.8, 2.62, and 3.11 mg/L, respectively. For comparison, produced water was also collected from the Bonsucesso treatment plant, State of Sergipe, Brazil and had average concentrations of 1397, 1263, and 312 µg/L for benzene, toluene, and xylene, respectively [17]. Similar results were also found in an oilfield wastewater platform in the Gulf of Mexico. Examination of oilfield wastewater in that area indicated that the concentrations of benzene, toluene, and xylene were 0.8–4.6, 1.0–3.5, and 0.2–0.7 mg/L, respectively [18]. In the Campos Basin, State of Rio de Janeiro, Brazil, the levels of benzene, toluene, and xylene were 283–1855, 87.04–2224, and 67.35–5969 mol/L, respectively [16].

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3 Results and Discussions

3.1 Membrane Flux Behaviour

Normalization of flux profiles (J/J_0) as a function of time is presented in Fig. 3. In general, the flux showed a declining trend during ultrafiltration. The reduction of membrane flux is a characteristic of membrane fouling, which can be generated by an increase in membrane resistance due to pore blocking, concentration polarization, and cake formation [24]. Fouling can be related to the accumulation of a substance (called foulant) on the membrane surface or inside the membrane pores. At the beginning of ultrafiltration, no foulant deposit was found on the membrane surface. As time increased, foulants accumulated on the membrane surface and generated a cake layer, leading to decreased flux value and normalized fluxes.

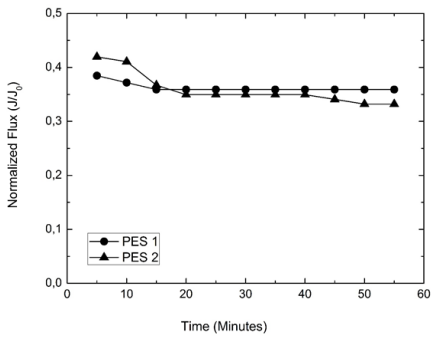

Fig. 3 Performance of membrane normalized fluxes as a function of time in treatment of produced water by using membranes with different pore sizes (TMP = 1 bar)

In the ultrafiltration treatment of produced water, its components, such as oil and other organic compounds, are significant sources of fouling. Ashaghi et al. [30] and Maguire-Boyle and Barron [31] proposed that fouling during filtration of produced water could be due to biofouling, scaling, organic fouling, and colloidal fouling. Fouling could also be attributed to microbial contaminants (biofouling), salt precipitation resulting in scaling, organic fouling due to pore plugging or pore coating by hydrocarbon compounds, and clay and silica accumulation on the membrane surface (colloidal fouling). However, flux reduction was relatively steady along with time because of the compression of the cake layer and its constant thickness.

The flux decline of the PES 2 membrane was more pronounced than that of the PES 1 membrane. The flux decline (final flux compared with the initial flux) values of PES 2 and PES 1 membranes were found to be 8.7% and 2.5 %, respectively. The flux decline can be explained by membrane fouling caused by pore blocking or membrane adsorption due to contaminants in the produced water. The pore size of the PES 1 membrane was slightly smaller than that of the PES 2 membrane. Contaminants with size bigger than the membrane pores have a tendency to form a cake layer on the membrane surface. By contrast, contaminants with size smaller than the membrane pores are likely to induce membrane pore blocking or adsorption. In the PES 2 membrane, contaminants most likely close the membrane pores strongly and accumulated on the membrane surface [32].

Two levels of trans membrane pressure (TMP) were applied to study its effect on membrane behaviour in produced water treatment (Fig. 4).

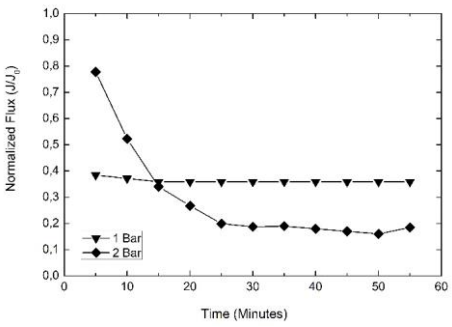

Fig. 4 Behavior of membrane normalized fluxes as a function of time in treatment of produced water under different trans membrane pressure levels (membrane : PES 1)

The initial normalized flux was high at high TMP but decreased at the end of the process. The flux decrease at TMP of 2 bar (59 %) was higher than that at 1 bar (2.5 %). As a general rule, the increase in TMP in ultrafiltration of oil exerts negative and positive influences on the permeate flux [33]. At high TMP, more oil droplets and solutes passed quickly through the membrane pores. However, more oil droplets contributed to oil droplet accumulation both on the membrane surface and in the pores. The accumulation of oil droplets led to the formation of a cake layer on the membrane surface. It is predicted that initially a gel layer is formed due to some solutes congeal on the membrane surface. A steady state of flux is obtained with assumption that the concentration does not increase. However, with the increase of pressure, the gel layer is transformed into cake layer. In cake layer, the fouling increases continuously and result in complete blocking with no flux. The use of high TMP also resulted in the formation of a cake layer covering the membrane pores, thereby inducing membrane fouling [34].

Fig. 5 represents the effect of ozonation pre-treatment on ultrafiltration behaviour.

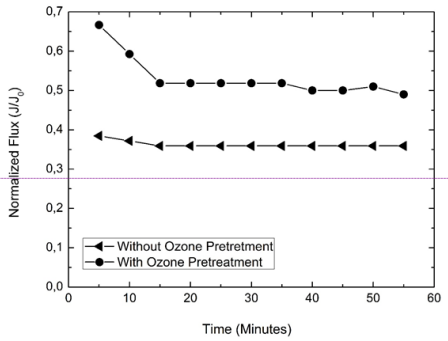

Fig. 5 Effect of ozonation pre-treatment on membrane normalized fluxes as a function of time for ultrafiltration of produced water (membrane: PES 1, TMP = 1 bar)

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The normalized flux of the PES 1 membrane with ozone pre-treatment was higher than without ozone pre-treatment, but the flux decrease after ozone pre-treatment remained high. The flux decline of the membrane with ozone pre-treatment was about 18.5%, whereas the flux decrease of the membrane without ozone pre-treatment was only about 2.5 %. Ozone can oxidize the majority of organic compounds (about 35 %) in produced water into smaller intermediate products, which are then decomposed into CO_2 and H_2O [20]. Ozonation of produced water could also generate new compounds, such as acids, amines, and aldehyde, which influence the fouling rate of membranes during filtration. Figure 6 reveals that ozone pre-treatment can diminish membrane fouling, as indicated by the superior normalized flux profile of the membrane subjected to UF with ozone pre-treatment over that subjected to UF only. The flux decline was significant in the first stage of filtration but became steady thereafter. Pre-ozonation can also reduce dissolved organic carbon by mineralization of small organic molecules. The breaking of large molecules was found to be the dominant principle for fouling reduction [23]. This finding was supported by the images of the SEM membrane illustrated in Fig. 6.

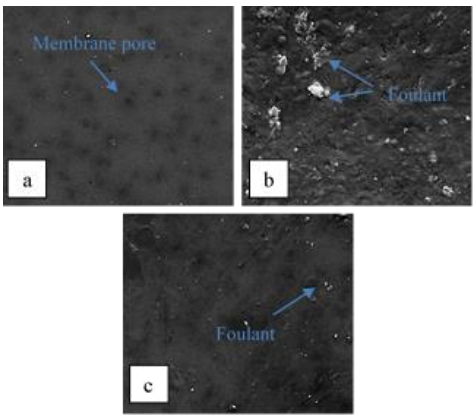

Fig. 6 SEM result of PES membranes (magnification of 20,000 ×: (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

Fig. 6 confirms the clean surface of the new membrane (Fig. 6.a) without any substances on its top. By contrast, Fig. 6.b shows some foulants deposited on the membrane surface when filtering produced water without pre-treatment. The foulant deposits formed a cake layer, with some small particles found above the cake layer. The foulants were almost certainly suspended solids and large-molecular-weight compounds, such as xylene, toluene, benzene, and phenol in the produced water; as such, the foulants blocked the membrane surface and then formed a cake layer. At a certain period, foulant particles accumulated and generated a thick cake layer, thereby promoting the deposition of the foulant on the cake surface. During the filtration of produced water feed with ozone pre-treatment (Figure 6.c), the membrane surface showed a better appearance. Some foulant deposits were observed, but their size was smaller than that in the deposits shown in Figure 6.b. Organic substances present in produced water are responsible for membrane fouling. Song et al. [35] also described that membrane fouling was produced by organic substances with a high molecular weight. Ozone may also oxidize organic compounds in produced water and effectively decrease the risk of fouling of the membrane. A similar result was also found by You et al. [26], who confirmed that the C=H bonds in the aromatic rings could be eliminated by ozone and more C–H and C–H bonds could be produced in the alkanes. Moreover, ozone can destroy aromatic rings to form few alkanes with a linear chain.

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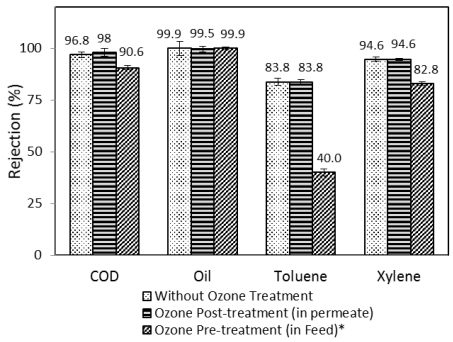
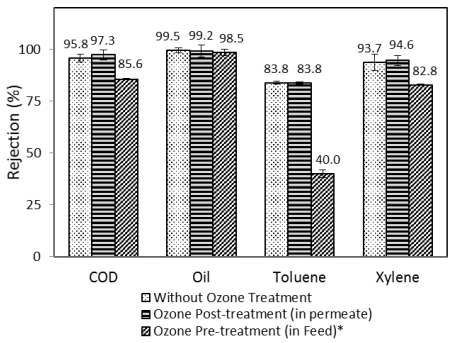
3.2 Membrane Rejection

In the ultrafiltration membrane, membrane selectivity is determined by membrane rejection. The ability of the PES membrane to selectively resist COD, oil, toluene and xylene in the produced water is shown in Fig. 7.



(a)



(b)

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2 * (C_t Toluene =C Toluene after feed ozonation = 0.10 mg/L).

The ultrafiltration membrane showed significantly high rejection rates for COD, oil and grease, toluene, and xylene under various conditions, except for toluene during ozone pre-treatment. The low value of toluene rejection did not indicate its high concentration in the permeate because ozone pre-treatment could significantly reduce the toluene concentration. The rejection of the PES 1 membrane for COD and oil and grease concentration was slightly greater than that of the PES 2 membrane, which has bigger pore size. In membranes with a large pore size, oil that accumulated on the membrane surface will possibly permeate through large pores, resulting in slightly higher oil concentration in the permeate. Rejection or removal efficiency of this system to decrease oil and grease was considerably high (in the range of 98-99.9 %) showing that almost all oil was removed. Physical treatment such as EPCON compact floatation unit reduced 50-70 % dispersed oil [34]. Applying a copolymer could absorb up to 85 % of oil in produced water [36]. On the other hand, utilizing biological treatment such as rotating disk, aerated biological filter was only able to reduce oil and grease to 74 % [37].

Oil can be categorized as an organic compound; hence, the value of COD in the permeate was high, corresponding to low COD rejection. Implementation of this system is able to reduce the COD in the range of 85.6-98%. This value of reduction is considerably high since the COD reduction by applying another method was low. Using electrochemical oxidation only removed up to 57% of initial COD concentration [38]. The sequence batch reactor SBR, with acclimated sewage sludge, had COD removal efficiencies varied from 30% to 50% [39] and applying microwave (MW)-assisted CWAO (Catalytic Wet Air Oxidation) in produced water treatment showed more than 90% of COD was removed [40]. This combined system of ultrafiltration – Ozone was also confirmed superior to the immobilization of microorganism for produced water treatment that was only removed 90% of initial COD at COD concentration of 2600 mg/L [41].

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Table 3 presents the characteristics of ultrafiltration permeate and the standard regulation of on-shore produced water in Indonesia. According to the table, permeates both with UF only and Ozone combined-UF are in the range of acceptable level for water discharge. The result is significant since this method was able to reduce the oil and grease to a very low level (<0.03 - 8.18 mg/L) compared to the existing method. It is reported that the conventional method of produced water treatment reduced the oil and grease concentrations to 30-40 mg/L [37]. In addition, almost all of benzene, toluene, and xylene were removed during the ultrafiltration of produced water under various conditions.

Table 3 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Phenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

* Permeate characteristic of the parameter was not tested because its value is below the standard limit
** Average value of PES 1 and PES 2 membrane, 1 atm
*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia

This result is superior compared to other methods of produced water treatment. It was reported that neutralized amine “tailored” zeolites were applied in produced water treatment, and only able to remove around 70 and 85% of

BTEX from saline produced water [37]. In addition, this Ultrafiltration-Ozone combined system achieved similar result with the commercially available method such as Macro-porous Polymer Extraction (MPPE) technology, which the MPPE achieved 99% removal of BTEX [37].

Produced water contains crude oil, which is a mixture of hydrocarbons, such as naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons (PAHs), and phenols. These hydrocarbons could not be dissolved but are dispersed in produced water. In this research, ultrafiltration membranes with molecular-weight cut-off (MWCO) values of 10.000 and 20.000 Da and pore sizes of 0,01 and 0,02 µm were used. The membranes rejected compounds with molecular weight within 10.000 and 20.000 Daltons. Produced water comprises organic compounds, such as benzene, toluene, and xylene (BTX), which have lower molecular weight than the molecular weight cut-off. When applying the "membrane-sieving principle", the BTX components should pass through the membrane pores. However, the results showed high rejection rates for toluene and xylene. BTX exists as dispersed oil and has size larger than that of the membrane pores; hence, BTX was rejected by the ultrafiltration membrane.

Ozonation pre-treatment significantly reduced the concentrations of toluene and xylene and COD. This method is accurate because ozone can degrade macromolecular matter into small organic matter [20] and change the composition and hydrophilicity of organic matter [42]. Šilhárová et al. [19] provided evidence that ozone treatment led to a low concentration of organic petroleum compound (BTEX). The removal efficiency of ozonation for xylene, toluene, and benzene reached 90%, 89 %, and 86 %, respectively. The removal efficiency was correlated with reaction kinetics of BTX and ozone. The reaction kinetic rates of ozone with benzene, toluene, and xylene were 4.75×10^{-2}, 7.30×10^{-2}, and 1.82×10^{-1} µg/m^3.h, respectively.

COD is the oxygen required to degrade biodegradable and non-biodegradable organic compounds. As shown in Table 3, the concentration of COD was decreased by both ultrafiltration and ozone pre- or post-treatment. This finding verifies that the amount of organic compounds decreased when produced water was subjected to ultrafiltration combined with ozonation pre- or post-treatment.

4 Conclusion

The quality of produced water was examined based on oil and grease content as well as COD, which were found to be higher than the standard limit of wastewater for oil and gas activities. Benzene, toluene, and xylene were also detected in the produced water. Two commercial Ultrafiltration PES membranes were used to treat the produced. Ultrafiltration was modified by combining it with feed ozonation (pre-treatment) and permeate ozonation (post-treatment). This experimental work demonstrated that ultrafiltration and its combination with ozone pre-treatment and post-treatment showed effective removal of COD, oil and grease, toluene, and xylene. It is also confirmed that almost oil and grease can be removed by using this combined system. Ultrafiltration with ozone pre-treatment led to higher flux profile than ultrafiltration only. This finding verifies that ozone pre-treatment did not only remove produced water pollutants but also diminished the fouling of the ultrafiltration membrane. In addition, it was confirmed that the quality of permeate satisfied the acceptable level to discharge.

Abbreviation list

A	Membrane area (m^2)
BTX	Benzene, toluene, and xylene
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
C_f	Concentration of a specific pollutant in the feed
C_p	Concentration of specific pollutants in permeate
J	Flux (L/ m^{2}h)
J/J_0	Normalization of flux profiles
J_0	Initial water flux
MWCO	Molecular weight cut off
PAH	Polyaromatic hydrocarbons
PES	Polyethersulfone
Q	Volume (L)
R	Rejection (%)
SEM	Scanning electron microscopy
t	Time interval (h)
TMP	Transmembrane pressure (bar)
TOC	Total organic compound
UF	Ultrafiltration
UV-Vis	Ultraviolet, visible spectrophotometer

Acknowledgement

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Periodica Polytechnica Chemical Engineering

Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

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Abstract

Oil exploration waste, also called produced water, contains hazardous pollutants, such as benzene; benzene, toluene, and xylene (BTX); naphthalene, phenanthrene, and dibenzothiophene (NDP); polyaromatic hydrocarbons (PAHs); and phenol. Produced water is characterized by high chemical oxygen demand (COD) and oil content, which exceed the standard limits of regulation. In this study, the combination of ultrafiltration (UF) and ozone pre-treatment and post-treatment were applied for treatment of produced water to minimize its environmental impact. Produced water and membrane were characterized, and their ultrafiltration performance for removal of oil content, benzene, toluene, xylene, and COD. Two commercial Polyethersulfone membranes, with molecular-weight cut-off values of 10 and 20 kDa, were used. The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Separation performance was evaluated based on flux profile and removal of COD, oil and grease content, toluene, and xylene. Significant finding was found where the combination of UF with ozone pre-treatment and post-treatment could significantly eliminate COD, oil content, toluene, and xylene. The rejection of these components was found higher than conventional process, which was in the range of 80% to 99%. In addition, almost oil and grease can be removed by using this combined system. Permeate quality of this system confirmed the acceptable level as water discharge.

Keywords

ultrafiltration, ozone, produced water, benzene, toluene, xylene

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1 Introduction

Oil explorations are the primary source of energy, and their corresponding activities generate a large volume of oilfield wastewater, also referred as produced water. For each barrel of oil, three barrels of produced water are generated [1]. In general, produced water is reused to enhance oil recovery or treated prior to discharge into the environment. Produced water comprises various organic and inorganic substances, which are potentially characterized as hazardous and toxic wastes. Produced water compound is categorized as organic substance, inorganic substance, and radionucleotide. Moreover, produced water contains some important compounds, such as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids, and dissolved gases [2]. Oils consist of monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAH), and related heterocyclic aromatic compounds [3]. BTEX and phenols are dissolved in water. Residual chemicals, such as corrosion and scale inhibitors, emulsion breakers, and biocides, are also present in produced water [4].

Compounds in produced water are toxic and adversely affect the environment. Bakke et al. [5] published a review of the environmental impact of produced water and oil drilling in the offshore petroleum industry. Alkylphenols, naphthenic acids, and PAHs from produced water may disrupt reproductive functions and affect several chemicals, biochemical, and genetic biomarkers. As a consequence of the lethal effects of produced water contaminants, many countries have implemented a stringent regulatory standard for discharging produced water to alleviate their adverse environmental impacts. Produced water quality can be represented as oil content or concentration and chemical oxygen demand (COD). The concentrations of oil and COD in produced water are relatively high, reaching 565 and 1220 mg/L, respectively [1]. The government of the Republic of Indonesia through Regulation of the Minister of State for Environment No. 19 set standard limits for wastewater for oil and gas activities in 2010. The permitted oil concentration and COD are within 20–50 and 200 mg/L, respectively. Hence, treatment of produced water is a responsibility for oil and gas explorations.

Membrane technology has been applied to treat produced water and reviewed comprehensively [6, 7]. Ultrafiltration membrane is also an appropriate method for produced water

treatment. Ultrafiltration (UF) is a low-pressure driven membrane filtration process operating at 2–10 bar [8]. The pore size of an UF membrane ranges from 0.001 µm to 0.1 µm; as such, the membrane rejects compounds with molecular weight of 1000 to 100.000 Da [9].

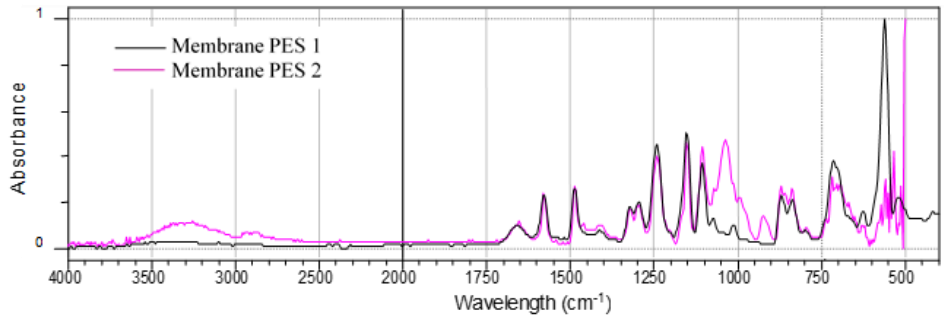

Fig. 1 FTIR results of PES 1 and PES 2 membranes

Several researchers have examined the use of UF membranes for handling produced water [10-14]. The previous study showed that UF treatment was able to reject 87.82 % of COD, 98.7 % of oil, 90.5 % of Total Organic Compound (TOC) from produced water by using 20 kDa UF membrane [12]. The treatment of oil-field produced water using UF ceramic membrane also presented a good removal of oil content with 99.15% of oil rejection [11].

However, studies on produced water treatment only investigated method performance through determination of general effluent parameters, such as COD, BOD, total dissolved solids, total suspended solids, oil content, and total organic carbon and analysis of anions and cations. Several studies have evaluated specific BTX content in produced water [15-17]. However, to the best of our knowledge, limited works have examined the performance of UF in BTX removal. The present study mainly aims to investigate the performance of ultrafiltration in treating produced water, specifically in filtering BTX pollutants. In detail, Polyethersulfone (PES) was selected as membrane material for ultrafiltration due to its hydrophilic property. To enhance the ultrafiltration performance, this research combined ultrafiltration and ozone pre-treatment and post-treatment for removal of produced water compounds. Ozone was selected because it can break up large organic molecules. Ozone can break complex molecular organic compounds in crude oil, which is a component of produced water [18-19]. Ziabari et al. [20] studied the removal of hydrocarbons from aqueous solution by ozonation. In addition, Zha et al. [21] reported that ozone could oxidize compounds having a large molecular weight to generate smaller compounds. Ozone can also reduce fouling associated with microfiltration and ultrafiltration [22-25]. Hence, we confirm the novelty of this research by implementing the combination of ultrafiltration and ozone to improve ultrafiltration performance for produced water treatment. The improvement was achieved not only in the term of permeate quality but also reduction of membrane fouling. Results provide novel significant findings in this research area.

2 Materials and Method

2.1 Membrane characterization

Two available commercial membranes made of PES (NADIR Filtration, Germany) were used to filter produced water. Membranes with molecular-weight cut-off of 10 and 20 kDa and were labelled as PES 1 and PES 2, respectively. Specific functional groups were identified using Fourier transform infrared spectroscopy (Shimadzu IR Prestige-21). Specific functional groups were examined based on their wavelength as a function of absorbance (Fig. 1).

Similar peaks at 1577.77 and 1485.19 cm^{-1} are characteristics of PES membrane. Peaks at 1485.19 and 1577.77cm^{-1} indicate the presence of aromatic components (C=C stretching) in benzene, and peaks at 1240.23 and 1242.16 cm^{-1} represent ether aromatic compounds [26-27]. In addition, peaks at 1151.5 and 1105.21 cm^{-1} exhibit SO_2

symmetrical stretching and are assigned to a sulfuric component. Peaks at 1656 and 1321 cm^{-1} are predicted as preservative PVP (poly-N-vinyl-2-pyrrolidone) because it is an additive polymer used for pore formation on PES and polysulfone membrane [27]. Moreover, a specific peak at 3500-3000 cm^{-1} is assigned to PES 2 membrane and indicates the existence of OH stretching radical. The PES 2 membrane was predicted to be more hydrophilic than the PES 1 membrane. To confirm this finding, the contact angle of the membrane was measured by using Optical Contact Angle Meter (DataPhysics, OCA 15LJ). The contact angle of the PES 1 and PES 2 membrane were 70.7° and 50.1°, respectively.

Table 1 summarizes the properties of UF membrane in relation to its pore size and water flux.

Table 1 Properties of UF membranes used in this work

Membrane	MWCO (Da)	Pure Water Flux ($L/m^2.hr$)
PES-1	10.000	11.25
PES-2	20.000	94.27

Table 1 shows that the pure water flux of the PES 2 membrane was higher than that of the PES 1 membrane. The pure water flux was mainly determined by membrane pore size and its surface hydrophilicity [28]. Given that the PES 2 membrane possessed a large pore size, it exhibited higher pure water flux. Membrane surface morphology was analyzed by scanning electron microscopy (FEI, Type Inspect-S50, Japan) at a specific magnification.

2.2 Ultrafiltration

Ultrafiltration experiments were conducted in a homemade laboratory-scale test cell. The apparatus consisted of a 500 mL feed tank, a pump (Kemflow, with nominal flow rate of 1.0 L/min, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar), a pressure gauge (JAKO, maximum pressure of 10.34 bar), and a stainless steel membrane cell. The pressure and flow rate were controlled using feed valve (Needle Valve, 1/4" FNPT x 1/4" FNPT, maximum pressure of 5000 psi, materials SS 316). Fig. 2 shows the schematic of the ultrafiltration cell.

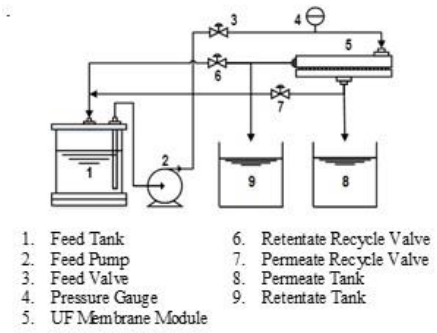

Fig. 2 Schematic of the ultrafiltration cell

All filtration runs were carried out at room temperature (25 ± 2°C). The membrane was compacted by filtering water through the membrane at a pressure of 2 bar for 0.5 h. For each experimental run, a new circular membrane sheet with an area of 13.85 cm^2 was used for measurement of initial water flux (J_0). Initial water flux (J_0) was determined by filtering pure water using a new clean membrane, then measuring the volume of water permeate collected at a specific recording time. Filtrations were carried out using total recycle mode, where both permeate, and retentate were recycled to the feed tank, to maintain the same concentration. Permeate flux (J) was determined by analytically weighting permeate collected at every 5 min intervals for 60 min. Membrane or permeate fluxes (J) were calculated by dividing the volume of permeate (Q) by the effective membrane area (A) and the sampling time (t), as defined in Eq. (1):

$$J = \frac{1}{A \cdot t} Q \quad (1)$$

where:

J: flux (L/m^2h), Q: volume (L), A: membrane area (m^2), and t: time interval (h).

The ability of the membrane for removing specific pollutants from produced water was determined by % rejection (%R). Membrane rejection was calculated by dividing the difference between the concentration of a specific pollutant in the feed (C_f) with the concentration of specific pollutants in permeate (C_p), as expressed in Eq. (2).

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

In this research, the term rejection and permeate and feed concentrations refers to rejection and concentrations of COD, total oil content, toluene, and xylene.

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2.3 Ozonation

Ozonation pre-treatment and post-treatment were conducted by Ozonizer, a generator (Krisbow) and flow meter. In the pre-treatment process, ozone was purged into the produced water feed. For the post-treatment, ozone was added into the permeate. Ozone concentration was tested using HI38054 Ozone Test kit. The ozone flow rate was set as 2 L/min, the contact time was 5 min, and the corresponding ozone concentration was 0.3 mg/L.

2.4 Produced Water Quality Analysis

Produced water was collected from offshore facilities in Cepu region, Central Java, Indonesia. Water quality was assessed using the produced water in the feed and permeate. COD of the feed and permeate samples were determined by Water quality was assessed using the produced water in the feed and permeate. The COD in the feed and permeate samples were determined by Test Tube Heater-COD Reactor (HANA HI 839800) for 2 hours at the temperature of 150ºC. Analysis of the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry (Perkin Elmer Lambda 20). The spectrophotometric analysis was performed based on the methods explained by Zadorojny et al. [29]. The similar method was adopted by Indonesian standard analysis (SNI 06-6989.30-2005). Table 2 shows the characteristics of produced water.

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	1872 mg/L
Oil and grease content	931.01 mg/L
Benzene	<0.8 mg/L
Toluene	2.62 mg/L
Xylene	3.11 mg/L
Phenol	<0.03 mg/L
Ammonia	0.22 mg/L
pH	8

According to Table 2, the mean levels of benzene, toluene, and xylene in the produced water sample were below 0.8, 2.62, and 3.11 mg/L, respectively. For comparison, produced water was also collected from the Bonsucesso treatment plant, State of Sergipe, Brazil and had average concentrations of 1397, 1263, and 312 μg/L for benzene, toluene, and xylene, respectively [16]. Similar results were also found in an oilfield wastewater platform in the Gulf of Mexico. Examination of oilfield wastewater in that area indicated that the concentrations of benzene, toluene, and xylene were 0.8–4.6, 1.0–3.5, and 0.2–0.7 mg/L, respectively [17]. In the Campos Basin, State of Rio de Janeiro, Brazil, the levels of benzene, toluene, and xylene were 283–1855, 87.04–2224, and 67.35–5969 mol/L, respectively [15].

3 Results and Discussions

3.1 Membrane Flux Behaviour

Normalization of flux profiles (J/J_0) as a function of time is presented in Fig. 3. In general, the flux showed a declining trend during ultrafiltration. The reduction of membrane flux is a characteristic of membrane fouling, which can be generated by an increase in membrane resistance due to pore blocking, concentration polarization, and cake formation [23]. Fouling can be related to the accumulation of a substance (called foulant) on the membrane surface or inside the membrane pores. At the beginning of ultrafiltration, no foulant deposit was found on the membrane surface. As time increased, foulants accumulated on the membrane surface and generated a cake layer, leading to decreased flux value and normalized fluxes.

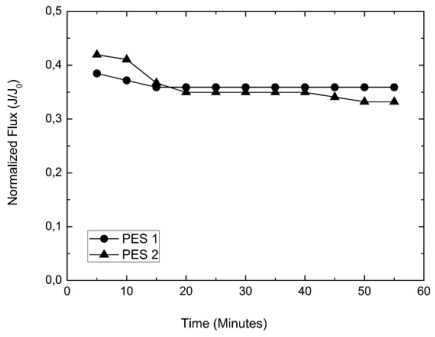

Fig. 3 Performance of membrane normalized fluxes as a function of time in treatment of produced water by using membranes with different pore sizes (TMP = 1 bar)

In the ultrafiltration treatment of produced water, its components, such as oil and other organic compounds, are significant sources of fouling. Ashaghi et al. [30] and Maguire-Boyle and Barron [31] proposed that fouling during filtration of produced water could be due to biofouling, scaling, organic fouling, and colloidal fouling. Fouling could also be attributed to microbial contaminants

(biofouling), salt precipitation resulting in scaling, organic fouling due to pore plugging or pore coating by hydrocarbon compounds, and clay and silica accumulation on the membrane surface (colloidal fouling). However, flux reduction was relatively steady along with time because of the compression of the cake layer and its constant thickness.

The flux decline of the PES 2 membrane was more pronounced than that of the PES 1 membrane. The flux decline (final flux compared with the initial flux) values of PES 2 and PES 1 membranes were found to be 8.7% and 2.5 %, respectively. The flux decline can be explained by membrane fouling caused by pore blocking or membrane adsorption due to contaminants in the produced water. The pore size of the PES 1 membrane was slightly smaller than that of the PES 2 membrane. Contaminants with size bigger than the membrane pores have a tendency to form a cake layer on the membrane surface. By contrast, contaminants with size smaller than the membrane pores are likely to induce membrane pore blocking or adsorption. In the PES 2 membrane, contaminants most likely close the membrane pores strongly and accumulated on the membrane surface [32].

Two levels of trans-membrane pressure (TMP) were applied to study its effect on membrane behaviour in produced water treatment (Fig. 4).

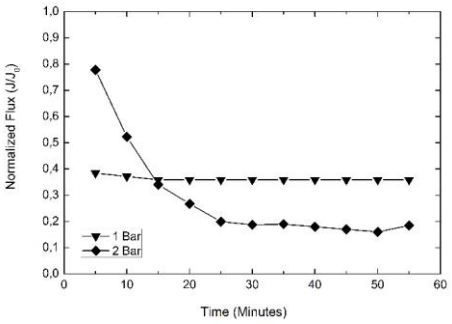

Fig. 4 Behavior of membrane normalized fluxes as a function of time in treatment of produced water under different trans membrane pressure levels (membrane : PES 1)

The initial normalized flux was high at high TMP but decreased at the end of the process. The flux decrease at TMP of 2 bar (59 %) was higher than that at 1 bar (2.5 %). As a general rule, the increase in TMP in ultrafiltration of oil exerts negative and positive influences on the permeate flux [33]. At high TMP, more oil droplets and solutes passed quickly through the membrane pores. However, more oil droplets contributed to oil droplet accumulation both on the membrane surface and in the pores. The accumulation of oil droplets led to the formation of a cake layer on the membrane surface. It is predicted that initially a gel layer is formed due to some solutes congeal on the membrane surface. A steady state of flux is obtained with assumption that the concentration does not increase. However, with the increase of pressure, the gel layer is transformed into cake layer. In cake layer, the fouling increases continuously and result in complete blocking with no flux. The use of high TMP also resulted in the formation of a cake layer covering the membrane pores, thereby inducing membrane fouling [34].

Fig. 5 represents the effect of ozonation pre-treatment on ultrafiltration behaviour.

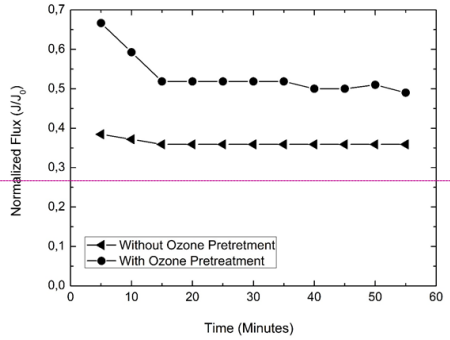

Fig. 5 Effect of ozonation pre-treatment on membrane normalized fluxes as a function of time for ultrafiltration of produced water (membrane: PES 1, TMP = 1 bar)

The normalized flux of the PES 1 membrane with ozone pre-treatment was higher than without ozone pre-treatment, but the flux decrease after ozone pre-treatment remained high. The flux decline of the membrane with ozone pre-treatment was about 18.5%, whereas the flux decrease of the membrane without ozone pre-treatment was only about 2.5 %. Ozone can oxidize the majority of organic compounds (about 35 %) in produced water into smaller intermediate products, which are then decomposed into CO_2 and H_2O [21]. Ozonation of produced water could also generate new compounds, such as acids, amines, and aldehyde, which influence the fouling rate of membranes during filtration. Figure 6 reveals that ozone pre-treatment can diminish membrane fouling, as indicated by the superior normalized flux profile of the membrane subjected

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to UF with ozone pre-treatment over that subjected to UF only. The flux decline was significant in the first stage of filtration but became steady thereafter. Pre-ozonation can also reduce dissolved organic carbon by mineralization of small organic molecules. The breaking of large molecules was found to be the dominant principle for fouling reduction [22]. This finding was supported by the images of the SEM membrane illustrated in Fig. 6.

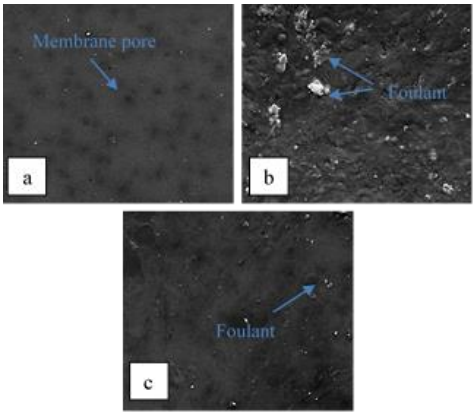
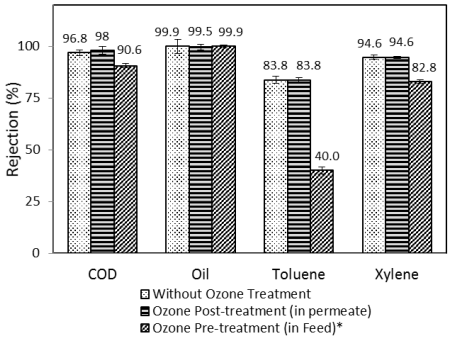


Fig. 6 SEM result of PES membranes (magnification of 20,000 ×: (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

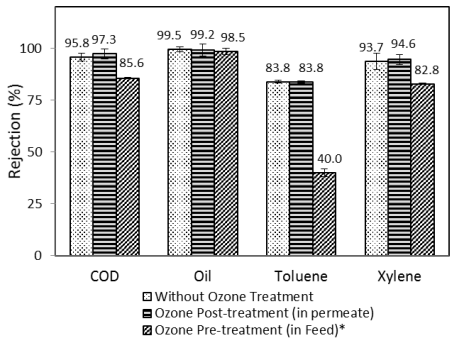
Fig. 6 confirms the clean surface of the new membrane (Fig. 6.a) without any substances on its top. By contrast, Fig. 6.b shows some foulants deposited on the membrane surface when filtering produced water without pre-treatment. The foulant deposits formed a cake layer, with some small particles found above the cake layer. The foulants were almost certainly suspended solids and large-molecular-weight compounds, such as xylene, toluene, benzene, and phenol in the produced water; as such, the foulants blocked the membrane surface and then formed a cake layer. At a certain period, foulant particles accumulated and generated a thick cake layer, thereby promoting the deposition of the foulant on the cake surface. During the filtration of produced water feed with ozone pre-treatment (Figure 6.c), the membrane surface showed a better appearance. Some foulant deposits were observed, but their size was smaller than that in the deposits shown in Figure 6.b. Organic substances present in produced water are responsible for membrane fouling. Song et al. [35] also described that membrane fouling was produced by organic substances with a high molecular weight. Ozone may also oxidize organic compounds in produced water and effectively decrease the risk of fouling of the membrane. A similar result was also found by You et al. [25], who confirmed that the C=H bonds in the aromatic rings could be eliminated by ozone and more C–H and C–H bonds could be produced in the alkanes. Moreover, ozone can destroy aromatic rings to form few alkanes with a linear chain.

3.2 Membrane Rejection

In the ultrafiltration membrane, membrane selectivity is determined by membrane rejection. The ability of the PES membrane to selectively resist COD, oil, toluene and xylene in the produced water is shown in Fig. 7.



(a)



(b)

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2 * (C_f Toluene =C Toluene after feed ozonation = 0.10 mg/L).

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The ultrafiltration membrane showed significantly high rejection rates for COD, oil and grease, toluene, and xylene under various conditions, except for toluene during ozone pre-treatment. The low value of toluene rejection did not indicate its high concentration in the permeate because ozone pre-treatment could significantly reduce the toluene concentration. The rejection of the PES 1 membrane for COD and oil and grease concentration was slightly greater than that of the PES 2 membrane, which has bigger pore size. In membranes with a large pore size, oil that accumulated on the membrane surface will possibly permeate through large pores, resulting in slightly higher oil concentration in the permeate. Rejection or removal efficiency of this system to decrease oil and grease was considerably high (in the range of 98-99.9 %) showing that almost all oil was removed. Physical treatment such as EPCON compact floatation unit reduced 50-70 % dispersed oil [36]. Applying a copolymer could absorb up to 85 % of oil in produced water [37]. On the other hand, utilizing biological treatment such as rotating disk, aerated biological filter was only able to reduce oil and grease to 74 % [38].

Oil can be categorized as an organic compound; hence, the value of COD in the permeate was high, corresponding to low COD rejection. Implementation of this system is able to reduce the COD in the range of 85.6-98%. This value of reduction is considerably high since the COD reduction by applying another method was low. Using electrochemical oxidation only removed up to 57% of initial COD concentration [39]. The sequence batch reactor SBR, with acclimated sewage sludge, had COD removal efficiencies varied from 30% to 50% [40] and applying microwave (MW)-assisted CWAO (Catalytic Wet Air Oxidation) in produced water treatment showed more than 90% of COD was removed [41]. This combined system of ultrafiltration–ozone was also confirmed superior to the immobilization of microorganism for produced water treatment that was only removed 90% of initial COD at COD concentration of 2600 mg/L [42].

Table 3 presents the characteristics of ultrafiltration permeate and the standard regulation of on-shore produced water in Indonesia. According to the table, permeates both with UF only and ozone combined-UF are in the range of acceptable level for water discharge. The result is significant since this method was able to reduce the oil and grease to a very low level (<0.03 - 8.18 mg/L) compared to the existing method. It is reported that the conventional method of produced water treatment reduced the oil and grease concentrations to 30-40 mg/L [37]. In addition, almost all of benzene, toluene, and xylene were removed during the ultrafiltration of produced water under various conditions.

Table 3 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Phenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

* Permeate characteristic of the parameter was not tested because its value is below the standard limit
** Average value of PES 1 and PES 2 membrane, 1 atm
*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia

This result is superior compared to other methods of produced water treatment. It was reported that neutralized amine "tailored" zeolites were applied in produced water treatment, and only able to remove around 70 and 85% of BTEX from saline produced water [38]. In addition, this ultrafiltration-ozone combined system achieved similar result with the commercially available method such as Macro-porous Polymer Extraction (MPPE) technology, which the MPPE achieved 99% removal of BTEX [38].

Produced water contains crude oil, which is a mixture of hydrocarbons, such as naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons (PAHs), and phenols. These hydrocarbons could not be dissolved but are dispersed in produced water. In this research, ultrafiltration membranes with molecular-weight cut-off (MWCO) values of 10.000 and 20.000 Da and pore sizes of 0,01 and 0,02 µm were used. The membranes rejected compounds with molecular weight within 10.000 and 20.000 Daltons.

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Produced water comprises organic compounds, such as benzene, toluene, and xylene (BTX), which have lower molecular weight than the molecular weight cut-off. When applying the "membrane-sieving principle", the BTX components should pass through the membrane pores. However, the results showed high rejection rates for toluene and xylene. BTX exists as dispersed oil and has size larger than that of the membrane pores; hence, BTX was rejected by the ultrafiltration membrane.

Ozonation pre-treatment significantly reduced the concentrations of toluene and xylene and COD. This method is accurate because ozone can degrade macromolecular matter into small organic matter [21] and change the composition and hydrophilicity of organic matter [35]. Šilhárová et al. [18] provided evidence that ozone treatment led to a low concentration of organic petroleum compound (BTEX). The removal efficiency of ozonation for xylene, toluene, and benzene reached 90%, 89 %, and 86 %, respectively. The removal efficiency was correlated with reaction kinetics of BTX and ozone. The reaction kinetic rates of ozone with benzene, toluene, and xylene were 4.75×10^{-2}, 7.30×10^{-2}, and 1.82×10^{-1} $\mu g/m^3.h$, respectively.

COD is the oxygen required to degrade biodegradable and non-biodegradable organic compounds. As shown in Table 3, the concentration of COD was decreased by both ultrafiltration and ozone pre- or post-treatment. This finding verifies that the amount of organic compounds decreased when produced water was subjected to ultrafiltration combined with ozonation pre- or post-treatment.

4 Conclusion

The quality of produced water was examined based on oil and grease content as well as COD, which were found to be higher than the standard limit of wastewater for oil and gas activities. Benzene, toluene, and xylene were also detected in the produced water. Two commercial Ultrafiltration PES membranes were used to treat the produced. Ultrafiltration was modified by combining it with feed ozonation (pre-treatment) and permeate ozonation (post-treatment). This experimental work demonstrated that ultrafiltration and its combination with ozone pre-treatment and post-treatment showed effective removal of COD, oil and grease, toluene, and xylene. It is also confirmed that almost oil and grease can be removed by using this combined system. Ultrafiltration with ozone pre-treatment led to higher flux profile than ultrafiltration only. This finding verifies that ozone pre-treatment did not only remove produced water pollutants but also diminished the fouling of the ultrafiltration membrane. In addition, it was confirmed that the quality of permeate satisfied the acceptable level to discharge.

Abbreviation list

A	Membrane area (m^2)
BTX	Benzene, toluene, and xylene
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
C_f	Concentration of a specific pollutant in the feed
C_p	Concentration of specific pollutants in permeate
J	Flux (L/ m^2h)
J/J_0	Normalization of flux profiles
J_0	Initial water flux
MWCO	Molecular weight cut off
PAH	Polyaromatic hydrocarbons
PES	Polyethersulfone
Q	Volume (L)
R	Rejection (%)
SEM	Scanning electron microscopy
t	Time interval (h)
TMP	Transmembrane pressure (bar)
TOC	Total organic compound
UF	Ultrafiltration
UV-Vis	Ultraviolet, visible spectrophotometer

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Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

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Abstract

Oil exploration waste, also called produced water, contains hazardous pollutants, such as benzene; benzene, toluene, and xylene (BTX); naphthalene, phenanthrene, and dibenzothiophene (NDP); polyaromatic hydrocarbons (PAHs); and phenol. Produced water is characterized by high chemical oxygen demand (COD) and oil content, which exceed the standard limits of regulation. In this study, the combination of ultrafiltration (UF) and ozone pre-treatment and post-treatment were applied for treatment of produced water to minimize its environmental impact. Produced water and membrane were characterized, and their ultrafiltration performance for removal of oil content, benzene, toluene, xylene, and COD. Two commercial Polyethersulfone membranes, with molecular-weight cut-off values of 10 and 20 kDa, were used. The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Separation performance was evaluated based on flux profile and removal of COD, oil and grease content, toluene, and xylene. Significant finding was found where the combination of UF with ozone pre-treatment and post-treatment could significantly eliminate COD, oil content, toluene, and xylene. The rejection of these components was found higher than conventional process, which was in the range of 80 % to 99 %. In addition, almost oil and grease can be removed by using this combined system. Permeate quality of this system confirmed the acceptable level as water discharge.

Keywords

ultrafiltration, ozone, produced water, benzene, toluene, xylene

1 Introduction

Oil explorations are the primary source of energy, and their corresponding activities generate a large volume of oilfield wastewater, also referred as produced water. For each barrel of oil, three barrels of produced water are generated [1]. In general, produced water is reused to enhance oil recovery or treated prior to discharge into the environment. Produced water comprises various organic and inorganic substances, which are potentially characterized as hazardous and toxic wastes. Produced water compound is categorized as organic substance, inorganic substance, and radionucleotide. Moreover, produced water contains some important compounds, such as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids, and dissolved gases [2]. Oils consist of monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAH), and related heterocyclic aromatic compounds [3]. BTEX and phenols are dissolved in water. Residual chemicals, such as corrosion and scale inhibitors, emulsion breakers, and biocides, are also present in produced water [4].

Compounds in produced water are toxic and adversely affect the environment. Bakke et al. [5] published a review of the environmental impact of produced water and oil drilling in the offshore petroleum industry. Alkylphenols, naphthenic acids, and PAHs from produced water may disrupt reproductive functions and affect several chemicals, biochemical, and genetic biomarkers. As a consequence of the lethal effects of produced water contaminants, many countries have implemented a stringent regulatory

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standard for discharging produced water to alleviate their adverse environmental impacts. Produced water quality can be represented as oil content or concentration and chemical oxygen demand (COD). The concentrations of oil and COD in produced water are relatively high, reaching 565 and 1220 mg/L, respectively [1]. The government of the Republic of Indonesia through Regulation of the Minister of State for Environment No. 19 set standard limits for wastewater for oil and gas activities in 2010. The permitted oil concentration and COD are within 20–50 and 200 mg/L, respectively. Hence, treatment of produced water is a responsibility for oil and gas explorations.

Membrane technology has been applied to treat produced water and reviewed comprehensively [6, 7]. Ultrafiltration membrane is also an appropriate method for produced water treatment. Ultrafiltration (UF) is a low-pressure driven membrane filtration process operating at 2–10 bar [8]. The pore size of an UF membrane ranges from 0.001 μm to 0.1 μm; as such, the membrane rejects compounds with molecular weight of 1000 to 100.000 Da [9].

Several researchers have examined the use of UF membranes for handling produced water [10-14]. The previous study showed that UF treatment was able to reject 87.82 % of COD, 98.7 % of oil, 90.5 % of Total Organic Compound (TOC) from produced water by using 20 kDa UF membrane [12]. The treatment of oil-field produced water using UF ceramic membrane also presented a good removal of oil content with 99.15% of oil rejection [11].

However, studies on produced water treatment only investigated method performance through determination of general effluent parameters, such as COD, BOD, total dissolved solids, total suspended solids, oil content, and total organic carbon and analysis of anions and cations. Several studies have evaluated specific BTX content in produced water [15-17]. However, to the best of our knowledge, limited works have examined the performance of UF in BTX removal. The present study mainly aims to investigate the performance of ultrafiltration in treating produced water, specifically in filtering BTX pollutants. In detail, Polyethersulfone (PES) was selected as membrane material for ultrafiltration due to its hydrophilic property. To enhance the ultrafiltration performance, this research combined ultrafiltration and ozone pre-treatment and post-treatment for removal of produced water compounds. Ozone was selected because it can break up large organic molecules. Ozone can break complex molecular organic compounds in crude oil, which is a component of produced water [18-19]. Ziabari et al. [20] studied the removal of hydrocarbons from aqueous solution by ozonation. In addition, Zha et al. [21] reported that ozone could oxidize compounds having a large molecular weight to generate smaller compounds. Ozone can also reduce fouling associated with microfiltration and ultrafiltration [22-25]. Hence, we confirm the novelty of this research by implementing the combination of ultrafiltration and ozone to improve ultrafiltration performance for produced water treatment. The improvement was achieved not only in the term of permeate quality but also reduction of membrane fouling. Results provide novel significant findings in this research area.

2 Materials and Method

2.1 Membrane characterization

Two available commercial membranes made of PES (NADIR Filtration, Germany) were used to filter produced water. Membranes with molecular-weight cut-off of 10 and 20 kDa and were labelled as PES 1 and PES 2, respectively. Specific functional groups were identified using Fourier transform infrared spectroscopy (Shimadzu IR Prestige-21). Specific functional groups were examined based on their wavelength as a function of absorbance (Fig. 1).

Similar peaks at 1577.77 and 1485.19 cm^{-1} are characteristics of PES membrane. Peaks at 1485.19 and 1577.77 cm^{-1}

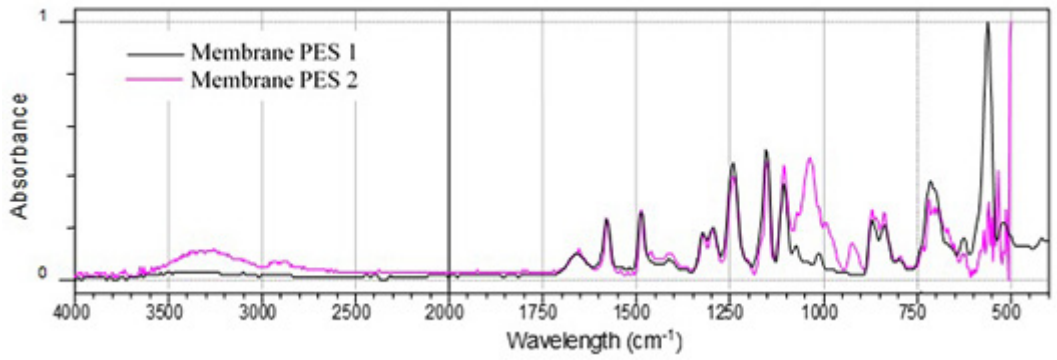

Fig. 1 FTIR results of PES 1 and PES 2 membranes

indicate the presence of aromatic components (C=C stretching) in benzene, and peaks at 1240.23 and 1242.16 cm^{-1} represent ether aromatic compounds [26-27]. In addition, peaks at 1151.5 and 1105.21 cm^{-1} exhibit SO_2 symmetrical stretching and are assigned to a sulfuric component. Peaks at 1656 and 1321 cm^{-1} are predicted as preservative PVP (poly-N-vinyl-2-pyrrolidone) because it is an additive polymer used for pore formation on PES and polysulfone membrane [27]. Moreover, a specific peak at 3500-3000 cm^{-1} is assigned to PES 2 membrane and indicates the existence of OH stretching radical. The PES 2 membrane was predicted to be more hydrophilic than the PES 1 membrane. To confirm this finding, the contact angle of the membrane was measured by using Optical Contact Angle Meter (DataPhysics, OCA 15LJ). The contact angle of the PES 1 and PES 2 membrane were 70.7° and 50.1°, respectively.

Table 1 summarizes the properties of UF membrane in relation to its pore size and water flux. Table 1 shows that the pure water flux of the PES 2 membrane was higher than that of the PES 1 membrane. The pure water flux was mainly determined by membrane pore size and its surface hydrophilicity [28]. Given that the PES 2 membrane possessed a large pore size, it exhibited higher pure water flux. Membrane surface morphology was analyzed by scanning electron microscopy (FEI, Type Inspect-S50, Japan) at a specific magnification.

2.2 Ultrafiltration

Ultrafiltration experiments were conducted in a homemade laboratory-scale test cell. The apparatus consisted of a 500 mL feed tank, a pump (Kemflow, with nominal flow rate of 1.0 L/min, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar), a pressure gauge (JAKO, maximum pressure of 10.34 bar), and a stainless steel membrane cell. The pressure and flow rate were controlled using feed valve (Needle Valve, 1/4" FNPT x 1/4" FNPT, maximum pressure of 5000 psi, materials SS 316). Fig. 2 shows the schematic of the ultrafiltration cell.

All filtration runs were carried out at room temperature (25 ± 2 °C). The membrane was compacted by filtering water through the membrane at a pressure of 2 bar for 0.5 h. For each experimental run, a new circular membrane sheet with an area of 13.85 cm^2 was used for measurement of

Table 1 Properties of UF membranes used in this work

Membrane	MWCO (Da)	Pure Water Flux (L/m².hr)
PES-1	10.000	11.25
PES-2	20.000	94.27

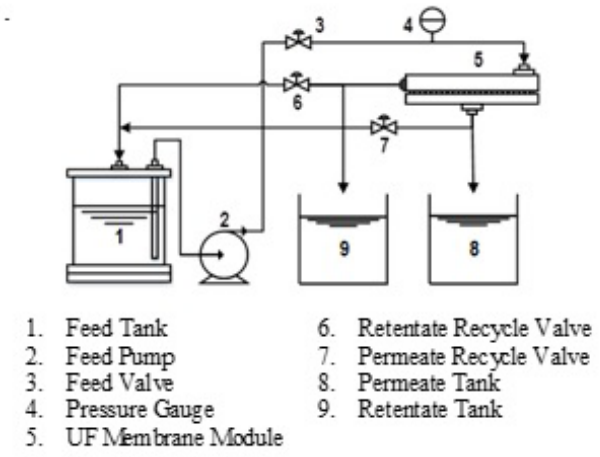

Fig. 2 Schematic of the ultrafiltration cell

initial water flux (J_0). Initial water flux (J_0) was determined by filtering pure water using a new clean membrane, then measuring the volume of water permeate collected at a specific recording time. Filtrations were carried out using total recycle mode, where both permeate, and retentate were recycled to the feed tank, to maintain the same concentration. Permeate flux (J) was determined by analytically weighting permeate collected at every 5 min intervals for 60 min. Membrane or permeate fluxes (J) were calculated by dividing the volume of permeate (Q) by the effective membrane area (A) and the sampling time (t), as defined in Eq. (1):

$$J = \frac{1}{A \cdot t} Q \tag{1}$$

where:

J: flux (L/ m^2h), Q: volume (L), A: membrane area (m^2), and t: time interval (h).

The ability of the membrane for removing specific pollutants from produced water was determined by % rejection (%R). Membrane rejection was calculated by dividing the difference between the concentration of a specific pollutant in the feed (C_f) with the concentration of specific pollutants in permeate (C_p), as expressed in Eq. (2).

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

In this research, the term rejection and permeate and feed concentrations refers to rejection and concentrations of COD, total oil content, toluene, and xylene.

2.3 Ozonation

Ozonation pre-treatment and post-treatment were conducted by Ozonizer, a generator (Krisbow) and flow meter. In the pre-treatment process, ozone was purged into the

produced water feed. For the post-treatment, ozone was added into the permeate. Ozone concentration was tested using HI38054 Ozone Test kit. The ozone flow rate was set as 2 L/min, the contact time was 5 min, and the corresponding ozone concentration was 0.3 mg/L.

2.4 Produced Water Quality Analysis

Produced water was collected from offshore facilities in Cepu region, Central Java, Indonesia. Water quality was assessed using the produced water in the feed and permeate. ~~COD of the feed and permeate samples were determined by Water quality was assessed using the produced water in the feed and permeate.~~ The COD in the feed and permeate samples were determined by Test Tube er-COD Reactor (HANA HI 839800) for 2 hours at ~~the~~ temperature of 150°C. Analysis of the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry (Perkin Elmer Lambda 20). The spectrophotometric analysis was performed based on the methods explained by Zadorojny et al. [29]. The similar method was adopted by Indonesian standard analysis (SNI 06-6989.30-2005). Table 2 shows the characteristics of produced water.

According to Table 2, the mean levels of benzene, toluene, and xylene in the produced water sample were below 0.8, 2.62, and 3.11 m, respectively. For comparison, produced wat /as ~~also~~ collected from Bonsucesso treatment plant, State of Sergipe, Brazil ~~and~~ had average concentrations of 1397, 1263, and 312 µg/L for benzene, toluene, and xylene, respectively [16]. Similar results were also found in an oilfield wastewater platform in the Gulf of Mexico. Examination of oilfield wastewater in that area indicated that the concentrations of benzene, toluene, and xylene were 0.8–4.6, 1.0–3.5, and 0.2–0.7 mg/L, respectively [17]. In the Campos Basin, State of Rio de Janeiro, Brazil, the levels of benzene, toluene, and xylene were 283–1855, 87.04–2224, and 67.35–5969 mol/L, respectively [15].

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	1872 mg/L
Oil and grease content	931.01 mg/L
Benzene	<0.8 mg/L
Toluene	2.62 mg/L
Xylene	3.11 mg/L
Phenol	<0.03 mg/L
Ammonia	0.22 mg/L
pH	8

3 Results and Discussions

3.1 Membrane Flux Behaviour

Normalization of flux profiles (J/J_0) as a function of time is presented in Fig. 3. In general, the flux showed a declining trend during ultrafiltration. The reduction of membrane flux is a characteristic of membrane fouling, which can be generated by an increase in membrane resistance due to pore blocking, concentration polarization, and cake formation [23]. Fouling can be related to the accumulation of a substance (called foulant) on the membrane surface or inside the membrane pores. At the beginning of ultrafiltration, no foulant deposit was found on the membrane surface. As time increased, foulants accumulated on the membrane surface and generated a cake layer, leading to decreased flux value and normalized fluxes.

In the ultrafiltration treatment of produced water, its components, such as oil and other organic compounds, are significant sources of fouling. Ashaghi et al. [30] and Maguire-Boyle and Barron [31] proposed that fouling during filtration of produced water could be due to biofouling, scaling, organic fouling, and colloidal fouling. Fouling could also be attributed to microbial contaminants (biofouling), salt precipitation resulting in scaling, organic fouling due to pore plugging or pore coating by hydrocarbon compounds, and clay and silica accumulation on the membrane surface (colloidal fouling). However, flux reduction was relatively steady along with time because of the compression of the cake layer and its constant thickness.

The flux decline of the PES 2 membrane was more pronounced than that of the PES 1 membrane. The flux decline (final flux compared with the initial flux) values of PES 2 and PES 1 membranes were found to be 8.7 % and 2.5 %,

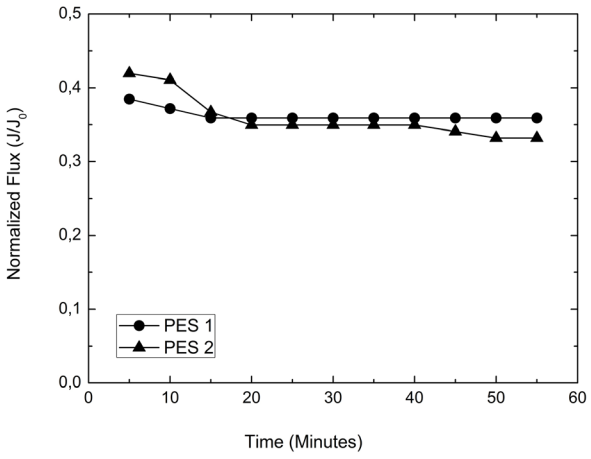

Fig. 3 Performance of membrane normalized fluxes as a function of time in treatment of produced water by using membranes with different pore sizes (TMP = 1 bar)

respectively. The flux decline can be explained by membrane fouling caused by pore blocking or membrane adsorption due to contaminants in the produced water. The pore size of the PES 1 membrane was slightly smaller than that of the PES 2 membrane. Contaminants with size bigger than the membrane pores have a tendency to form a cake layer on the membrane surface. By contrast, contaminants with size smaller than the membrane pores are likely to induce membrane pore blocking or adsorption. In the PES 2 membrane, contaminants most likely close the membrane pores strongly and accumulated on the membrane surface [32].

Two levels of trans-membrane pressure (TMP) were applied to study its effect on membrane behaviour in produced water treatment (Fig. 4).

The initial normalized flux was high at high TMP but decreased at the end of the process. The flux decrease at TMP of 2 bar (59 %) was higher than that at 1 bar (2.5 %). As a general rule, the increase in TMP in ultrafiltration of oil exerts negative and positive influences on the permeate flux [33]. At high TMP, more oil droplets and solutes passed quickly through the membrane pores. However, more oil droplets contributed to oil droplet accumulation both on the membrane surface and in the pores. The accumulation of oil droplets led to the formation of a cake layer on the membrane surface. It is predicted that initially a gel layer is formed due to some solutes congeal on the membrane surface. A steady state of flux is obtained with assumption that the concentration does not increase. However, with the increase of pressure, the gel layer is transformed into cake layer. In cake layer, the fouling increases continuously and result in complete blocking with no flux. The use of high TMP also resulted in the formation of a cake layer covering the membrane pores, thereby inducing membrane fouling [34].

Fig. 5 represents the effect of ozonation pre-treatment on ultrafiltration behaviour.

The normalized flux of the PES 1 membrane with ozone pre-treatment was higher than without ozone pre-treatment, but the flux decrease after ozone pre-treatment remained high. The flux decline of the membrane with ozone pre-treatment was about 18.5%, whereas the flux decrease of the membrane without ozone pre-treatment was only about 2.5 %. Ozone can oxidize the majority of organic compounds (about 35 %) in produced water into smaller intermediate products, which are then decomposed into CO_2 and H_2O [21]. Ozonation of produced water could also generate new compounds, such as acids, amines, and aldehyde, which influence the fouling rate of membranes during filtration. Fig. 6 reveals that ozone pre-treatment can diminish membrane fouling, as indicated by the superior normalized flux profile of the membrane subjected to UF with ozone pre-treatment over that subjected to UF only. The flux decline was significant in the first stage of filtration but became steady thereafter. Pre-ozonation can also reduce dissolved organic carbon by mineralization of small organic molecules. The breaking of large molecules was found to be the dominant principle for fouling reduction [22]. This finding was supported by the images of the SEM membrane illustrated in Fig. 6.

Fig. 6 confirms the clean surface of the new membrane (Fig. 6(a)) without any substances on its top. By contrast, Fig. 6(b) shows some foulants deposited on the membrane surface when filtering produced water without pre-treatment. The foulant deposits formed a cake layer, with some small particles found above the cake layer. The foulants

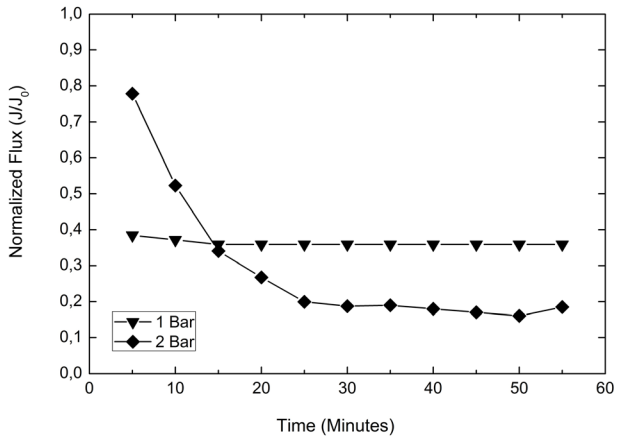

Fig. 4 Behavior of membrane normalized fluxes as a function of time in treatment of produced water under different trans membrane pressure levels (membrane : PES 1)

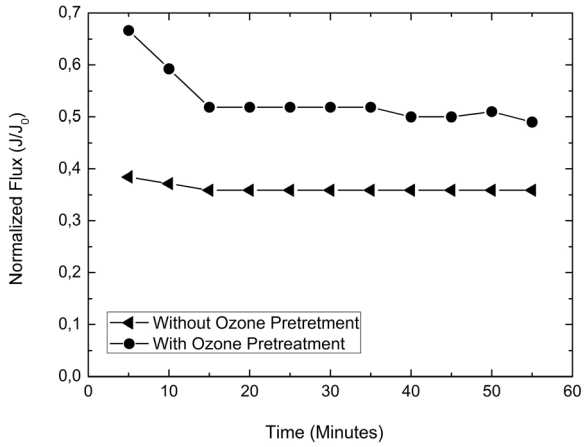

Fig. 5 Effect of ozonation pre-treatment on membrane normalized fluxes as a function of time for ultrafiltration of produced water (membrane: PES 1, TMP = 1 bar)

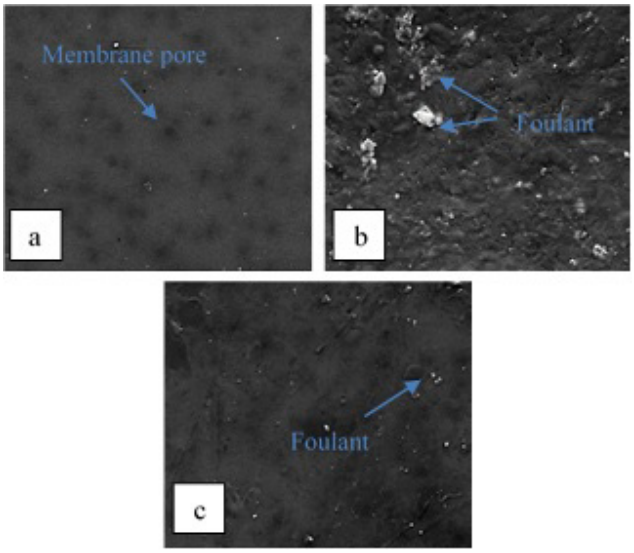

Fig. 6 SEM result of PES membranes (magnification of 20,000 ×: (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

were almost certainly suspended solids and large-molecular-weight compounds, such as xylene, toluene, benzene, and phenol in the produced water; as such, the foulants blocked the membrane surface and then formed a cake layer. At a certain period, foulant particles accumulated and generated a thick cake layer, thereby promoting the deposition of the foulant on the cake surface. During the filtration of produced water feed with ozone pre-treatment (Fig. 6(c)), the membrane surface showed a better appearance. Some foulant deposits were observed, but their size was smaller than that in the deposits shown in Fig. 6(b). Organic substances present in produced water are responsible for membrane fouling. Song et al. [35] also described that membrane fouling was produced by organic substances with a high molecular weight. Ozone may also oxidize organic compounds in produced water and effectively decrease the risk of fouling of the membrane. A similar result was also found by You et al. [25], who confirmed that the C=H bonds in the aromatic rings could be eliminated by ozone and more C–H and C–H bonds could be produced in the alkanes. Moreover, ozone can destroy aromatic rings to form few alkanes with a linear chain.

3.2 Membrane Rejection

In the ultrafiltration membrane, membrane selectivity is determined by membrane rejection. The ability of the PES membrane to selectively resist COD, oil, toluene and xylene in the produced water is shown in Fig. 7.

The ultrafiltration membrane showed significantly high rejection rates for COD, oil and grease, toluene, and xylene under various conditions, except for toluene during ozone pre-treatment. The low value of toluene rejection did not indicate its high concentration in the permeate because ozone pre-treatment could significantly reduce the toluene concentration. The rejection of the PES 1 membrane for COD and oil and grease concentration was slightly greater than that of the PES 2 membrane, which has bigger pore size. In membranes with a large pore size, oil that accumulated on the membrane surface will possibly permeate through large pores, resulting in slightly higher oil concentration in the permeate. Rejection or removal efficiency of this system to decrease oil and grease was considerably high (in the range of 98-99.9 %) showing that almost all oil was removed. Physical treatment such as EPCON

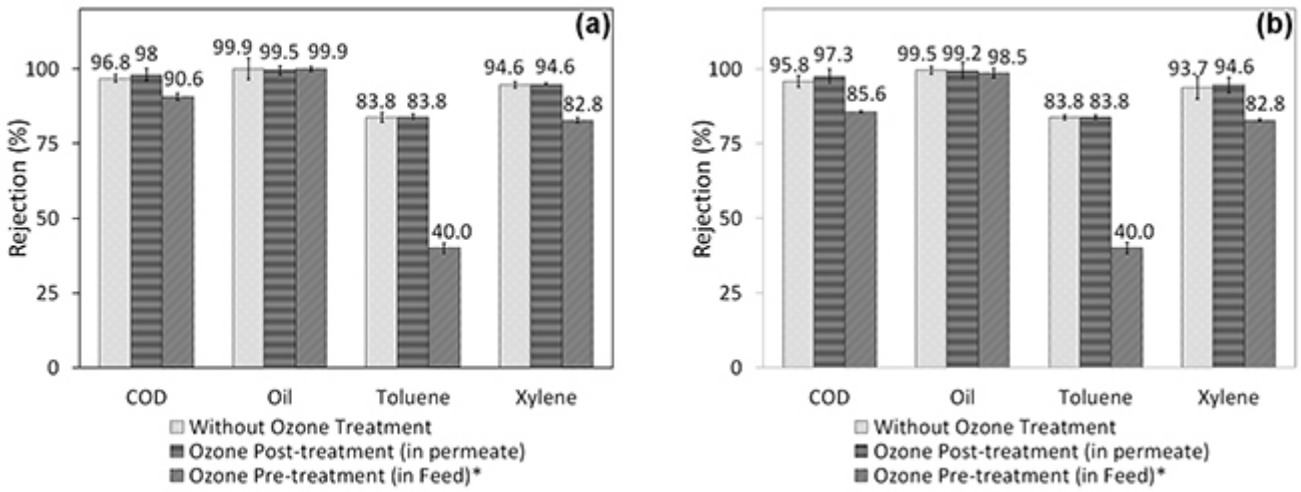

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2
* (C_fToluene =C Toluene after feed ozonation = 0.10 mg/L).

compact floatation unit reduced 50-70 % dispersed oil [36]. Applying a copolymer could absorb up to 85 % of oil in produced water [37]. On the other hand, utilizing biological treatment such as rotating disk, aerated biological filter was only able to reduce oil and grease to 74 % [38].

Oil can be categorized as an organic compound; hence, the value of COD in the permeate was high, corresponding to low COD rejection. Implementation of this system is able to reduce the COD in the range of 85.6-98%. This value of reduction is considerably high since the COD reduction by applying another method was low. Using electrochemical oxidation only removed up to 57% of initial COD concentration [39]. The sequence batch reactor SBR, with acclimated sewage sludge, had COD removal efficiencies varied from 30% to 50% [40] and applying microwave (MW)-assisted CWAO (Catalytic Wet Air Oxidation) in produced water treatment showed more than 90 % of COD was removed [41]. This combined system of ultrafiltration–ozone was also confirmed superior to the immobilization of microorganism for produced water treatment that was only removed 90% of initial COD at COD concentration of 2600 mg/L [42].

Table 3 presents the characteristics of ultrafiltration permeate and the standard regulation of on-shore produced water in Indonesia. According to the table, permeates both with UF only and ozone combined-UF are in the range of acceptable level for water discharge. The result is significant since this method was able to reduce the oil and grease to a very low level (<0.03 - 8.18 mg/L) compared to the existing method. It is reported that the conventional method of produced water treatment reduced the oil and grease concentrations to 30-40 mg/L [37]. In addition, almost all of benzene, toluene, and xylene were removed during the ultrafiltration of produced water under various conditions.

This result is superior compared to other methods of produced water treatment. It was reported that neutralized amine "tailored" zeolites were applied in produced water treatment, and only able to remove around 70 and 85% of BTEX from saline produced water [38]. In addition, this ultrafiltration-ozone combined system achieved similar result with the commercially available method such as Macro-porous Polymer Extraction (MPPE) technology, which the MPPE achieved 99% removal of BTEX [38].

Produced water contains crude oil, which is a mixture of hydrocarbons, such as naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons (PAHs), and phenols. These hydrocarbons could not be dissolved but are dispersed in produced water. In this research, ultrafiltration membranes with molecular-weight cut-off (MWCO) values of 10.000 and 20.000 Da and pore sizes of 0.01 and 0.02 µm were used. The membranes rejected compounds with molecular weight within 10.000 and 20.000 Daltons. Produced water comprises organic compounds, such as benzene, toluene, and xylene (BTX), which have lower molecular weight than the molecular weight cut-off. When applying the "membrane-sieving principle", the BTX components should pass through the membrane pores. However, the results showed high rejection rates for toluene and xylene. BTX exists as dispersed oil and has size larger than that of the membrane pores; hence, BTX was rejected by the ultrafiltration membrane.

Ozonation pre-treatment significantly reduced the concentrations of toluene and xylene and COD. This method is accurate because ozone can degrade macromolecular matter into small organic matter [21] and change the composition and hydrophilicity of organic matter [35]. Šilhárová et al. [18] provided evidence that ozone treatment led to a low concentration of organic petroleum compound (BTEX).

Table 3 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Phenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

* Permeate characteristic of the parameter was not tested because its value is below the standard limit

** Average value of PES 1 and PES 2 membrane, 1 atm

*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia

The removal efficiency of ozonation for xylene, toluene, and benzene reached 90%, 89 %, and 86 %, respectively. The removal efficiency was correlated with reaction kinetics of BTX and ozone. The reaction kinetic rates of ozone with benzene, toluene, and xylene were 4.75×10^{-2}, 7.30×10^{-2}, and 1.82×10^{-1} μg/m^3.h, respectively.

COD is the oxygen required to degrade biodegradable and non-biodegradable organic compounds. As shown in Table 3, the concentration of COD was decreased by both ultrafiltration and ozone pre- or post-treatment. This finding verifies that the amount of organic compounds decreased when produced water was subjected to ultrafiltration combined with ozonation pre- or post-treatment.

4 Conclusion

The quality of produced water was examined based on oil and grease content as well as COD, which were found to be higher than the standard limit of wastewater for oil and gas activities. Benzene, toluene, and xylene were also detected in the produced water. Two commercial Ultrafiltration PES membranes were used to treat the produced. Ultrafiltration was modified by combining it with feed ozonation (pre-treatment) and permeate ozonation (post-treatment). This experimental work demonstrated that ultrafiltration and its combination with ozone pre-treatment and post-treatment showed effective removal of COD, oil and grease, toluene, and xylene. It is also confirmed that almost oil and grease can be removed by using this combined system. Ultrafiltration with ozone pre-treatment led to higher flux profile than ultrafiltration only. This finding verifies that ozone pre-treatment did not only remove produced water pollutants but also diminished the fouling of the ultrafiltration membrane. In addition, it was confirmed that the quality of permeate satisfied the acceptable level to discharge.

Abbreviations

A	Membrane area (m^2)
BTX	Benzene, toluene, and xylene
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
C_f	Concentration of a specific pollutant in the feed
C_p	Concentration of specific pollutants in permeate
J	Flux (L/ m^{2}h)
J/J_0	Normalization of flux profiles
J_0	Initial water flux
MWCO	Molecular weight cut off
PAH	Polyaromatic hydrocarbons
PES	Polyethersulfone
Q	Volume (L)
R	Rejection (%)
SEM	Scanning electron microscopy
t	Time interval (h)
TMP	Transmembrane pressure (bar)
TOC	Total organic compound
UF	Ultrafiltration
UV-Vis	Ultraviolet, visible spectrophotometer

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LIST OF CORRECTION :

1. **Page 4 :**
   After sub section 2.4:
   - Remove the sentence "*COD of the feed and permeate samples were determined by Water quality was assessed using the produced water in the feed and permeate.*"
   - **Remove** "the" in sentence *"The COD in the feed and permeate samples were determined by Test Tube HeaterCOD Reactor (HANA HI 839800) for 2 hours at ~~the~~ temperature of 150 ^{o}C".*
   - 2nd paragraph of sub section 2.4:
     Add "which", **remove** "also" and "and" in sentence : "For comparison, produced water which was ~~also~~ collected from the Bonsucesso treatment plant, State of Sergipe, Brazil ~~and~~ had average concentrations of 1397, 1263, and 312 µg/L for benzene, toluene, and xylene, respectively [16]".
2. **Page 7 :**
   2nd paragraph :
   Add bracket after "SBR" → (SBR)
   Change : "*CWAO (Catalytic Wet Air Oxidation)*" → Catalytic Wet Air Oxidation (CWAO)

correction is attached in separated file.

Many thanks.

Regards,

Nita

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Best regards,

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Dear Cecilia

Thank you very much. According to the final version of my paper, I confirm that there is no correction. The paper is ready for further process.

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Performance of Ultrafiltration–Ozone Combined System for Produced Water Treatment

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Abstract

Oil exploration waste, also called produced water, contains hazardous pollutants, such as benzene; benzene, toluene, and xylene (BTX); naphthalene, phenanthrene, and dibenzothiophene (NDP); polyaromatic hydrocarbons (PAHs); and phenol. Produced water is characterized by high chemical oxygen demand (COD) and oil content, which exceed the standard limits of regulation. In this study, the combination of ultrafiltration (UF) and ozone pre-treatment and post-treatment were applied for treatment of produced water to minimize its environmental impact. Produced water and membrane were characterized, and their ultrafiltration performance for removal of oil content, benzene, toluene, xylene, and COD. Two commercial Polyethersulfone membranes, with molecular-weight cut-off values of 10 and 20 kDa, were used. The membrane flux profile illustrated that ozone pre-treatment had higher normalized flux than UF only. Separation performance was evaluated based on flux profile and removal of COD, oil and grease content, toluene, and xylene. Significant finding was found where the combination of UF with ozone pre-treatment and post-treatment could significantly eliminate COD, oil content, toluene, and xylene. The rejection of these components was found higher than conventional process, which was in the range of 80 % to 99 %. In addition, almost oil and grease can be removed by using this combined system. Permeate quality of this system confirmed the acceptable level as water discharge.

Keywords

ultrafiltration, ozone, produced water, benzene, toluene, xylene

1 Introduction

Oil explorations are the primary source of energy, and their corresponding activities generate a large volume of oilfield wastewater, also referred as produced water. For each barrel of oil, three barrels of produced water are generated [1]. In general, produced water is reused to enhance oil recovery or treated prior to discharge into the environment. Produced water comprises various organic and inorganic substances, which are potentially characterized as hazardous and toxic wastes. Produced water compound is categorized as organic substance, inorganic substance, and radionucleotide. Moreover, produced water contains some important compounds, such as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids, and dissolved gases [2]. Oils consist of monocyclic aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAH), and related heterocyclic aromatic compounds [3]. BTEX and phenols are dissolved in water. Residual chemicals, such as corrosion and scale inhibitors, emulsion breakers, and biocides, are also present in produced water [4].

Compounds in produced water are toxic and adversely affect the environment. Bakke et al. [5] published a review of the environmental impact of produced water and oil drilling in the offshore petroleum industry. Alkylphenols, naphthenic acids, and PAHs from produced water may disrupt reproductive functions and affect several chemicals, biochemical, and genetic biomarkers. As a consequence of the lethal effects of produced water contaminants, many countries have implemented a stringent regulatory

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standard for discharging produced water to alleviate their adverse environmental impacts. Produced water quality can be represented as oil content or concentration and chemical oxygen demand (COD). The concentrations of oil and COD in produced water are relatively high, reaching 565 and 1220 mg/L, respectively [1]. The government of the Republic of Indonesia through Regulation of the Minister of State for Environment No. 19 set standard limits for wastewater for oil and gas activities in 2010. The permitted oil concentration and COD are within 20–50 and 200 mg/L, respectively. Hence, treatment of produced water is a responsibility for oil and gas explorations.

Membrane technology has been applied to treat produced water and reviewed comprehensively [6, 7]. Ultrafiltration membrane is also an appropriate method for produced water treatment. Ultrafiltration (UF) is a low-pressure driven membrane filtration process operating at 2–10 bar [8]. The pore size of an UF membrane ranges from 0.001 μm to 0.1 μm; as such, the membrane rejects compounds with molecular weight of 1000 to 100.000 Da [9].

Several researchers have examined the use of UF membranes for handling produced water [10-14]. The previous study showed that UF treatment was able to reject 87.82 % of COD, 98.7 % of oil, 90.5 % of Total Organic Compound (TOC) from produced water by using 20 kDa UF membrane [12]. The treatment of oil-field produced water using UF ceramic membrane also presented a good removal of oil content with 99.15% of oil rejection [11].

However, studies on produced water treatment only investigated method performance through determination of general effluent parameters, such as COD, BOD, total dissolved solids, total suspended solids, oil content, and total organic carbon and analysis of anions and cations. Several studies have evaluated specific BTX content in produced water [15-17]. However, to the best of our knowledge, limited works have examined the performance of UF in BTX removal. The present study mainly aims to investigate the performance of ultrafiltration in treating produced water, specifically in filtering BTX pollutants. In detail, Polyethersulfone (PES) was selected as membrane material for ultrafiltration due to its hydrophilic property. To enhance the ultrafiltration performance, this research combined ultrafiltration and ozone pre-treatment and post-treatment for removal of produced water compounds. Ozone was selected because it can break up large organic molecules. Ozone can break complex molecular organic compounds in crude oil, which is a component of produced water [18-19]. Ziabari et al. [20] studied the removal of hydrocarbons from aqueous solution by ozonation. In addition, Zha et al. [21] reported that ozone could oxidize compounds having a large molecular weight to generate smaller compounds. Ozone can also reduce fouling associated with microfiltration and ultrafiltration [22-25]. Hence, we confirm the novelty of this research by implementing the combination of ultrafiltration and ozone to improve ultrafiltration performance for produced water treatment. The improvement was achieved not only in the term of permeate quality but also reduction of membrane fouling. Results provide novel significant findings in this research area.

2 Materials and Method

2.1 Membrane characterization

Two available commercial membranes made of PES (NADIR Filtration, Germany) were used to filter produced water. Membranes with molecular-weight cut-off of 10 and 20 kDa and were labelled as PES 1 and PES 2, respectively. Specific functional groups were identified using Fourier transform infrared spectroscopy (Shimadzu IR Prestige-21). Specific functional groups were examined based on their wavelength as a function of absorbance (Fig. 1).

Similar peaks at 1577.77 and 1485.19 cm^{-1} are characteristics of PES membrane. Peaks at 1485.19 and 1577.77 cm^{-1}

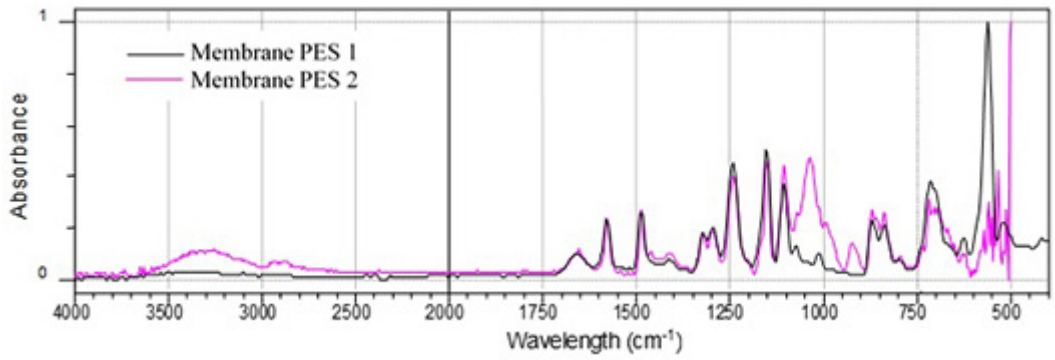

Fig. 1 FTIR results of PES 1 and PES 2 membranes

indicate the presence of aromatic components (C=C stretching) in benzene, and peaks at 1240.23 and 1242.16 cm^{-1} represent ether aromatic compounds [26-27]. In addition, peaks at 1151.5 and 1105.21 cm^{-1} exhibit SO_2 symmetrical stretching and are assigned to a sulfuric component. Peaks at 1656 and 1321 cm^{-1} are predicted as preservative PVP (poly-N-vinyl-2-pyrrolidone) because it is an additive polymer used for pore formation on PES and polysulfone membrane [27]. Moreover, a specific peak at 3500-3000 cm^{-1} is assigned to PES 2 membrane and indicates the existence of OH stretching radical. The PES 2 membrane was predicted to be more hydrophilic than the PES 1 membrane. To confirm this finding, the contact angle of the membrane was measured by using Optical Contact Angle Meter (DataPhysics, OCA 15LJ). The contact angle of the PES 1 and PES 2 membrane were 70.7° and 50.1°, respectively.

Table 1 summarizes the properties of UF membrane in relation to its pore size and water flux. Table 1 shows that the pure water flux of the PES 2 membrane was higher than that of the PES 1 membrane. The pure water flux was mainly determined by membrane pore size and its surface hydrophilicity [28]. Given that the PES 2 membrane possessed a large pore size, it exhibited higher pure water flux. Membrane surface morphology was analyzed by scanning electron microscopy (FEI, Type Inspect-S50, Japan) at a specific magnification.

2.2 Ultrafiltration

Ultrafiltration experiments were conducted in a homemade laboratory-scale test cell. The apparatus consisted of a 500 mL feed tank, a pump (Kemflow, with nominal flow rate of 1.0 L/min, maximum pump output of 7.58 bar, maximum inlet pressure of 4.14 bar), a pressure gauge (JAKO, maximum pressure of 10.34 bar), and a stainless steel membrane cell. The pressure and flow rate were controlled using feed valve (Needle Valve, 1/4" FNPT x 1/4" FNPT, maximum pressure of 5000 psi, materials SS 316). Fig. 2 shows the schematic of the ultrafiltration cell.

All filtration runs were carried out at room temperature (25 ± 2 °C). The membrane was compacted by filtering water through the membrane at a pressure of 2 bar for 0.5 h. For each experimental run, a new circular membrane sheet with an area of 13.85 cm^2 was used for measurement of

Table 1 Properties of UF membranes used in this work

Membrane	MWCO (Da)	Pure Water Flux (L/m².hr)
PES-1	10.000	11.25
PES-2	20.000	94.27

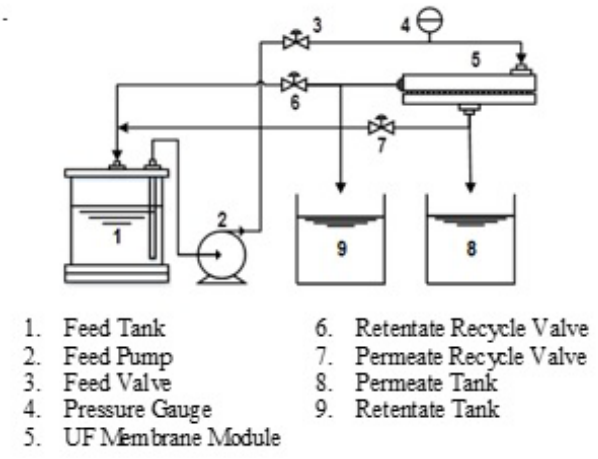

Fig. 2 Schematic of the ultrafiltration cell

initial water flux (J_0). Initial water flux (J_0) was determined by filtering pure water using a new clean membrane, then measuring the volume of water permeate collected at a specific recording time. Filtrations were carried out using total recycle mode, where both permeate, and retentate were recycled to the feed tank, to maintain the same concentration. Permeate flux (J) was determined by analytically weighting permeate collected at every 5 min intervals for 60 min. Membrane or permeate fluxes (J) were calculated by dividing the volume of permeate (Q) by the effective membrane area (A) and the sampling time (t), as defined in Eq. (1):

$$J = \frac{1}{A \cdot t} Q \tag{1}$$

where:

J: flux (L/ m^2h), Q: volume (L), A: membrane area (m^2), and t: time interval (h).

The ability of the membrane for removing specific pollutants from produced water was determined by % rejection (%R). Membrane rejection was calculated by dividing the difference between the concentration of a specific pollutant in the feed (C_f) with the concentration of specific pollutants in permeate (C_p), as expressed in Eq. (2).

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

In this research, the term rejection and permeate and feed concentrations refers to rejection and concentrations of COD, total oil content, toluene, and xylene.

2.3 Ozonation

Ozonation pre-treatment and post-treatment were conducted by Ozonizer, a generator (Krisbow) and flow meter. In the pre-treatment process, ozone was purged into the

produced water feed. For the post-treatment, ozone was added into the permeate. Ozone concentration was tested using HI38054 Ozone Test kit. The ozone flow rate was set as 2 L/min, the contact time was 5 min, and the corresponding ozone concentration was 0.3 mg/L.

2.4 Produced Water Quality Analysis

Produced water was collected from offshore facilities in Cepu region, Central Java, Indonesia. Water quality was assessed using the produced water in the feed and permeate. The COD in the feed and permeate samples were determined by Test Tube Heater-COD Reactor (HANA HI 839800) for 2 hours at temperature of 150 °C. Analysis of the contents of oil, BTX was conducted through gas chromatography. Ammonia value was obtained using UV-Vis spectrophotometry (Perkin Elmer Lambda 20). The spectrophotometric analysis was performed based on the methods explained by Zadorojny et al. [29]. The similar method was adopted by Indonesian standard analysis (SNI 06-6989.30-2005). Table 2 shows the characteristics of produced water.

According to Table 2, the mean levels of benzene, toluene, and xylene in the produced water sample were below 0.8, 2.62, and 3.11 mg/L, respectively. For comparison, produced water which was collected from the Bonsucesso treatment plant, State of Sergipe, Brazil had average concentrations of 1397, 1263, and 312 μg/L for benzene, toluene, and xylene, respectively [16]. Similar results were also found in an oilfield wastewater platform in the Gulf of Mexico. Examination of oilfield wastewater in that area indicated that the concentrations of benzene, toluene, and xylene were 0.8–4.6, 1.0–3.5, and 0.2–0.7 mg/L, respectively [17]. In the Campos Basin, State of Rio de Janeiro, Brazil, the levels of benzene, toluene, and xylene were 283–1855, 87.04–2224, and 67.35–5969 mol/L, respectively [15].

Table 2 Characteristics of produced water used in this study

Parameter	Value
COD	1872 mg/L
Oil and grease content	931.01 mg/L
Benzene	<0.8 mg/L
Toluene	2.62 mg/L
Xylene	3.11 mg/L
Phenol	<0.03 mg/L
Ammonia	0.22 mg/L
pH	8

3 Results and Discussions

3.1 Membrane Flux Behaviour

Normalization of flux profiles (J/J_0) as a function of time is presented in Fig. 3. In general, the flux showed a declining trend during ultrafiltration. The reduction of membrane flux is a characteristic of membrane fouling, which can be generated by an increase in membrane resistance due to pore blocking, concentration polarization, and cake formation [23]. Fouling can be related to the accumulation of a substance (called foulant) on the membrane surface or inside the membrane pores. At the beginning of ultrafiltration, no foulant deposit was found on the membrane surface. As time increased, foulants accumulated on the membrane surface and generated a cake layer, leading to decreased flux value and normalized fluxes.

In the ultrafiltration treatment of produced water, its components, such as oil and other organic compounds, are significant sources of fouling. Ashaghi et al. [30] and Maguire-Boyle and Barron [31] proposed that fouling during filtration of produced water could be due to biofouling, scaling, organic fouling, and colloidal fouling. Fouling could also be attributed to microbial contaminants (biofouling), salt precipitation resulting in scaling, organic fouling due to pore plugging or pore coating by hydrocarbon compounds, and clay and silica accumulation on the membrane surface (colloidal fouling). However, flux reduction was relatively steady along with time because of the compression of the cake layer and its constant thickness.

The flux decline of the PES 2 membrane was more pronounced than that of the PES 1 membrane. The flux decline (final flux compared with the initial flux) values of PES 2 and PES 1 membranes were found to be 8.7 % and 2.5 %,

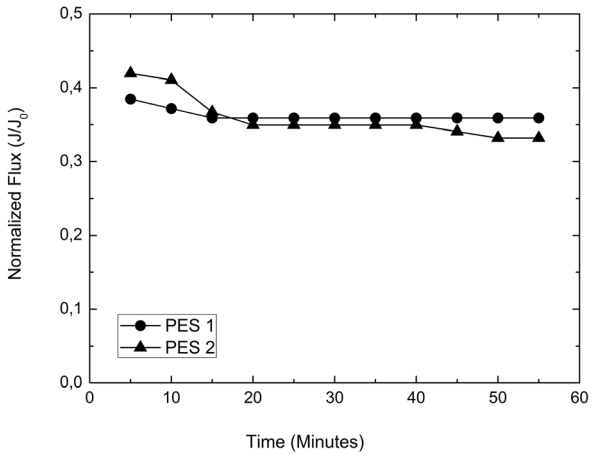

Fig. 3 Performance of membrane normalized fluxes as a function of time in treatment of produced water by using membranes with different pore sizes (TMP = 1 bar)

respectively. The flux decline can be explained by membrane fouling caused by pore blocking or membrane adsorption due to contaminants in the produced water. The pore size of the PES 1 membrane was slightly smaller than that of the PES 2 membrane. Contaminants with size bigger than the membrane pores have a tendency to form a cake layer on the membrane surface. By contrast, contaminants with size smaller than the membrane pores are likely to induce membrane pore blocking or adsorption. In the PES 2 membrane, contaminants most likely close the membrane pores strongly and accumulated on the membrane surface [32].

Two levels of trans-membrane pressure (TMP) were applied to study its effect on membrane behaviour in produced water treatment (Fig. 4).

The initial normalized flux was high at high TMP but decreased at the end of the process. The flux decrease at TMP of 2 bar (59 %) was higher than that at 1 bar (2.5 %). As a general rule, the increase in TMP in ultrafiltration of oil exerts negative and positive influences on the permeate flux [33]. At high TMP, more oil droplets and solutes passed quickly through the membrane pores. However, more oil droplets contributed to oil droplet accumulation both on the membrane surface and in the pores. The accumulation of oil droplets led to the formation of a cake layer on the membrane surface. It is predicted that initially a gel layer is formed due to some solutes congeal on the membrane surface. A steady state of flux is obtained with assumption that the concentration does not increase. However, with the increase of pressure, the gel layer is transformed into cake layer. In cake layer, the fouling increases continuously and result in complete blocking with no flux. The use of high TMP also resulted in the formation of a cake layer covering the membrane pores, thereby inducing membrane fouling [34].

Fig. 5 represents the effect of ozonation pre-treatment on ultrafiltration behaviour.

The normalized flux of the PES 1 membrane with ozone pre-treatment was higher than without ozone pre-treatment, but the flux decrease after ozone pre-treatment remained high. The flux decline of the membrane with ozone pre-treatment was about 18.5%, whereas the flux decrease of the membrane without ozone pre-treatment was only about 2.5 %. Ozone can oxidize the majority of organic compounds (about 35 %) in produced water into smaller intermediate products, which are then decomposed into CO_2 and H_2O [21]. Ozonation of produced water could also generate new compounds, such as acids, amines, and aldehyde, which influence the fouling rate of membranes during filtration. Fig. 6 reveals that ozone pre-treatment can diminish membrane fouling, as indicated by the superior normalized flux profile of the membrane subjected to UF with ozone pre-treatment over that subjected to UF only. The flux decline was significant in the first stage of filtration but became steady thereafter. Pre-ozonation can also reduce dissolved organic carbon by mineralization of small organic molecules. The breaking of large molecules was found to be the dominant principle for fouling reduction [22]. This finding was supported by the images of the SEM membrane illustrated in Fig. 6.

Fig. 6 confirms the clean surface of the new membrane (Fig. 6(a)) without any substances on its top. By contrast, Fig. 6(b) shows some foulants deposited on the membrane surface when filtering produced water without pre-treatment. The foulant deposits formed a cake layer, with some small particles found above the cake layer. The foulants

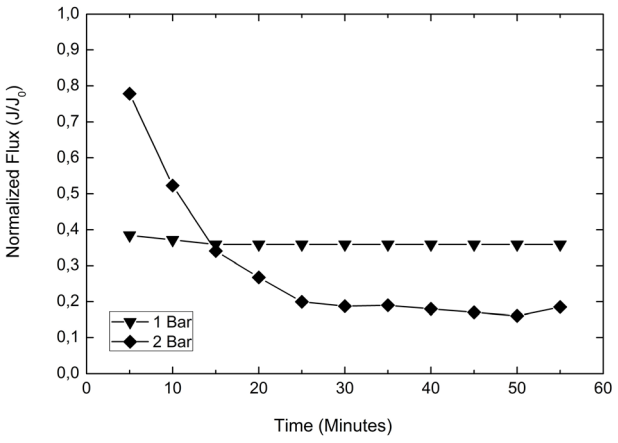

Fig. 4 Behavior of membrane normalized fluxes as a function of time in treatment of produced water under different trans membrane pressure levels (membrane : PES 1)

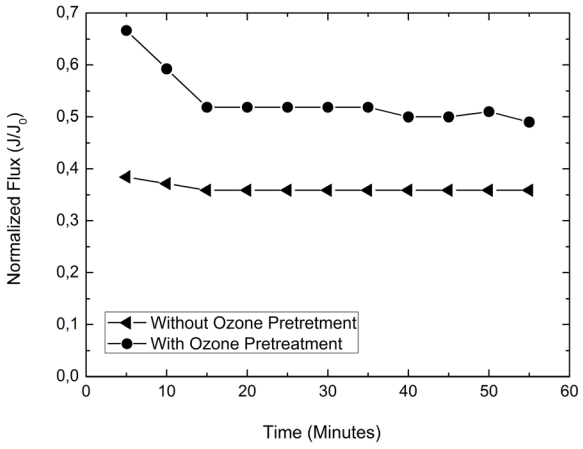

Fig. 5 Effect of ozonation pre-treatment on membrane normalized fluxes as a function of time for ultrafiltration of produced water (membrane: PES 1, TMP = 1 bar)

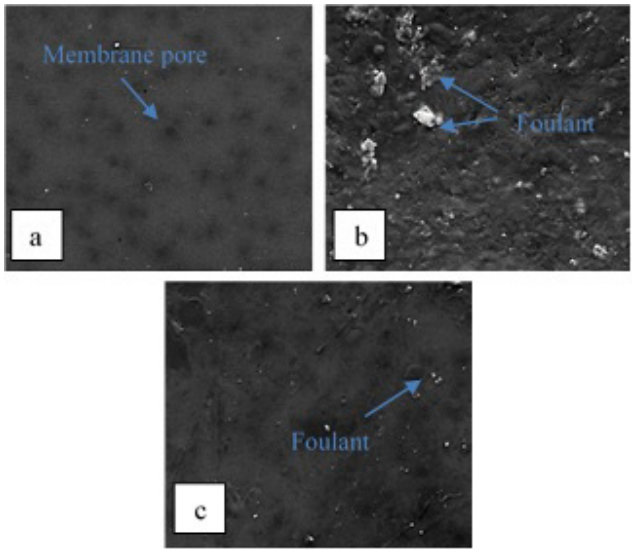

Fig. 6 SEM result of PES membranes (magnification of 20,000 ×: (a) clean membrane (before filtration), (b) membrane after filtration without ozone pre-treatment, and (c) membrane after filtration with ozone pre-treatment. (membrane PES 1, TMP = 1 bar)

were almost certainly suspended solids and large-molecular-weight compounds, such as xylene, toluene, benzene, and phenol in the produced water; as such, the foulants blocked the membrane surface and then formed a cake layer. At a certain period, foulant particles accumulated and generated a thick cake layer, thereby promoting the deposition of the foulant on the cake surface. During the filtration of produced water feed with ozone pre-treatment (Fig. 6(c)), the membrane surface showed a better appearance. Some foulant deposits were observed, but their size was smaller than that in the deposits shown in Fig. 6(b). Organic substances present in produced water are responsible for membrane fouling. Song et al. [35] also described that membrane fouling was produced by organic substances with a high molecular weight. Ozone may also oxidize organic compounds in produced water and effectively decrease the risk of fouling of the membrane. A similar result was also found by You et al. [25], who confirmed that the C=H bonds in the aromatic rings could be eliminated by ozone and more C–H and C–H bonds could be produced in the alkanes. Moreover, ozone can destroy aromatic rings to form few alkanes with a linear chain.

3.2 Membrane Rejection

In the ultrafiltration membrane, membrane selectivity is determined by membrane rejection. The ability of the PES membrane to selectively resist COD, oil, toluene and xylene in the produced water is shown in Fig. 7.

The ultrafiltration membrane showed significantly high rejection rates for COD, oil and grease, toluene, and xylene under various conditions, except for toluene during ozone pre-treatment. The low value of toluene rejection did not indicate its high concentration in the permeate because ozone pre-treatment could significantly reduce the toluene concentration. The rejection of the PES 1 membrane for COD and oil and grease concentration was slightly greater than that of the PES 2 membrane, which has bigger pore size. In membranes with a large pore size, oil that accumulated on the membrane surface will possibly permeate through large pores, resulting in slightly higher oil concentration in the permeate. Rejection or removal efficiency of this system to decrease oil and grease was considerably high (in the range of 98-99.9 %) showing that almost all oil was removed. Physical treatment such as EPCON

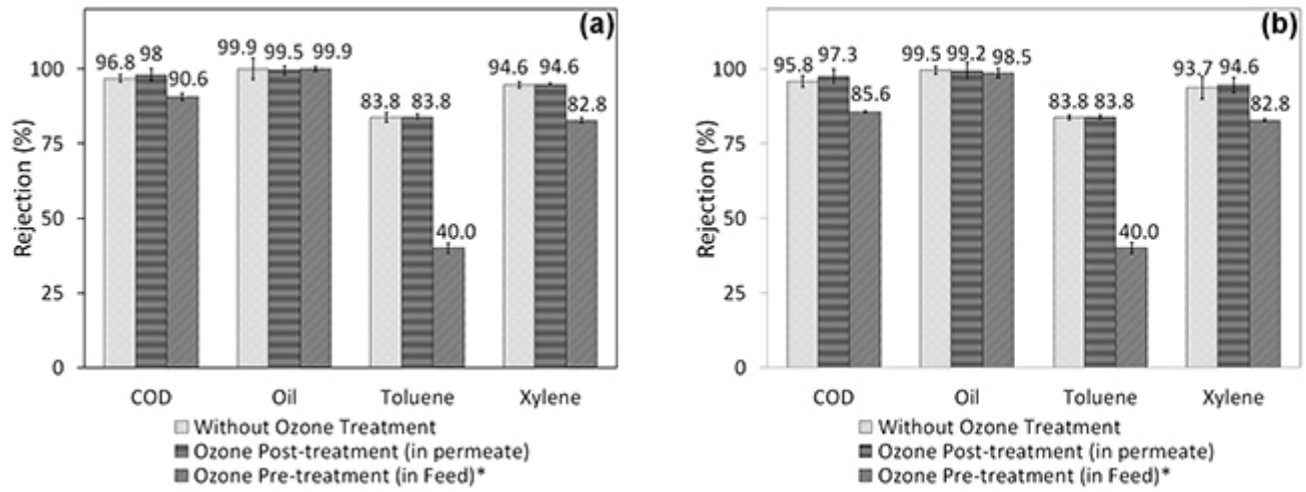

Fig. 7 Rejection of COD, oil, toluene, and xylene under various conditions (TMP = 1 bar): (a) PES 1 and (b) PES 2
* (C_f Toluene =C Toluene after feed ozonation = 0.10 mg/L).

compact floatation unit reduced 50-70 % dispersed oil [36]. Applying a copolymer could absorb up to 85 % of oil in produced water [37]. On the other hand, utilizing biological treatment such as rotating disk, aerated biological filter was only able to reduce oil and grease to 74 % [38].

Oil can be categorized as an organic compound; hence, the value of COD in the permeate was high, corresponding to low COD rejection. Implementation of this system is able to reduce the COD in the range of 85.6-98 %. This value of reduction is considerably high since the COD reduction by applying another method was low. Using electrochemical oxidation only removed up to 57 % of initial COD concentration [39]. The sequence batch reactor (SBR), with acclimated sewage sludge, had COD removal efficiencies varied from 30 % to 50 % [40] and applying microwave (MW)-assisted Catalytic Wet Air Oxidation (CWAO) in produced water treatment showed more than 90 % of COD was removed [41]. This combined system of ultrafiltration–ozone was also confirmed superior to the immobilization of microorganism for produced water treatment that was only removed 90 % of initial COD at COD concentration of 2600 mg/L [42].

Table 3 presents the characteristics of ultrafiltration permeate and the standard regulation of on-shore produced water in Indonesia. According to the table, permeates both with UF only and ozone combined-UF are in the range of acceptable level for water discharge. The result is significant since this method was able to reduce the oil and grease to a very low level (<0.03-8.18 mg/L) compared to the existing method. It is reported that the conventional method of produced water treatment reduced the oil and grease concentrations to 30-40 mg/L [37]. In addition, almost all of benzene, toluene, and xylene were removed during the ultrafiltration of produced water under various conditions.

This result is superior compared to other methods of produced water treatment. It was reported that neutralized amine "tailored" zeolites were applied in produced water treatment, and only able to remove around 70 and 85 % of BTEX from saline produced water [38]. In addition, this ultrafiltration-ozone combined system achieved similar result with the commercially available method such as Macro-porous Polymer Extraction (MPPE) technology, which the MPPE achieved 99 % removal of BTEX [38].

Produced water contains crude oil, which is a mixture of hydrocarbons, such as naphthalene, phenanthrene, dibenzothiophene, polyaromatic hydrocarbons (PAHs), and phenols. These hydrocarbons could not be dissolved but are dispersed in produced water. In this research, ultrafiltration membranes with molecular-weight cut-off (MWCO) values of 10.000 and 20.000 Da and pore sizes of 0.01 and 0.02 μm were used. The membranes rejected compounds with molecular weight within 10.000 and 20.000 Daltons. Produced water comprises organic compounds, such as benzene, toluene, and xylene (BTX), which have lower molecular weight than the molecular weight cut-off. When applying the "membrane-sieving principle", the BTX components should pass through the membrane pores. However, the results showed high rejection rates for toluene and xylene. BTX exists as dispersed oil and has size larger than that of the membrane pores; hence, BTX was rejected by the ultrafiltration membrane.

Ozonation pre-treatment significantly reduced the concentrations of toluene and xylene and COD. This method is accurate because ozone can degrade macromolecular matter into small organic matter [21] and change the composition and hydrophilicity of organic matter [35]. Šilhárová et al. [18] provided evidence that ozone treatment led to a low concentration of organic petroleum compound (BTEX).

Table 3 Comparison of the quality of feed and permeate

Parameter	Value			
	Feed with ozonation	Permeate**	Permeate with ozonation**	Standard Limits***
COD	790 mg/L	64.2 mg/L	56.9 mg/L	200 mg/L
Oil and Grease	351.61 mg/L	8.18 mg/L	< 0.03	25 mg/L
Benzene	<0.08 mg/L	n.a.*	n.a.*	n.a.
Toluene	0.10 mg/L	0.37 mg/L	< 0.06	n.a.
Xylene	1.67	<0.05 mg/L	<0.05 mg/L	n.a.
Phenol	n.a.*	n.a.*	n.a.*	2 mg/L
Ammonia	n.a.*	n.a.*	n.a.*	5 mg/L
pH	n.a*	n.a*	n.a*	6-9

* Permeate characteristic of the parameter was not tested because its value is below the standard limit

** Average value of PES 1 and PES 2 membrane, 1 atm

*** Standard limits based on Regulation of the Minister of State for Environment, Republic of Indonesia

The removal efficiency of ozonation for xylene, toluene, and benzene reached 90%, 89 %, and 86 %, respectively. The removal efficiency was correlated with reaction kinetics of BTX and ozone. The reaction kinetic rates of ozone with benzene, toluene, and xylene were 4.75×10^{-2}, 7.30×10^{-2}, and 1.82×10^{-1} μg/m^3.h, respectively.

COD is the oxygen required to degrade biodegradable and non-biodegradable organic compounds. As shown in Table 3, the concentration of COD was decreased by both ultrafiltration and ozone pre- or post-treatment. This finding verifies that the amount of organic compounds decreased when produced water was subjected to ultrafiltration combined with ozonation pre- or post-treatment.

4 Conclusion

The quality of produced water was examined based on oil and grease content as well as COD, which were found to be higher than the standard limit of wastewater for oil and gas activities. Benzene, toluene, and xylene were also detected in the produced water. Two commercial Ultrafiltration PES membranes were used to treat the produced. Ultrafiltration was modified by combining it with feed ozonation (pre-treatment) and permeate ozonation (post-treatment). This experimental work demonstrated that ultrafiltration and its combination with ozone pre-treatment and post-treatment showed effective removal of COD, oil and grease, toluene, and xylene. It is also confirmed that almost oil and grease can be removed by using this combined system. Ultrafiltration with ozone pre-treatment led to higher flux profile than ultrafiltration only. This finding verifies that ozone pre-treatment did not only remove produced water pollutants but also diminished the fouling of the ultrafiltration membrane. In addition, it was confirmed that the quality of permeate satisfied the acceptable level to discharge.

Abbreviations

A	Membrane area (m^2)
BTX	Benzene, toluene, and xylene
BTEX	Benzene, toluene, ethylbenzene and xylene
COD	Chemical oxygen demand
C_f	Concentration of a specific pollutant in the feed
C_p	Concentration of specific pollutants in permeate
J	Flux (L/ m^{2}h)
J/J_0	Normalization of flux profiles
J_0	Initial water flux
MWCO	Molecular weight cut off
PAH	Polyaromatic hydrocarbons
PES	Polyethersulfone
Q	Volume (L)
R	Rejection (%)
SEM	Scanning electron microscopy
t	Time interval (h)
TMP	Transmembrane pressure (bar)
TOC	Total organic compound
UF	Ultrafiltration
UV-Vis	Ultraviolet, visible spectrophotometer

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