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A Novel Poly (vinylidene) Fluoride/TiO_2/Spent Bleaching Earth for Enhancing Hydrophilic Hollow Fibre Membrane

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ABSTRACT

Nowadays, polymer as the raw material has been utilized in the development of Hollow Fibre (HF) membranes. PVDF is a commonly used for HF membrane material. However, it has hydrophobicity properties and lead membrane becomes low permeability and fouling. Therefore, to avoid these membranes problems, the incorporation of inorganic nanoparticles into PVDF membranes matrix is necessary to be applied for significantly improving PVDF membranes performance. This study investigates the characteristics and performance of PVDF-TiO_2 HF membranes using spent bleaching earth (SBE) as a promising material from industrial waste as a renewable inorganic nanoparticle. This novel PVDF-TiO_2-SBE HF membrane was fabricated using the subsequent steps: The preparation process incorporates SBE revival through solvent extraction and thermal treatment alongside the wet spinning technique for membrane fabrication. The Fourier transform infrared (FTIR) functional groups, scanning electron microscope (SEM) morphology, water contact angle and pure water flux performance were investigated to specifically understand the performance of this typical HF membranes. The IR results show that Si-O-Si groups were found in the membrane matrices due to the addition of SBE material. The addition of TiO_2-SBE particles also indicate a sandwich (sponge-finger-like) morphological structure on the cross-sectional, a rough and porous surface structures. The hydrophilic properties of the HF membrane and pure water flux performance are determined by the composition of the TiO_2-SBE mixture added as an additive material. The minimum contact angle found at 74.33°, while the water flux is 5.81 $kg.m^{-2}.h^{-1}$ on the identical HF membrane. Accordingly, this approach significantly enhances the properties of the pure PVDF HF membrane.

1. Introduction

Secure drinking water availability is a critical concern that cannot be ignored. It is not always necessary that the number of water sources must increase in order to meet the demands of a growing community [1, 2]. On a world scale, the availability of clean water barely 2,5% [3, 4]. According to the

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WHO assessment, nearly half the world's population would live in water-deprived regions by 2025 [5]. To meet the demand for water, various low-quality water resources are utilized, including river, wetland water, seawater, and wastewater. In addition, a water treatment process is very important to remove pollutants in the water especially for wastewater. One of the most frequently used water treatment processes is the hollow fiber membrane technology [6, 7]

Today, hollow fiber (HF) membrane is a vital component in water treatment processes, providing plentiful benefits, including high surface area, efficient separation capabilities, and a compacter design [8-10]. The development of these membranes has progressed significantly in recent years, resulting in superior performance and increased application [11, 12]. Numerous studies have demonstrated that the development of hollow fiber membranes typically centres on modifying or creating new membranes to obtain desirable properties, including porosity, permeability, rejection, hydrophilicity, thermal stability, and mechanical stability [13-16].

In recent years, polymer materials have been utilized in the development of HF membrane technology [17]. Various chemical and physical methods, including blending, coating, chemical and plasma treatments, surface grafting, enzyme immobilisation, nanostructured fillers, photo-modification, amongst others, were used to augment membrane performance and physicochemical properties [17]. Membrane modification by various chemical and physical functionalization (such as blending, coating, chemical treatment, plasma treatment, surface grafting, enzyme immobillization, nanostructured fillers, photo-modification, etc.) were employed to develop a novel membrane with superior performance and physicochemical properties [18, 19]. Incorporating inorganic nanoparticles into polymeric membranes has significantly improved performance and membrane properties [20, 21].

One of potential HF membrane additive is spent bleaching earth, an inorganic particle that results from the refining process of crude palm oil using bentonite clay. SBE comprises high concentrations of Al_2O_3 and SiO_2, rendering it a promising replacement for synthetic inorganic materials as a renewable membrane additive [22, 23]. Several studies have been conducted with regard to the application of hollow fiber membranes. Mokhtar [24] investigated the addition of bentonite to composite hollow fiber membranes, resulting in a flux performance of up to 4 $kg.m^{-2}.h^{-1}$. Similarly, other studies have shown that the addition of bentonite can increase the hydrophilicity of a PSF membrane, reducing its water contact angle to 66° [25]. In addition to being an eco-friendly waste management solution, the incorporation of SBE in membranes is currently being researched. The use of SBE as an additive allows for the efficient utilization of waste materials, hence decreasing their environmental impact and supporting sustainability. This novelty work aims to examine the impact of SBE addition onto PVDF-TiO_2 hollow fiber membranes and their performance in terms of pure water flux.

2. Methodology

2.1 Materials and Chemicals

Spent bleaching earth (SBE) was collected from PT. Sime Darby Oil, Kotabaru, South Kalimantan-Indonesia. The chemicals employed in this work is Polyvinylidene fluoride (PVDF) (Solef 6012) as the hollow fiber membrane's basic polymer. N, N-Dimethylacetamide (DMAC) (Sigma-Aldrich) was utilized as a solvent to dissolve PVDF during the dope preparation. Titanium oxide (TiO_2) (Merck) as a hollow fiber membrane additive, Ethanol and n-Hexane (Merck). All of the chemicals were analytical reagent grade and were used exactly as supplied.

2.2 SBE Regeneration

SBE was regenerated by solvent extraction and thermal treatment to remove oil and any organics debris. n-Hexane as a solvent is dissolved in SBE. Then, the SBE was calcined after being extracted from the solvent. The regenerated SBE was then ready to be integrated into HF membrane. The detailed techniques are carried out based on our previous work [22].

2.3 Membrane Preparation

Firstly, a solution was prepared by dissolving TiO_2 and regenerated SBE in DMAC, as outlined in Table 1. The solution was mixed at 70°C for 24 hours. Then, 18% of PVDF was added to the dope solution and stirred at 70°C until homogenous. After cooling the dope solution, it was poured into the dope tank for the HF membrane spinning process. The dope solution was extruded using the HF membrane spinning set up as show in Figure 1. The spinning conditions are presented in Table 2. The resulting HF membrane was soaked in tap water for 24 hours, followed by 1-hour immersion in 50% ethanol and another immersion in 98% ethanol. Subsequently, the HF membrane was air-dried at room temperature for 24 hours.

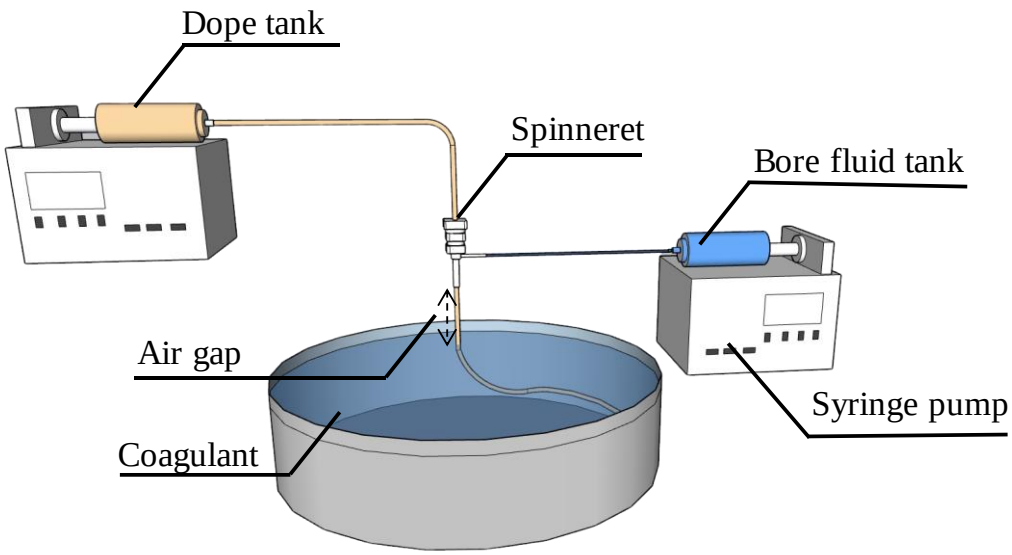

Fig. 1. Schematic of hollow fiber membrane spinning set up

Table 1
Dope Solution compositions of hollow fiber membranes

Membrane code	PVDF (% mass)	DMAC (% mass)	TiO_2 (% mass)	SBE (% mass)
3:0			3	0
2:1			2	1
1.5:1.5	18	79	1.5	1.5
1:2			1	2
0:3			0	3

Table 2
Spinning conditions of hollow fiber membranes

Spinning conditions	Unit	Value
Dope extrusion rate	mL/min	4
Bore fluid flow rate	mL/min	2
Bore fluid composition	-	Demineralize water
Coagulation medium	-	Tap water
Spinneret OD/ID	mm	
Air gap	mm	0
Dope solution's temperature	°C	25
External coagulation's temperature	°C	25

2.4 Membrane Characterization

The functional groups present in the HF membrane were obtained via the attenuated total reflectance (ATR) technique using Bruker Diamond at a wavenumber of 4,000-500 cm. Functional groups will be identified based on the FTIR spectra graph data. The morphology of the HF membrane was characterised using a scanning electron microscope (SEM). The contact angles of the membranes were determined using the sessile drop technique. This involved placing a droplet of pure water on the dry membrane surface and capturing an image shortly after contact. For each repetition, contact angle measurements were captured at various locations utilizing the ImageJ software.

2.5 Membrane Performance Operation

The ability of the HF membrane pure water flux was determined using a series of cross-flow filtration equipment as shown in the Figure 2. Filtration conditions run with a pressure of 1 bar at room temperature. One end of the membrane has previously been blocked. The pure water flux was determined using the formula in the equation below. The m is permeate mass (kg), A is the active surface area of the membrane (m^2) and Δt is the time required to obtain permeate mass (hour) as shown on Eq. (1).

$$\text{Flux permeate} = \frac{m}{A \times \Delta t} \tag{1}$$

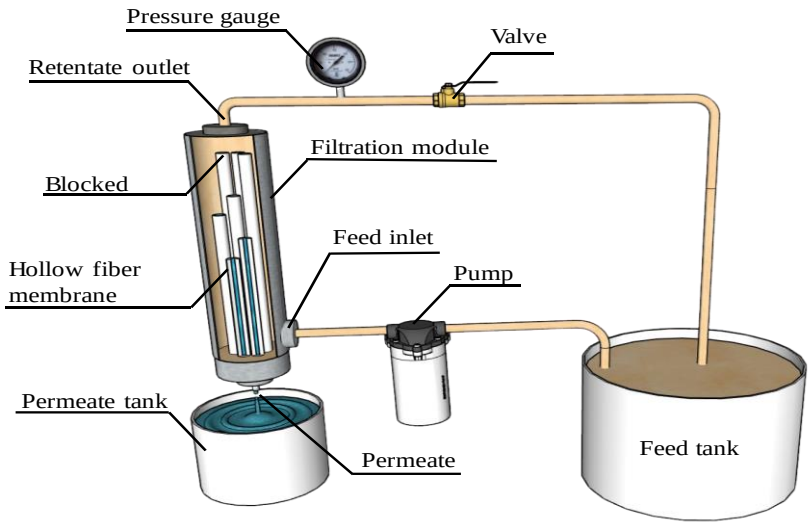

Fig. 2. Schematic system of hollow fiber membrane cross-flow filtration

3. Results

3.1 Characterization of SBE as Raw Material

The analysis of the SBE regeneration outcomes involved the use of FTIR testing, which can discern essential information about a material's chemical bonds and functional groups [2]. Figure 3 displays the FTIR spectra of the regenerated SBE. The FTIR graph displays the vanishing of particular functional group peaks that identify the oil and organic matter as a result of the SBE regeneration procedure. The existence of oil carbon chains and unbound fatty acids is indicated by C-H bonds at 2923 cm^{-1} and 2853 cm^{-1} as well as -C=O ester bonds at 1745 cm^{-1}. Furthermore, there are also sections with -OH bonds at wavelengths surpassing 3000 cm^{-1} [26]. The results of the regeneration process have retained only certain essential functional groups in SBE, including the silica matrix (exhibiting Si-O-Si stretching vibrations) at a wavelength of 1031 cm^{-1} and silica or quartz (displaying Si-O vibrations) at 795 cm^{-1} [22, 27, 28].

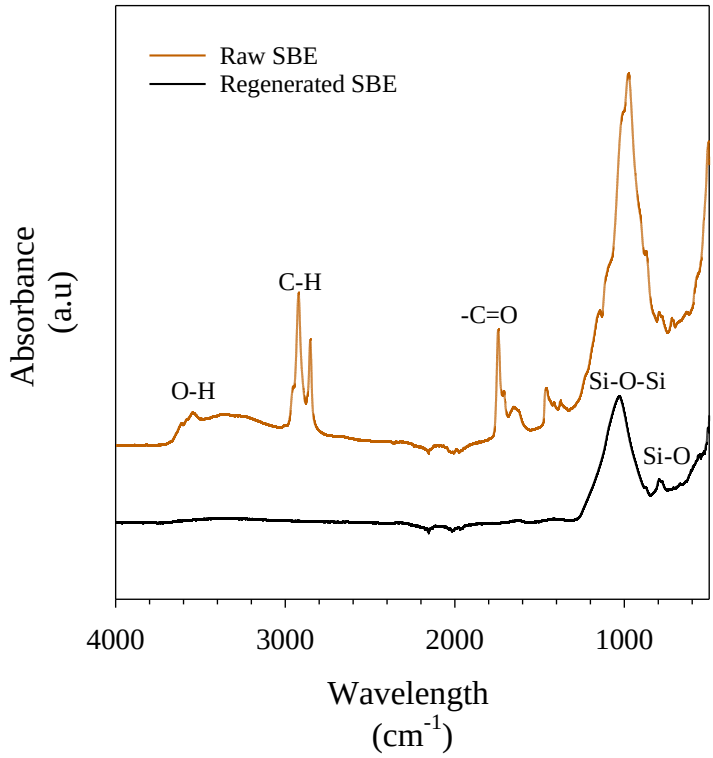

Fig. 3. FTIR spectra of spent bleaching earth

3.2 Functionalization of Hollow Fiber Membranes

Figure 4 shows the FTIR spectra of all PVDF HF membranes at different particle addition and the FTIR spectrum of a regenerated SBE at wavenumber 4000-500 cm^{-1}. The FTIR spectra of SBE indicate a montmorillonite structure, as evidenced by the peak at wavenumber 3549 cm^{-1}, indicative of Al-O-H stretching leading to the montmorillonite structure [29]. Absorption spectra of Si-O groups are seen at wavenumber 2099 cm^{-1} (stretching) in regenerated SBE. Wavenumber 776-794 cm^{-1} reveal vibrational group of Si-O with quartz impurities. Spectrum 611-676 cm^{-1} show Si-O vibration in the form of kaolinite Si-C, and the other spectrum 969 cm^{-1} reflect Si-OH [22].

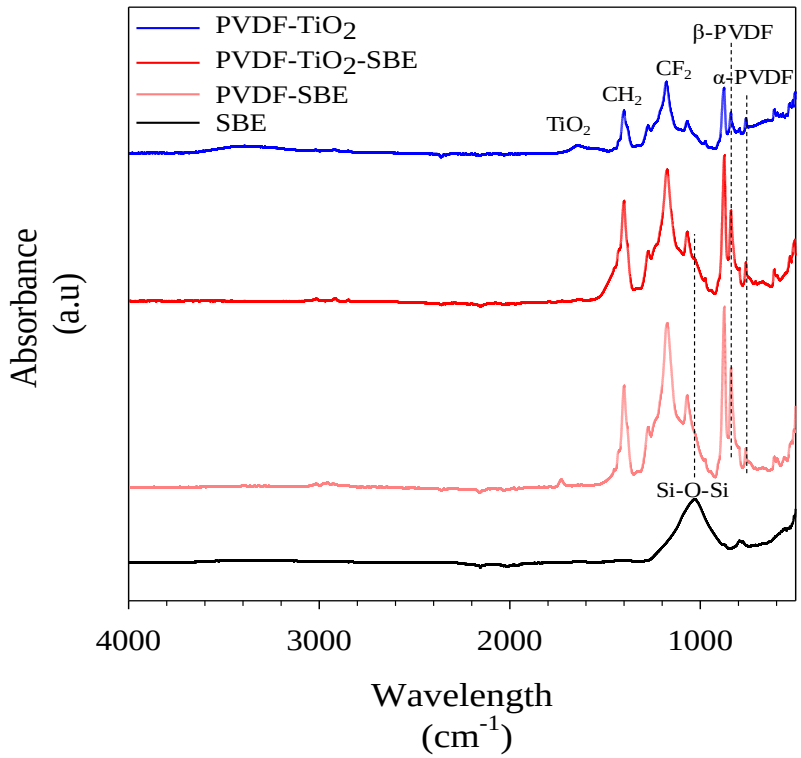

Fig. 4. FTIR spectra of hollow fiber membrane with variation composition

SBE addition in to PVDF HF membrane led to appear Si-O-Si functional groups at wavenumber 1060 cm^{-1} [22, 30]. The peak clearly visible at PVDF-TiO_2-SBE and PVDF-SBE HF membrane. And the other hand, PVDF-TiO_2 HF membrane without SBE addition show the low peak of Si-O-Si functional group. it proves with SBE addition, so the PVDF HF membrane strength characteristic can be improved by the presence of silica [31, 32].

The PVDF spectra also define its crystalline phase. the phase depends on its preparation method [14]. the figure shows the a-phase found at wavenumber 763 cm^{-1} and the b-phase at 840 cm^{-1}. The difference of SBE-TiO_2 addition into PVDF HF membrane led to different β-phase. The FTIR spectra determine that the larger β-phase is PVDF-TiO_2-SBE, which lead to the most hydrophilic than other membrane because the β-phase showed the polar nature of PVDF [33].

3.3 Membranes Morphology

The morphology of the membrane was examined by scanning electron microscopy (SEM). SEM provides high resolution images of the surface and cross-section of the HF membrane [15]. SEM enables the observation of the general structure This technique for characterisation enables the uniformity and integrity of membrane to be determined, as well as the presence of defects and fouling [34]. Figure 5 gives the morphology of the fabricated HF membrane.

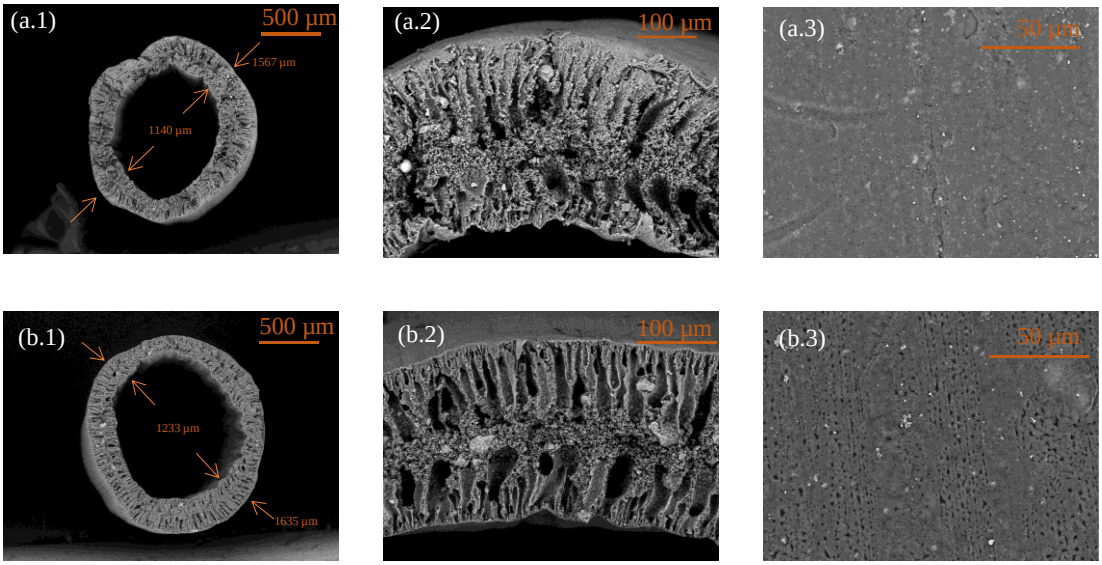

Fig. 5. SEM morphology of hollow fiber membrane's cross section and surface (a) PVDF-TiO_2-SBE (b) PVDF-SBE

Figure 5 illustrates the cross-section and surface area of the resultant asymmetric HF membrane, as shown in Figure 5 (a.1), (a.2), (b.1), and (b.1) as membranes cross section. The PVDF-TiO_2-SBE HF membrane obtained has an outer diameter of 1567 µm, while the PVDF-SBE HF membrane reaches 1635 µm. Figure 5 (a.2) and (b.2), display the HF membrane structures, which consist of finger-like structures at the top and bottom layers, with a sponge layer between them. These structures are commonly referred to as a sandwich structure in HF membranes [35, 36]. This formation is due to the instability of the suspension/coagulant interface that occurs during phase inversion [37]. The spongy structure permits the membrane to exhibit good mechanical robustness even when the thickness is low. Additionally, it supports the transmission of mass in water [38, 39].

The characteristics and pore size of the membrane surface play a key role in influencing the selectivity and performance of the HF membrane [40, 41]. The surface structure depicted in Figure 5 (a.3) and (b.3) of the HF membrane illustrates the pore structures' formation resulting from the phase inversion process [35]. White patches on the membrane surface indicate the presence of a homogeneous distribution of TiO_2 and SBE inorganic particles. Increasing the quantity of TiO_2 and SBE within the polymer membrane results in further hydrophilic properties of the membrane and subsequently enhances its flux performance. However, excessive particle loading can lead to aggregation or agglomeration, which can eventually block the membrane pores [42, 43]. The distribution of SBE particles on the membrane surface is also influenced by the hydrophilic interaction between SBE and water molecules that migrate towards the coagulant during the phase inversion process [44].

3.4 Membranes Surface Hydrophilicity

The hydrophilicity of the membrane surface is a crucial membrane property [8]. The water contact angle, determined by the angle formed between the surface of the liquid and solid particles and the surface of the liquid and gas during droplet formation, is used to classify membranes. In general, a membrane with a water contact angle of less than 90º is described as having hydrophilic properties [45]. Based on the Figure 6 it is evident that all of the manufactured HF membranes have a contact angle value ranging from 74.3° to 87.7°. This signifies that the HF membranes are characterized by low hydrophilicity, which can be linked to the hydrophobic properties of the PVDF

polymer material [14, 46, 47]. Moreover, a previous study conducted by Dzinun, Othman [35] reports a pristine PVDF HF membrane with a contact angle value of 91°.

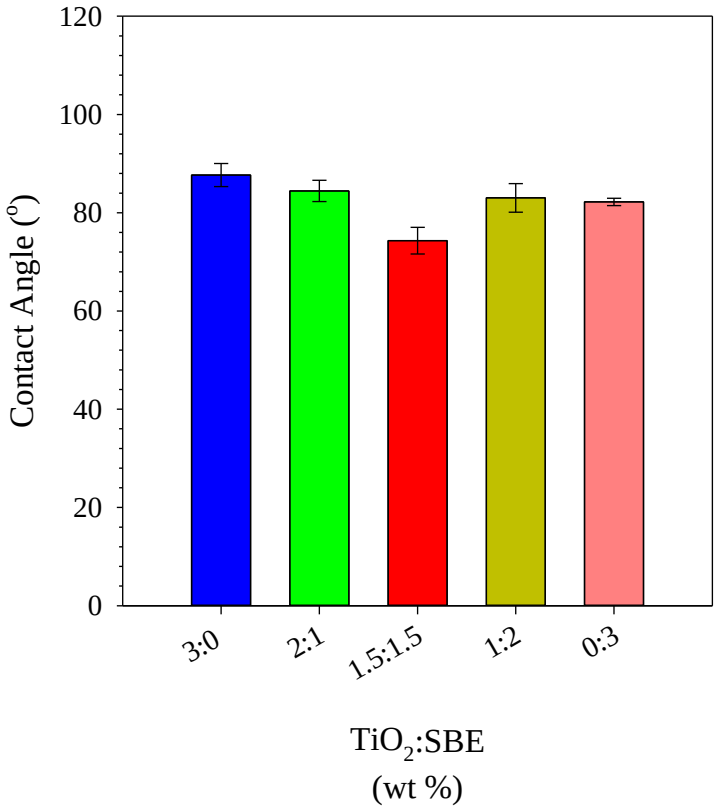

Fig. 6. Water contact angle of hollow fiber membrane

In this experiment, the modification of the PVDF HF membrane was successful. The addition of SBE and TiO_2 resulted in improved hydrophilicity, with the contact angle reaching 74.33º. Additionally, when comparing the loading of only SBE or TiO_2 in the HF membrane, it indicated that the improvement in hydrophilicity was not as significant as when both were used in combination. The study suggests that the number of hydrophilic functional groups present in a HF membrane plays a significant role in the results obtained [48, 49]. As the most hydrophilic property, the PVDf-TiO_2-SBE HF membrane has larger hydrophilic functional groups from the acquired FTIR spectra, such as hydroxyl, carboxyl, and the β-phase of PVDF crystallinity.

3.5 Pure Water Flux of Membrane

The study employed the ultrafiltration process to evaluate the efficiency of the produced HF membrane. Water permeate flux is a crucial measure of HF membrane performance, denoting the speed of pure water travelling via the membrane per unit area under a pressure gradient imposed on the membrane [50]. Figure 7 shows pure water flux performances of HF membranes.

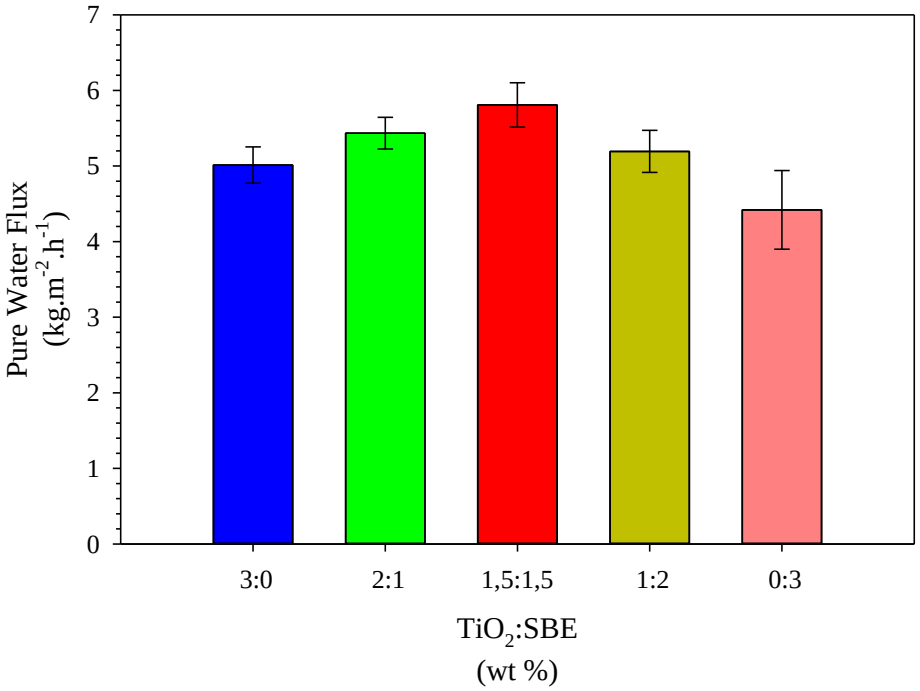

Fig. 1. Pure Water Flux Performance of varied hollow fiber membrane with different TiO_2:SBE wt% addition (under pressure filtration 1 bar at 25 °C temperature)

The process for determining pure water flux utilises a HF membrane filtration method that employs a cross-flow. This filtration system runs at an operating pressure of 1 bar. The graph shows pure water flux permeate of the obtained HF membranes has various results. The HF membrane with the addition of 1.5% TiO_2 and 1.5% SBE has the highest permeate water flux. The pure water flux achieved a value of 5.81 $kg.m^{-2}.h^{-1}$. The variation in permeate flux among each variation of HF membrane is influenced by the variation in the addition of additive particles to the membrane [2, 51-53]. Furthermore, a number of factors influence the permeate flux of the membrane, including its morphology and water contact angle. Membranes exhibiting lower water contact angles display a hydrophilic nature, allowing water to readily permeate the membrane's pores [45]. This is demonstrated by the 1.5% TiO_2:1.5% SBE membrane, which records a lower water contact angle value compared to the other membranes, indicating that it possesses the most hydrophilic properties. Furthermore, the structure of the membrane has an impact on its capacity to allow water to pass through [35, 54].

Permeate flux and rejection of turbidity and colour performance of PVDF membrane with addition 1:1 wt.% ratio of TiO_2 and SBE for palm oil mill effluent (POME) wastewater application shown on Figure 8. The permeate flux of its membrane under different trans membrane pressure from 1-3 bar exhibit 4.3-9.5 $kg.m^{-2}.h^{-1}$. The membrane flux of POME filtration is just slightly lower than pure water filtration about half percent. It demonstrates the PVDF-TiO_2-SBE membrane able to treating of POME wastewater specially to remove turbidity and colour parameters. Rejection of colour parameter obtained slightly low about range 54.7-60.5%. However, interestingly the turbidity rejection of all pressure filtration process shows greatly high up to 98.4-99.8% at 1 to 3 bar.

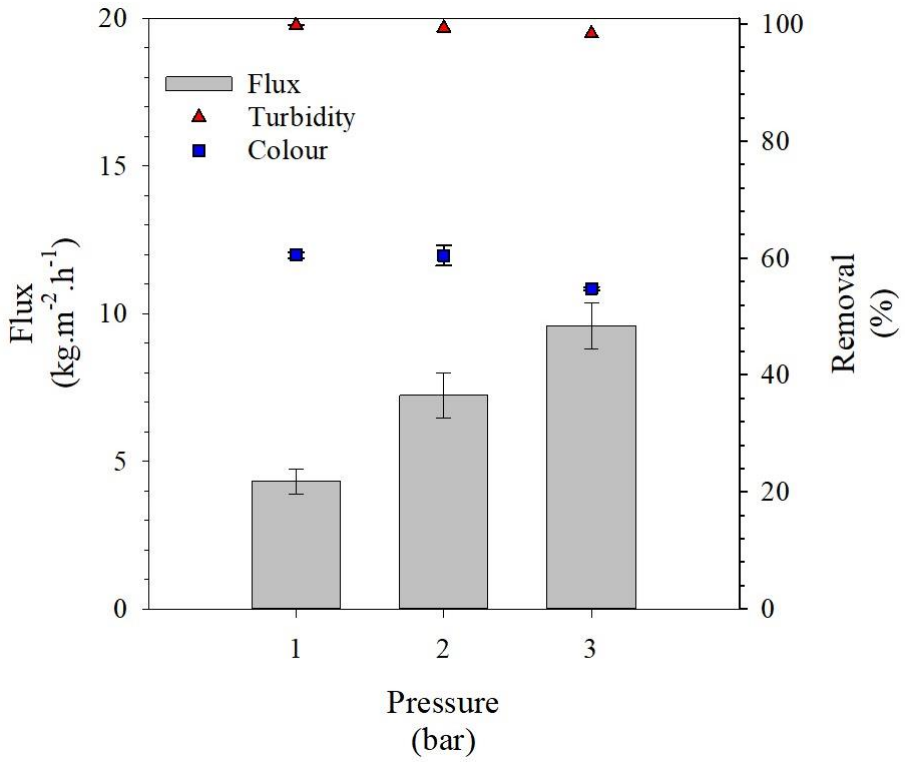

Fig. 8. Flux performance and rejection of turbidity and color parameter of PVDF-TiO_2-SBE membrane at 1:1 wt% ratio of inorganic additive loading for palm oil mill effluent filtration (under pressure filtration 1 bar at 25 °C temperature)

The color rejection of this PVDF-TiO_2-SBE HF membrane is slightly lower than reported by Mokhtar [55] using PVDF-bentonite HF membrane for POME application. It is due to the different filtration process have been used, in this work using driven pressure membrane separation process meanwhile the PVDF-bentonite HF membrane applied under thermally driven separation process. Therefore, the color parameter can not removed up to 60%. In other hand, turbidity removal of PVDF-TiO_2-SBE HF membrane in this work is more higher than other previous work which is only 80% by direct contact membrane distillation with pretreatmnet [56]. It conluded the PVDF HF membrane by modification with TiO_2 and SBE loading into the membrane matrices is affordable to remove the turbidity via pressure driven separation process.

4. Conclusions

The produced membrane comprises Si-O-Si and SBE. The HF membrane, with added TiO_2-SBE particles, displays a sandwich (sponge-finger-like) morphological structure on the cross-section, and a rough and porous structure on the surface. The composition of the TiO_2-SBE mixture, added as an additive, dictates both the hydrophilic properties of the HF membrane and the flux performance of pure water. The approach significantly enhances the properties of the PVDF HF membrane as evidenced by the resulting lowest contact angle value of 74.33°. Then the water flux of this membrane was 5.81 $kg.m^{-2}.h^{-1}$. This performance shows a better value when compared to other works

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