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Preparation and Performance Evaluation of TiO_2 incorporated Fly Ash-Kaolin Ceramic Membrane for Oil/Water Separation

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Abstract. This study aimed to prepare ceramic membranes from low-cost materials for oil/water separation. TiO_2 was incorporated into fly ash/kaolin-based ceramic membrane matrix via the impregnation method to enhance membrane performance. The scanning electron microscope (SEM) results exhibited random distribution of pores along the membrane surface with an estimated pore size of 0.001- 0.13 µm. The porosity of the TiO_2-incorporated fly ash/kaolin ceramic membrane ranged from 42.82%-50.22%, where the sintering temperature played an important role in the water absorption and porosity properties. The X-ray diffraction (XRD) pattern showed an orthorhombic kyanite phase with the presence of three characteristic peaks at 2θ of 26.30°: 27.87° and 35.90°. The XRD pattern of all formulated membranes showed almost no change, however, the crystal intensity varied due to the different ceramic compositions. P hysicochemical properties evaluation showed that the membrane with fly ash, kaolin, and alumina of 20 : 30 : 40 wt% has reached the best characteristic. The casted membrane with a compaction pressure of 30 bar with sintering temperature of 1200°C for 7 h had the highest compressive strength. The performance showed that the TiO_2 incorporated membrane achieved over 95% oil rejection efficiency and significant decrease of several parameters such as Pb, Fe, Mn, nitrate, nitrite, total dissolved solid (TDS), Cl and total organic matter without sacrificing the permeate water flux up to 116 L/m^2/h. These experimental results suggest that the TiO_2-incorporated Fly ash/kaolin ceramic membrane has great potential for reclaiming oily wastewater into clean water.

Keywords: Ceramic membrane; Fly ash; Impregnation; Kaolin; Oily wastewater; Titania

1. Introduction

A growing worldwide population followed by the rapid growth of industrial sectors such as oil and gas, petrochemical, pharmaceutical, agricultural, metallurgical, and food industries have led to high consumption of clean water (Van-Vliet *et al.*, 2021). The decrease of water resources due to inevitable wastewater discharge of human activity caused the present surface water resources to be no longer adequate to meet the needs of future generations. As the world's fourth most populous country, Indonesia has been facing increasingly severe water scarcity due to insufficient water resources resulting from over-withdrawal of both surface water and groundwater in many regions (Istirokhatun *et al.*,

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2021; Masduqi, Nugroho, and Wilujeng, 2020). This condition is aggravated by the release of inconvenient oily wastewater from many industries that significantly harms the environment, especially surface water. The utilization of local natural resources such as raw kaolin for wastewater remediation has been reported to have great potential as well as an economical solution (Asbollah *et al.*, 2022). However, the presence of oil in water will form an emulsion that is difficult to separate, thus reducing the efficiency of processing. To overcome these problems, it is necessary to have an alternative technology that can work better and be economically competitive.

Several advanced techniques, including conventional physical and chemical methods, have been developed to manage the wastewater with oil droplet contamination. These techniques include adsorption using activated carbon (Wang *et al.,* 2022), diatomite clay (Kusworo *et al.,* 2018), resin (Kang *et al.,* 2021), graphene oxide-polyurethane composite sponge (Addina *et al.,* 2022; Kusrini *et al.,* 2022) etc., modified sand filter (Liu *et al.,* 2018), cyclone (He *et al.,* 2018), settling gravitational API separators (Jaworski and Meng, 2009), and evaporation (Tudu *et al.,* 2020) are the physical treatments that are relatively low cost; however, they have poor separation efficiency. The chemical treatments such as advanced oxidation processes (AOPs) (Mirza *et al.,* 2020), electrochemical, photocatalytic treatments, ozone treatment, ionic de-emulsifiers have shown high separation efficiencies with several drawbacks such as high cost, potential using toxic compounds, and generation of complex secondary pollutants (Padaki *et al.,* 2015). Among advanced technologies, the membrane is a promising technology due to continuous research and development. Additionally, membrane technology is recognized as an efficient technique to separate oil/water emulsion with high separation performance (Ye *et al.,* 2022). Its possibility to produce reclaimed water from wastewater, and membrane-based separation becomes a potential method for addressing the water scarcity issues. One of the membrane classifications that possesses practical feasibility for wastewater treatment is a ceramic membrane (Diana, Zaharani, and Fona, 2018).

Ceramic membranes are artificial membranes synthesized from inorganic materials such as alumina, zirconia, titania, silica, etc., in the form of metal oxides, carbides, or nitrides. The development of porous ceramic materials is increasing because of their application that covers all fields, especially those that prioritize high temperatures. Ceramic membranes provide many advantages over polymer membranes because ceramic membranes are stable at high temperatures and have good mechanical strength, and have properties that do not expand quickly in water but quickly form suspensions to coat the membrane as support (Dong *et al.,* 2010). Compared to polymeric membranes, ceramic membranes have the advantages of being able to be operated at higher temperatures, more extreme chemical conditions, and higher mechanical conditions to conditions. However, they also have limitations, including limited availability of raw materials, more complicated manufacturing, and more expensive. In general, the constituent materials of ceramic membranes are alumina, titania, and silica. The availability of these materials is relatively limited, causing the ceramic membranes more expensive. The price of commercial Al_2O_3 and ZrO_2-based ceramic membranes are in the range of \$500 - \$3000/m^2, which is much higher than commercial polymeric membranes (~\$20 – \$200/m^2) (Mestre *et al.,* 2019). The price of waste-based or natural mineral-based ceramic membranes is tremendously decreased, ranging from \$2 to \$130/m^2 (Dong *et al.,* 2022). Therefore, it is necessary to utilize low-cost alternative materials as raw materials for ceramic membrane manufacturing. Kaolin, fly ash and clay seem to be interesting as alternative natural-based materials. Moreover, the combination of Kaolin-titania has been reported to exhibit photocatalytic degradation activity under UV irradiation towards pollutants in wastewater, thereby increasing the overall removal efficiency of wastewater treatment (Kamaluddin *et al.,* 2021). Hence, the combination of Kaolin, fly ash, and titania is expected to provide synergetic effect in enhancing the removal efficiencies as well as reducing the production cost.

Fly ash is a coal combustion residue from thermal power plants that has attracted considerable interest because of its unique properties, i.e., low density and cost and smooth spherical surfaces. The main components of fly ash are oxides of silica, aluminum, iron, and calcium (Janani and Santhi, 2018). Recent studies have reported that fly ash has the potential to be used as a raw material for ceramic membrane preparation (Goswami, Pakshirajan, and Pugazhenthi, 2022; Agmalini, Lingga, and Nasir, 2013). Therefore, in this study, fly ash was developed as an alternative material for the preparation of ceramic membranes.

The development of ceramic membranes using natural materials such as clay, coal, zeolite, and other inorganic materials is widely carried out because of the lower cost that can be applied as filters (Jedidi *et al.,* 2009). Fu *et al.* (2021) developed a superhydrophobic fly-ash based ceramic membrane by immersing the membrane in a silane compound for the grafting process. This membrane is suitable for separating the water in oil emulsion rather than oil in water. Chathurappan and Jayapal (2022) utilized coal fly ash for preparing ultrafiltration ceramic membranes. They reported that the membrane has a porosity of 39.8% with an average pore size of 41 nm, 11.31 m^3/m^2 of pure water flux, and 95% rejection of rhodamine B. In another study by Zou *et al.* (2019), fly ash ceramic membrane was successfully composited with alumina via spray-coating, resulting in high oil/water separation efficiency of 99% and high permeability of up to 445 $L/m^2/h/bar$. These results suggested the possibility of improving the fly-ash based ceramic membrane through a composite approach. Later, Zou *et al.* (2021) developed a fly ash/kaolin-based ceramic membrane to afford lower-cost membrane with remarkable water permeability up to 3650 $L/m^2/h/bar$ however the oil/water separation slightly decreased to 98.5%. According to Liang *et al.* (2021), the performance of ceramic membranes was influenced by composition specifications; additionally, it is also influenced by operating conditions, including pressure, concentration gradient, pH of the inlet solution, and operating temperature. In addition, fly ash also contains other minor minerals such as magnesium, sulfur, sodium, potassium, and carbon (Susanto *et al.,* 2020). However, the application of membranes for wastewater treatment is majorly restricted by fouling formation that extensively deteriorates the membrane performance. Therefore, it is necessary to develop composite ceramic membranes from low-cost natural sources with anti-fouling and self-cleaning properties.

In this study, the inorganic composite ceramic membranes were manufactured by exploring the potential of natural resources combination, i.e., fly ash, kaolin, alumina, and TiO_2. Fly ash was used as the main material for producing ceramic membranes, and kaolin was considered as a reinforcement material. TiO_2 was used as an additive to improve the membrane performance. The performance of the membrane was evaluated for separating the synthetic oil/water emulsion and real wastewater containing oil & grease contaminants. This study aims to obtain the best composition of fly ash, kaolin, and TiO_2 for producing high-performance ceramic membranes in terms of mechanical properties, separation efficiency, and water permeability. Therefore, the fly ash-based ceramic membranes could be practically feasible wastewater treatment applications.

2. Methods

2.1. Materials

The materials used in this research included fly ash obtained from the local power plant Paiton Energy Ltd., Probolinggo, East Java, Indonesia. Natural kaolin powder was purchased from Brataco Chemical, Semarang, Indonesia. Carboxymethyl cellulose (CMC) and Magnesium sulfate ($MgSO_4$) ±95% were purchased from Merck, Singapore Science Park, Singapore. Sodium citrate, TiO_2, Alumina (Al_2O_3), and Polyethylene glycol (PEG) 99% were purchased from Sigma Aldrich, Pasir Panjang, Singapore. Deionized water was produced from a laboratory-made RO-Ion exchange deionized water unit in Chemical Process Laboratory, Chemical Engineering Department, Universitas Dionegoro, Semarang, Indonesia.

2.2. Methods

2.2.1 Manufacturing of Fly Ash Ceramic

First of all, the ceramic support membrane was prepared using fly ash (200 mesh/ ~75 µm), kaolin, and alumina. In addition, carboxymethyl cellulose (CMC), sodium citrate, polyethylene glycol, and $MgSO_4$ were added as a binder and reinforcing materials. Table 1 shows the composition of materials used during ceramic support membrane preparation. Those materials were mixed until homogenous paste dough was achieved. The paste dough was then left at room temperature for 30 min and kept away from direct sunlight for the aging process (Otitoju *et al.*, 2020). Thereafter, the paste dough was molded in tubular form with an external diameter of 8.5 cm and an inside diameter of 4.5 cm. The resulting ceramic support membrane was then dried at 250°C for one hour to remove the organic content, followed by calcination at 1000°C, 1100°C and 1200°C for 7 hours. A schematic illustration of membrane preparation is presented in Figure 1.

Table 1 Composition of materials used during ceramic support membrane preparation (% wt)

Membrane	Fly ash	Kaolin	Alumina	CMC	Sodium citrate	PEG	$MgSO_4$	Deionized water
M1	55	32	5	1	1	2	1	3
M2	45	42	5	1	1	2	1	3
M3	35	52	5	1	1	2	1	3

2.2.2 TiO_2 Ceramic Membrane Manufacturing

The process of producing TiO2 ceramic membrane in the first stage involves material preparation, mixing of constituent materials and additives, pugging, aging, and printing. The second stage of making TiO_2 - Fly ash impregnation by dissolving 1 gr of TiO_2 into a 0.1 M 100 ml NaOH solution and then stirring using a magnetic stirrer for 2 hours, and the ceramic membrane is immersed in a solution of TiO_2. Then the membrane is sintered at a temperature of 1000^{o}C, 1100^{o}C, and 1200^{o}C for 7 hours after sintering the membrane was cooled to room temperature. The resulting membrane was then characterized using XRD (X-Ray Diffraction) to determine the crystallinity phase of the membrane before and after modification with TiO_2 and to determine the morphology of the membrane characterized using SEM.

2.2.3 Membrane performance evaluation

The performance evaluation of prepared ceramic membranes was performed for synthetic oily wastewater and real wastewater treatment. The synthetic oily wastewater was prepared by dispersing 200 mg of cooking oil into 1 L of deionized water to make oily wastewater with a concentration of 200 mg/L. The oil was emulsified into the water using ultrasonic induction for 1 h. The concentration of permeate water was determined using a UV-Vis spectrophotometer (Shimadzu, Japan). The real wastewater was obtained from municipal sewage in Tembalang, Semarang, Central Java, Indonesia. The evaluated performance parameters were permeate flux, oil rejection, and other pollution rejections such as heavy metal, TDS, and organic matter. Figure 1(B) shows schematic filtration apparatus for membrane performance evaluation. The pollutant rejection efficiency and permeate water flux were calculated using equations (1) and (2), respectively.

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

$$J = \frac{V}{A \times \Delta t} \quad (2)$$

Where R is the rejection efficiency (%), Cp is the concentration of unwanted pollutants in permeate stream, and Cf is the concentration of unwanted pollutants in feed. J is the permeate flux (L/m2/h), V is the permeate volume (L), A is the effective membrane area (m2), and Δt is the filtration time (h).

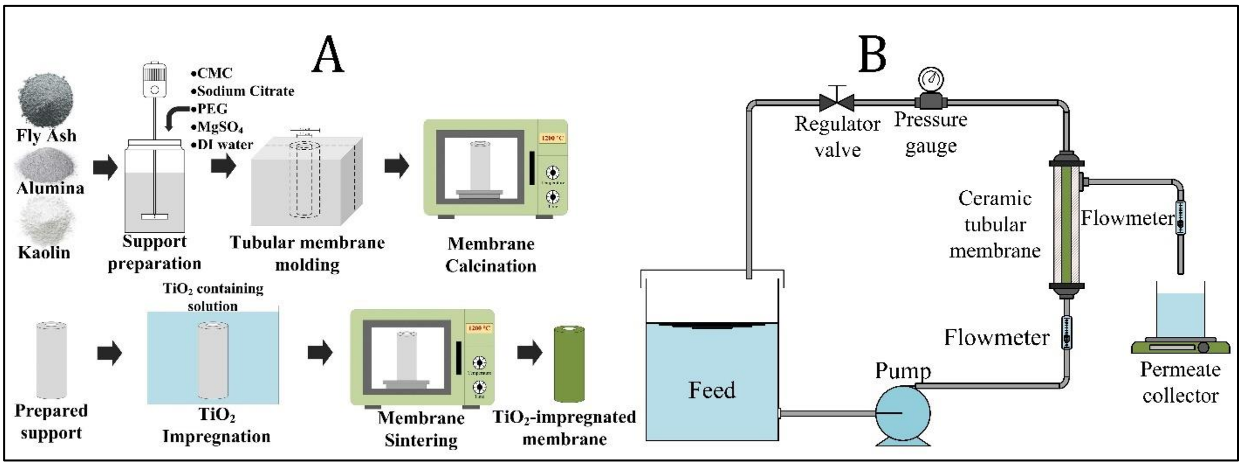

Figure 1 (A) Schematic illustration of ceramic membrane preparation (B) Membrane filtration scheme

3. Results and Discussion

3.1. Characteristics of Fly ash Ceramic Membrane Support

Fly ash used in this work was a natural compound that was a waste from the steam power plant industry and was classified as hazardous and toxic waste. This solid waste can be solidified and can be used as a basic material in the manufacture of ceramic. membranes (Chasri, 2015). The chemical composition of fly ash was identified using Energy Dispersive X-ray (EDX), and the quantitative analysis of metal content was analyzed using Atomic Absorption Spectrophotometer (AAS). Based on the results of the EDX and AAS analysis, the chemical composition of fly ash was mainly SiO_2 up to 39.85% and Al_2O_3 up to 12.74%. The complete analysis results of fly ash using AAS can be seen in Table 2.

Table 2 Mineral Content of Fly Ash

No	Component	Composition (%)
1	SiO_2	39.85
2	Al_2O_3	12.74
3	FeO	18.31
4	CaO	21.58
5	MgO	5.68
6	S	0.67
7	Na_2O	0.59
8	MnO	0.34
9	ZnO	0.12
10	P_2O_5	0.11
11	V_2O_5	0.04
12	Cr_2O_7	<0.01

3.2. Porosity test

The porosity test is carried out to determine the amount of substance or components that are absorbed by the membrane. The porosity test is usually carried out on water to see how much water can be absorbed by the membrane. The method used to carry out the porosity test is by immersing the membrane in water for 24 hours at room temperature, then weighing the membrane. After that, the membrane is dried in an oven at 60°C for 48 hours, then, burned, and then burned, it is weighed. This test is carried out by immersing the ceramic membrane in boiling water, then analyzing it, while the value of the membrane porosity can be calculated using equation (3) (Kusworo *et al.,* 2024).

$$\varepsilon(\%) = \frac{(W_w - W_D)/\rho_W}{(W_w - W_D)/\rho_W + (W_D/\rho_m)} \tag{3}$$

The W_w and W_D are the wet and dry membrane mass, respectively (g), ρ_w and ρ_m are the density of the pure water and membrane, respectively (g/cm^3). Figure 2(a) displays the results of the porosity analysis, indicating that the TiO_2-fly ash membrane produced exhibited porosity properties ranging from 42.82% to 50.22%. The higher the heating, the higher the porosity properties.

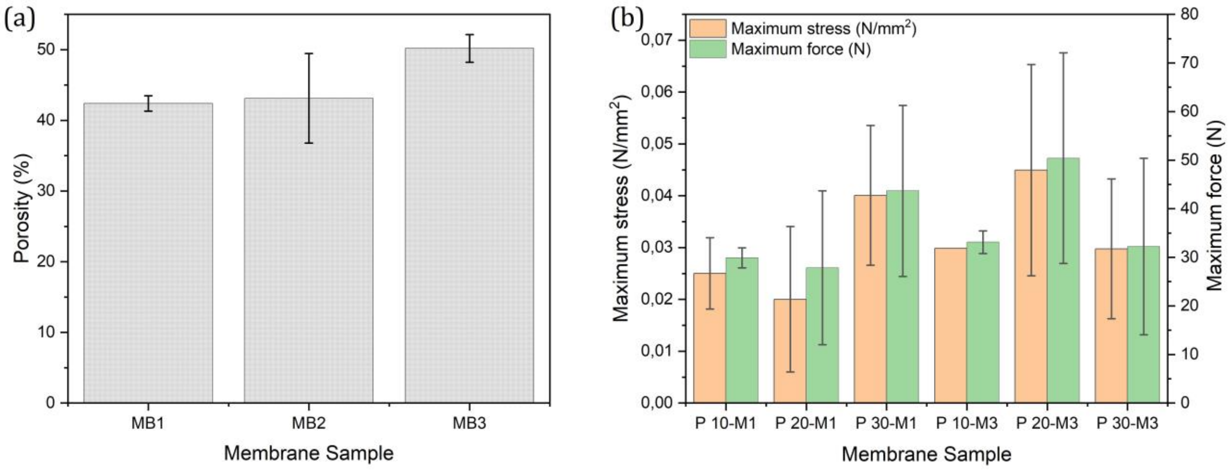

Figure 2 (a) Porosity value of TiO_2-Fly Ash ceramic membranes, (b) Compression test of the fabricated membranes expressed as maximum stress and force

3.3. Compression Test

The compressive test was carried out in this study with the aim of knowing the mechanical strength of the membrane support layer when subjected to compressive forces. The prepared M3 membrane compression tests at pressures of 10, 20, and 30 bar with fly ash compositions of 20%, 40%, and 30% were shown in Figure 2(b). It shows that ceramic membranes at 40% fly ash composition have the greatest membrane compressive strength of 65.45 kg/cm^2. The membrane compression test was influenced by the sintering. Temperature in the study used a combustion temperature of 1200^{o}C for 7 hours. The higher the combustion temperature, the higher the compressive strength obtained.

3.4. Membrane Characterization Test

The membrane characterization test was carried out to determine the morphology of the membrane pore size using SEM (JEOL JSM-651OLA). The SEM photo shows the surface structure of the TiO_2-fly ash membrane, which is formed unevenly due to uneven immersion. Judging from the pores formed are small enough so that they can be used in the microfiltration process with a size of 0.001-0.13μm. Based on Figure 4. It can be seen that the surface of the TiO_2 membrane is uneven in thickness, but the pore size formed is already small (less than 0.1 m).

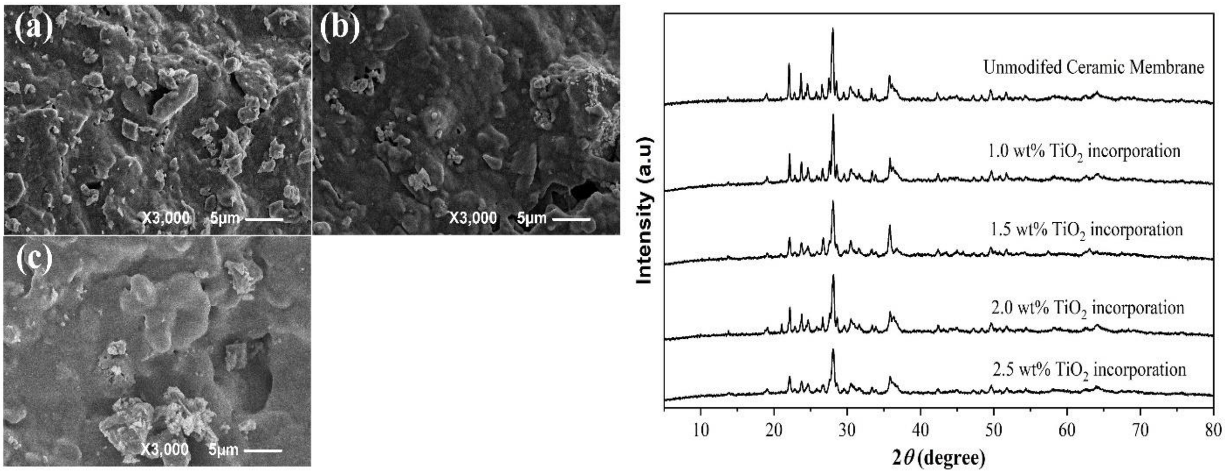

Figure 3 SEM images of the membrane with different calcination temperatures (a) 1000ºC, (b) 1100ºC, (c) 1300ºC, and XRD pattern of prepared ceramic membranes

Figure 3 reveals that the titanium peaks are not visible in any of the TiO_2-fly ash samples, even though there is titanium present on the surface of the fly ash membrane. This is due to the diffractogram produced from the fly ash membrane prior to modification, and the lack of significant changes observed in the fly ash membrane after modification with TiO_2. As shown in the image, a peak corresponding to the fly ash mineral can be observed, specifically andalusite ($Al_2(SiO_4)O$) and kyanite (Al_2SiO_5), which are both orthorhombic in structure (Liu *et al.,* 2022). That is at 2θ = 19.62º; 20.9º; 24.97º; 26.10º; 26.30º; 27.87º; 35.9º of the XRD diffractogram for orthorhombic kyanite was found at the three highest peaks at 2θ = 26.30º; 27.87º and 35.90º. The weak diffraction peaks at 2θ angles of 24.8º; 26.7°; 55.2°; and 63.0° correspond with the kaolinite structure as mentioned in the previous work (Kamaluddin *et al.,* 2021). The diffractogram produced from fly ash and modified fly ash almost shows no change, but at the peak, there is a change in crystal intensity. Intensity is a parameter that indicates the number or number of crystal planes that are measured. The intensity change that occurs is due to the addition of titanium dioxide (TiO_2) metal which affects the crystallinity, from the TiO_2-Fly Ash diffractogram data located at the main 2θ angle, namely 26.43º and 27.97º. The suitability of the diffractogram pattern indicated that the addition of TiO_2 to fly ash did not change the crystal structure of Andalusite $Al_2(SiO_4)$ and kyanite orthorhombic Al_2SiO_5 from the TiO_2 – Fly ash sample, the intensity decreased with an increasing amount of TiO_2. The decrease in peak intensity in the TiO_2 - fly ash sample has proven that titanium is on the fly ash surface. The peak shown in the modified XRD diffractogram shows a slight shift due to the phase change after the titanium is attached to the fly ash. This is because the type of tool and the accuracy of the tool used has the same accuracy and working method.

3.5. Membrane Performance Evaluation

The excellent property of the developed membrane for wastewater treatment is indicated by the high permeability of permeate water and oil rejection. The flux profile and oil rejection of membranes for synthetic wastewater treatment are presented in Figure 4. The average permeate flux of the M1, M2, and M3 membranes were 94.93, 95.83, and 116.16 $L/m^2/h$, respectively. Within 120 min of filtration time, the highest initial permeate can reach ~ 127 $L/m^2/h$. The similar flux profile of M1 and M2 could be due to the similar pore properties of the membrane, where the pore structure of the membrane strongly influenced the water permeability. Chen *et al.* (2022) reported that the flux of oily wastewater using ceramic membrane was about 300 – 700 L/m^2/h. The permeate water fluxes of this study were lower than that of previous studies, which could be attributed to the higher oil concentration of feed water. However, the oil rejection, according to Figure 4B, was around 93 – 96% which was higher than the previous report (Chen *et al.* 2022). The higher oil rejection could be due to the presence of hydrophilic channels provided by TiO_2, kaolin, and fly ash matrix. The Si/Al ratio also plays an important role in enhancing the oil-water separation in the membrane process. Si/Al ratio influenced the crystallinity of the membrane where a higher Si/Al ratio resulted in a high crystallinity membrane. Moreover, by increasing Si/Al ratio, the hydrophilicity of the membrane is increased then the hydrophobic oil is effectively rejected. This result is in accordance with a previous study by Jiang *et al.* (2019) where they reported that ceramic membranes with Si/Al ratio > 2.9 had shown the highest separation factor. In this work, the Si/Al ratio was 3.13 indicating the membrane was favourable for oil-water separation. The hydrophilic surface tends to reject hydrophobic substances such as cooking oil dispersed in wastewater. This result suggests the effectiveness of the developed ceramic membrane for separating oily wastewater. To evaluate the potential application of the membrane in wastewater treatment, the filtration experiment using real oily wastewater was performed. The characteristics of feed wastewater and permeate water are shown in Table 3.

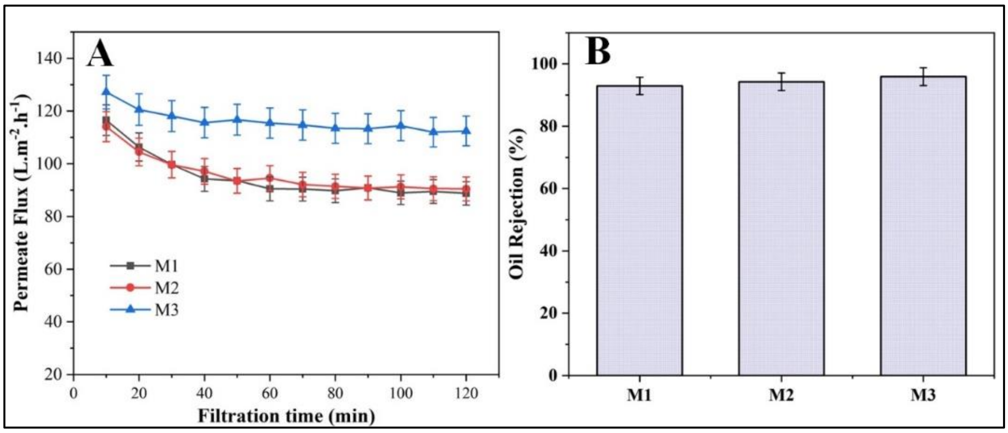

Figure 4 Performance evaluation for filtrating synthetic oily wastewater (A) permeate flux, (B) oil rejection

Table 3 Test result of real wastewater treatment using ceramic membrane fly ash/kaolin-TiO_2

No.	Parameter	unit	Real WW	Pre-treated	Membrane Treated wastewater			Standard
					M1	M2	M3	
1.	pH	mg/L	2.59	7. 32	6.59	6.8	7.3	6.5 – 8.5
2.	TSS	mg/L	16	16.5	14	15	12	Max 10
3.	TDS	mg/L	2313	2082	1876	1903	1562	Max 1500
4.	Turbidity	NTU	47.94	19	2.5	3.1	3.8	Max 5
5.	Organic matter	mg/L	278	254	191.2	187.3	179.4	-
6.	Oil & Grease	mg/L	35	29	1.5	1.8	<1	-
7.	$CaCO_3$	mg/L	29.36	20.23	9.91	7.24	6.84	Max 500
8.	Iron (Fe)	mg/L	9.79	6.7	2.3	1.7	1.0	Max 0,3
9.	Manganese (Mn)	mg/L	6.6	1.6	0.4	0.3	0.2	Max 0,1
10.	Nitrate (NO_3)	mg/L	0.86	0.259	0.765	0.665	0.754	Max 1
11.	Nitrite (NO_2)	mg/L	4.764	2.27	0.752	0.662	0.845	Max 1
12.	Sulfate (SO_4)	mg/L	39	35.8	30.12	29.85	33.17	Max 400
13.	Chloride (Cl)	mg/L	3.3	8.8	0.052	0.065	0.036	Max 250

Based on Table 3, there was a significant decrease in TSS, TDS, turbidity, organic substances, and hardness on ceramic membranes (M1, M2, M3) in the real wastewater treatment trial. This shows the effectiveness of the purification of the water treatment system, where the pre-treatment carried out on the ceramic membrane was indicated by a decrease in Fe content from 9.79 to 1,0 – 2.3 mg/L dan Mn content from 6.6 mg/L to 0.2 – 0.4 mg/L, the decrease in impurities was caused by solutes being retained by the ceramic membrane and forming a precipitate that served as a filter for TSS flow. Turbidity in real wastewater indicated the level of suspended organic matter in the solution. Parameters of successful filtration can be expressed by the amount of substance lost. The decrease in the levels of cations and anions after passing through the ceramic membrane indicated that the resulting ceramic membrane has fairly good permeability. The decrease of ionic dissolved solids could be due to Gibbs-Donnan's exclusion mechanism, where the charged particles are excluded as the result of electrostatic charge repulsion between charged particles with a membrane surface containing TiO_2. According to Rasouli *et al.* (2021), the accumulation of charged particles around the membrane surface significantly enhanced the charge density and created counter-ion concentration with higher ionic strength, which reduced electrostatic attraction toward organic molecules. Hence, higher oil and ionic pollutants rejections are achieved. These results suggested that tubular ceramic membranes made from fly ash, kaolin, and TiO_2 can be used to treat oily wastewater into clean water that has fairly met the Indonesia Health Ministry regulation for clean water quality standard No. 416/MENKES/XII/1990.

4. Conclusions

The research demonstrates that the ceramic membrane exhibits a water porosity range of 42.82%-50.22%, with the M3 membrane achieving the highest compressive strength of 65.45 kg/cm^2. The incorporation of fly ash influences membrane pore formation, while XRD analysis reveals the orthorhombic kyanite structure in both pristine and modified membranes. The M3 membrane, with a fly ash: kaolin: alumina: TiO_2 composition ratio of 20%: 40%: 30% and a combustion temperature of 1200°C, performs excellently in river water treatment, achieving >95% oil rejection and a permeate flux of 116 $L/m^2/h$. Modifications with TiO_2 significantly improve the membrane surface properties, enhancing hydrophilicity, permeate flux, pollutant rejection, and fouling resistance. However, the higher production cost of ceramic membranes compared to polymeric membranes remains a limitation. Despite this, the findings offer promising implications for clean water reclamation, as these durable ceramic membranes could provide a sustainable solution for wastewater treatment, contributing to global water scarcity solutions with further optimization in production processes.

References

Addina, S.N., Alhamid, M.I., Usman, A., Prasetyanto, E.A., Sufyan, M., Kusrini, E., 2022. Economic Analysis of Graphene Aerogel Polyurethane Sponge Production as Adsorbent for Oil-Water Separation. *Materials Today: Proceedings,* Volume 51, pp. 1896–1907. DOI: https://doi.org/10.1016/j.matpr.2022.01.313

Agmalini, S., Lingga, N.N., Nasir, S., 2013. Peningkatan Kualitas Air Rawa Menggunakan Membran Keramik Berbahan Tanah Liat Alam Dan Abu Terbang Batubara (Improving Swamp Water Quality Using Ceramic Membranes Made from Natural Clay and Coal Fly Ash). *Jurnal Teknik Kimia*, Volume 19(2), pp. 59 – 68. DOI: https://www.e-jurnal.com/2015/03/peningkatan-kualitas-air-rawa.html.

Asbollah, M.A., Sahid, M.S.M., Padmosoedarso, K.M., Mahadi, A.H., Kusrini, E., Hobley, J., Usman, A., 2022. Individual and Competitive Adsorption of Negatively Charged Acid Blue 25 and Acid Red 1 Onto Raw Indonesian Kaolin Clay. *Arabian Journal for Science and Engineering,* Volume 47(5), pp. 6617–6630. DOI: https://doi.org/10.1007/s13369-021-06498-3

Chasri, N., 2015. The Utilization of Coal Fly Ash as Ceramic Membranes for the Unit of Peat Water Treatment. Jurnal Dinamika Kimia *(Journal of Chemical Dynamics),* Volume 26(2), pp. 95–105. DOI: https://media.neliti.com/media/publications/178436-ID-pemanfaatan-fly-ash-batubara-sebagai-bah.pdf.

Chathurappan, R., Jayapal, A., 2022. Synthesis and Characterization of Coal Fly Ash Based Multipurpose Ultrafiltration Membrane. *Materialia,* Volume 25, p. 101548. DOI: https://doi.org/10.1016/j.mtla.2022.101548

Chen, J., Lv, Q., Meng, Q., Liu, X., Xiao, X., Li, X., Gao, P., 2022. Study on Treatment of Low Concentration Oily Wastewater Using Alumina Ceramic Membranes. *Crystals,* Volume 12(2), p. 127. DOI: https://doi.org/10.3390/cryst12020127.

Diana, S., Zaharani, L., Fona, Z., 2018, Utilization of Fly and Clay in Making Ceramic Membranes with the Addition of PVA as Adhesives for Rejection of TSS on River Water, *In:* Prosiding Seminar Nasional Politeknik Negeri Lhkseumawe *(Proceedings of Lhokseumawe State Polytechnic National Seminar),* Volume 2(1), pp. 91–95. DOI: -.

Dong, Y., Hampshire, S., Zhou, J.E., Lin, B., Ji, Z., Zhang, X., Meng, G., 2010. Recycling of Fly Ash for Preparing Porous Mullite Membrane Supports with Titania Addition. *Journal of Hazardous Material,* Volume 180, pp. 173–180. DOI: https://doi.org/10.1016/j.jhazmat.2010.04.010.

Dong, Y., Wu, H., Yang, F., Gray, S., 2022. Cost and Efficiency Perspectives of Ceramic Membranes for Water Treatment. *Water Research,* Volume 220, p. 118629. DOI: https://doi.org/10.1016/j.watres.2022.118629

Fu, H., Li, Z., Zhang, Y., Zhang, H., Chen, H., 2022. Preparation, Characterization and Properties Study of a Superhydrophobic Ceramic Membrane Based on Fly Ash. *Ceramics International,* Volume 48(8), pp. 11573–11587. DOI: https://doi.org/10.1016/j.ceramint.2022.01.014

Goswami, K.P., Pakshirajan, K., Pugazhenthi, G., 2022. Process Intensification Through Waste Fly Ash Conversion and Application as Ceramic Membranes: A Review. *Science of The Total Environment,* Volume 808, p. 151968. DOI: https://doi.org/10.1016/j.scitotenv.2021.151968

He, L., Yang, G., Xiaohan, P., Guoxing, Z., Lichen, Z., 2018. Progress and Prospect of Downhole Cyclone Oil-Water Separation with Single-Well Injection-Production Technology. *Acta Petrolei Sinica,* Volume 39(4), pp. 463–471. DOI: http://dx.doi.org/10.7623/syxb201804010

Istirokhatun, T., Susanto, H., Budihardjo, M.A., Septiyani, E., Wibowo, A.R., Karamah, E.F., 2021. Treatment of Batik Industry Wastewater Plant Effluent using Nanofiltration. *International Journal of Technology,* Volume 12(4), pp. 770–780. DOI: https://doi.org/10.14716/ijtech.v12i4.4645

Janani, S., Santhi, A.S., 2018. Multiple Linear Regression Model for Mechanical Properties and Impact Resistance of Concrete with Fly Ash and Hooked-end Steel Fibers. *International Journal of Technology,* Volume 9(3), pp. 526–536. DOI: https://doi.org/10.14716/ijtech.v9i3.763

Jaworski, A.J., Meng, G., 2009. On-Line Measurement of Separation Dynamics in Primary Gas/Oil/Water Separators: Challenges and Technical Solutions—A Review. *Journal of*

Petroleum Science and Engineering, Volume 68(1-2), pp. 47–59. DOI: https://doi.org/10.1016/j.petrol.2009.06.007

Jedidi, I., Saidi, S., Khmakem, S., Larbot, A., Ammar, N.E., Fourati, A., Charfi, A., Amar, R.B., 2009. Elaboration of New Ceramic Microfiltration Membranes from Mineral Coal Fly Ash Applied to Waste Water Treatment. *Journal of Hazardous Materials,* Volume 172(1), pp. 152–158. DOI: https://doi.org/10.1016/j.jhazmat.2009.06.151

Jiang, J., Peng, L., Wang, X., Qiu, H., Ji, M., Gu, X., 2019. Effect of Si/Al Ratio in the Framework on the Pervaporation Properties of Hollow Fiber CHA Zeolite Membranes. *Microporous and Mesoporous Materials,* Volume 273, pp. 196–202. DOI: https://doi.org/10.1016/j.micromeso.2018.07.015

Kamaluddin, M.R., Zamri, N.I.I., Kusrini, E., Prihandini, W.W., Mahadi, A.H., Usman, A., 2021. Photocatalytic Activity of Kaolin–Titania Composites to Degrade Methylene Blue Under UV Light Irradiation; Kinetics, Mechanism and Thermodynamics. *Reaction Kinetics, Mechanisms and Catalysis,* Volume 133(1), pp. 517–529. DOI: https://doi.org/10.1007/s11144-021-01986-x.

Kang, L., Shi, L., Zeng, Q., Liao, B., Wang, B., Guo, X., 2021. Melamine Resin-Coated Lignocellulose Fibers with Robust Superhydrophobicity for Highly Effective Oil/Water Separation. *Separation and Purification Technology,* Volume 279, p. 119737. DOI: http://dx.doi.org/10.1016/j.seppur.2021.119737

Kusrini, E., Ramadhani, I., Alhamid, M.I., Voo, N.Y., Usman, A., 2022. Synthesis and Adsorption Performance of Graphene Oxide-Polyurethane Sponge for Oil-Water Separation. *Engineering Journal,* Volume 26(1), pp. 1–9. DOI: https://doi.org/10.4186/ej.2022.26.1.1

Kusworo, T.D., Aryanti, N., Inamullah, A.M.A., Astuti, D.A.P., Utomo, D.P., 2024. Advanced Photocatalytic Membrane GO-NiFe@ SiO2/PVDF for Efficient Decontamination of Synthetic Dyes in Batik Wastewater with Superior Antifouling Features. *Journal of Water Process Engineering,* Volume 66, p. 105953. DOI: https://doi.org/10.1016/j.jwpe.2024.105953

Kusworo, T.D., Aryanti, N., Utomo, D.P., 2018. Oilfield Produced Water Treatment to Clean Water Using Integrated Activated Carbon-Bentonite Adsorbent and Double Stages Membrane Process. *Chemical Engineering Journal,* Volume 347, pp. 462–471. DOI: https://doi.org/10.1016/j.cej.2018.04.136

Liang, D., Huang, J., Zhang, H., Fu, H., Zhang, Y., Chen, H., 2021. Influencing Factors on the Performance of Tubular Ceramic Membrane Supports Prepared by Extrusion. *Ceramics International,* Volume 47(8), pp. 10464–10477. DOI: https://doi.org/10.1016/j.ceramint.2020.12.235

Liu, P., Niu, L., Tao, X., Li, X., Zhang, Z., Yu, L., 2018. Preparation of Superhydrophobic-Oleophilic Quartz Sand Filter and its Application in Oil-Water Separation. *Applied Surface Science,* Volume 447, pp. 656–663. DOI: https://doi.org/10.1016/j.apsusc.2018.04.030

Liu, Y., Xu, L., Chen, M., Zhang, D., 2022. Effects of Andalusite and Kyanite Addition on The Microstructure, Thermo-Mechanical Properties and Corrosion Resistance of Ultralow-Cement Bauxite-Corundum Castables. *Ceramics International,* Volume 48(10), pp. 14141–14150. DOI: https://doi.org/10.1016/j.ceramint.2022.01.300

Masduqi, A., Nugroho, A.R., Wilujeng, S.A., 2020. Solution to Water Scarcity in The Eastern Indonesia: A Case Study of The Lembata Regency. *GEOMATE Journal,* Volume 19(71), pp. 69–76. DOI: https://geomatejournal.com/geomate/article/view/831.

Mestre, S., Gozalbo, A., Lorente-Ayza, M.M., Sánchez, E., 2019. Low-Cost Ceramic Membranes: A Research Opportunity for Industrial Application. *Journal of the*

European Ceramic Society, Volume 39(12), pp. 3392–3407. DOI: https://doi.org/10.1016/j.jeurceramsoc.2019.03.054

Mirza, N. R., Huang, R., Du, E., Peng, M., Pan, Z., Ding, H., Xie, Z., 2020. A Review of the Textile Wastewater Treatment Technologies with Special Focus on Advanced Oxidation Processes (AOPs), Membrane Separation and Integrated AOP-Membrane Processes. *Desalination and Water Treatment,* Volume 206, pp. 83–107. DOI: https://doi.org/10.5004/dwt.2020.26363

Otitoju, T.A., Okoye, P.U., Chen, G., Li, Y., Okoye, M.O., Li, S., 2020. Advanced Ceramic Components: Materials, Fabrication, and Applications*. Journal of Industrial and Engineering Chemistry,* Volume 85, pp. 34–65. DOI: http://dx.doi.org/10.1016/j.jiec.2020.02.002

Padaki, M., Murali, R.S., Abdullah, M.S., Misdan, N., Moslehyani, A., Kassim, M.A., Ismail, A.F., 2015. Membrane Technology Enhancement in Oil–Water Separation. A review. *Desalination,* Volume 357, pp. 197–207. DOI: https://doi.org/10.1016/j.desal.2014.11.023

Rasouli, S., Rezaei, N., Hamedi, H., Zendehboudi, S., Duan, X., 2021. Design, Fabrication, and Characterization of a Facile Superhydrophobic and Superoleophilic Mesh-Based Membrane for Selective Oil-Water Separation. *Chemical Engineering Science*, Volume 236, p. 116354. DOI: https://doi.org/10.1016/j.ces.2020.116354.

Susanto, H., Fahmi, Y., Hutami, A.T., Hadi, Y.T., 2020. Effects of Fly Ash Loading on the Characteristics of PVC-Based Cation Exchange Membranes for Reverse Electrodialysis. *International Journal of Technology,* Volume 11(3), pp. 544–553. DOI: https://doi.org/10.14716/ijtech.v11i3.3773

Tudu, B.K., Gupta, V., Kumar, A., Sinhamahapatra, A., 2020. Freshwater Production via Efficient Oil-Water Separation and Solar-Assisted Water Evaporation Using Black Titanium Oxide Nanoparticles. *Journal of Colloid and Interface Science,* Volume 566, pp. 183–193. DOI: https://doi.org/10.1016/j.jcis.2020.01.079

Van-Vliet, M.T., Jones, E.R., Flörke, M., Franssen, W.H.P., Hanasaki, N., Wada, Y., Yearsley, J.R., 2021. Global Water Scarcity Including Surface Water Quality and Expansions of Clean Water Technologies. *Environmental Research Letters,* Volume 16(2), p. 024020. DOI: 10.1088/1748-9326/abbfc3

Wang, J., Duan, H., Wang, M., Shentu, Q., Xu, C., Yang, Y., Yao, Y., 2022. Construction of Durable Superhydrophilic Activated Carbon Fibers Based Material for Highly-Efficient Oil/Water Separation and Aqueous Contaminants Degradation. *Environmental Research,* Volume 207, p. 112212. DOI: https://doi.org/10.1016/j.envres.2021.112212

Ye, Q., Xu, J.M., Zhang, Y.J., Chen, S.H., Zhan, X.Q., Ni, W., Tsai, F.C., 2022. Metal-Organic Framework Modified Hydrophilic Polyvinylidene Fluoride Porous Membrane for Efficient Degerming Selective Oil/Water Emulsion Separation. *Nature Partner Journals Clean Water,* Volume 5(1), p. 23. DOI: https://ui.adsabs.harvard.edu/link_gateway/2022npjCW...5...23Y/doi:10.1038/s41545-022-00168-z

Zou, D., Fan, W., Xu, J., Drioli, E., Chen, X., Qiu, M., Fan, Y., 2021. One-Step Engineering of Low-Cost Kaolin/Fly Ash Ceramic Membranes for Efficient Separation of Oil-Water Emulsions. *Journal of Membrane Science,* Volume 621, p. 118954. DOI: http://dx.doi.org/10.1016/j.memsci.2020.118954

Zou, D., Xu, J., Chen, X., Drioli, E., Qiu, M., Fan, Y., 2019. A Novel Thermal Spraying Technique to Fabricate Fly Ash/Alumina Composite Membranes for Oily Emulsion and Spent Tin Wastewater Treatment. *Separation and Purification Technology,* Volume 219, pp. 127–136. DOI: https://doi.org/10.1016/j.seppur.2019.02.051