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Preparation and Characterization of Polysulfone Composite Membrane Blended with Kenaf Cellulose Fibrils

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ABSTRACT

Polysulfone (PSF) is widely used material for ultrafiltration (UF) membranes, which has outstanding mechanical properties, great chemical resistance, good thermal stability and wide pH operation range. The hydrophobic property of the PSF membrane seriously limits its application. Hence, blending with hydrophilic material as additives such as cellulose have been intensively studied to improve the hydrophilicity of membranes. Cellulose fibrils are composed of nano-sized elements, which have high hydrophilicity, strength, and biodegradation. A composite membrane was prepared by the phase inversion induced by an immersion process. The characteristics of the composite membrane were investigated with Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopic (SEM). The pure water flux of the composite membrane increased dramatically with the increase of cellulose fibrils. Mean pore size and porosity were significantly increased. Both mechanical properties and hydrophilicity were enhanced due to the addition of the cellulose fibrils.

1. Introduction

Since the twentieth century, there have undoubtedly been significant efforts made by researchers and industrialists in the development of water treatment processes to extract fresh water from the polluted water [1-3]. Ultrafiltration (UF) membranes have been commonly applied in modern industry, including applications in water treatment, food industry, and pharmaceuticals [2,3]. The recent development in material science provides a broad range of raw ingredients that could be utilized for membrane synthesis. The economic empowerment of cellulosic materials such as the cellulose fibrils, bacterial nano cellulose, cellulose nanocrystals, and diverse cellulose derivatives not just relies on the membrane fabrication process, yet additionally on their potential in water treatment [1]. Therefore, choosing the proper fillers or raw materials for synthesis and surface tailoring is crucial to putting together an effective membrane for water treatment.

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Polysulfone (PSF) is widely used in formulation of an asymmetric UF membrane. This is due to its advantageous characteristics of good strength, firm support material, temperature tolerances, porous nature and high dimensional stability to be fabricated into membranes in various conditions for UF [3]. The asymmetric UF membrane can be simply prepared using phase inversion method [4]. Hyper selectivity and permeability are controlled by the surface layer of the membrane. However, due to the hydrophobic property of PSF material, pure PSF membrane is vulnerable to fouling effect in water treatment. Severe problems related to protein can occur during the operation where a layer can easily form on a PSF membrane surface under hydrophobic conditions [5]. Moreover, membrane fouling results in not only limiting UF membrane performance and reducing its life-span, but also in increasing the operating cost. Hydrophobicity definitely restricts the application of PSF membranes. However, the hydrophilicity of membranes can be enhanced by blending with hydrophilic materials. Blending is known to be a very effective method of formulating and fabricating membranes with upgrading of membrane properties. Some inorganic particles, such as TiO_2 and SiO_2, have been used to enhance the mechanical properties of membranes [6]. Nevertheless, the most crucial in the blending process is to disperse particles uniformly into the polymer solution.

Cellulose is a natural biopolymer that can be easily and abundantly found in the world, and has favorable characteristics of flexibility in processing, biodegradability, sustainability and low cost, hydrophilicity and environmental friendliness. Because it is the most prevalent and highly hydrophilic natural material, cellulose has received a lot of attention. One significant concern among researchers is the development of cellulose fibrils. Cellulose fibrils can be synthesized into nano and micro scales [7,8]. Different forms of cellulose (C) are available, such as cellulose fibrils (CF), nanocellulose (NC), Nano fiber and microcrystalline cellulose (MCC) [1,8-10]. Due to their low density, renewable, biodegradable nature, and good mechanical qualities, all of these forms have been successfully used in a variety of fields. Additionally, the various forms of cellulose have been successfully blended with other polymers like polyaniline, poly (caprolactone), polyvinylidene difluoride (PVDF), and epoxy to produce materials with the desired properties [9,10]. This has been made possible by the presence of bulk -OH groups on the cellulose backbone. Mechanical and chemical treatment were typically used to produce cellulose fibrils. The chemical method, using strong acid hydrolysis, produces size-controlled fibrils with fractional removal of the amorphous sections of raw materials such as wood fibers and agricultural waste [7]. Whereas, the mechanical method includes a grinder process, a high-pressure homogenizer and refiner treatment [11]. Cellulose fibrils extracted from cellulose pulp have much larger specific surface area, low density and higher stiffness compared with the inorganic particles [8]. In addition, the presence of hydroxyl (-OH) groups on cellulose fibrils give better hydrophilic properties. Hence, the cellulose fibrils are very attractive for enhancing the hydrophilic character when preparing composite materials.

In this study, some hydrophilic cellulose fibrils extracted from Kenaf fibers have been blended with PSF to improve the hydrophilicity of PSF membranes. Composite membranes were prepared by embedded microcrystalline kenaf cellulose as the additives into PSF membrane. The composite membranes are fabricated by an interfacial polymerization method. Then, UF properties of composite membranes were evaluated directly by an ultrafiltration process. An obtained composite membrane was characterized by Fourier transform infra-red spectrometry (FT-IR) and Scanning electron Microscopy (SEM).

2. Methodology

2.1 Extraction of Cellulose

Using the Elementary Chlorine Free (ECF) method, kenaf cellulose was extracted. The Forest Research Institute Malaysia (FRIM) carried out the extraction process. The Kenaf extraction approach was used in earlier study [12]. Initially, 500g of kenaf bast were cut into pieces that were about 3 mm long. Afterwards, 6.0% sodium hydroxide (NaOH) and 0.1% anthraquinone were used to pulp and bleach kenaf bast. Approximately 150 psi and 170 °C of temperature were employed for a 1-hour treatment. These procedures were carried out five times until white color samples were acquired. Each stage involved spinning the samples in a spin dryer to remove the alcohol. During one hour at 70°C, the samples were treated with hydrochloric acid (HCl) at a 1:20 ratio to bleached pulp. To ensure that the desired texture and color of the sample was achieved, the mixed sample was refluxed for an additional hour. The samples were then dry milled or sieved to obtain acceptable sizes, ranging from 10-0.1 microns, after being rinsed with distilled water.

2.2 Materials of Composite Membrane

The composite membrane consists of a polymer, solvent and two types of additives. PSF provided by Sigma-Aldrich Company with average molecular weight of 35 000 g/mol have been chosen as the main polymer in this research. PSF has been used as an asymmetric membrane because of their porous behaviour and rigid support material in composite membrane. The solvent used to prepare the dope solution was N-Methyl 2-Pyrolidone (NMP) supplied by MERCK, Malaysia since this solvent dissolve a wide variety of polymers, and solution casting based on this precipitate rapidly when immersed in water to give porous, very anisotropic membranes. The blending of one or more additives technique has also been used for a surface improvement and pore formation. The Polyvinylpyrolidone (PVP K30) used in this research is supplied by Sigma-Aldrich Co. with molecular weight of 30000 g/mole and 99% purity. Cellulose fibrils were chosen as a second additive for base polymer PSF-PVP to produce a membrane with greater degree of hydrophilicity.

2.3 Preparation of Composite Membrane

The Loeb and Sorirajan phase inversion method was used to prepare the composite membrane [7]. The kenaf cellulose fibrils at various weight percent (wt.%) from 1 wt% to 9 wt.% were dispersed in the NMP by ultrasonic treatment for 30 min at 30 °C and 100 Hz. Then, PSF (20.5 wt %) and PVP K30 (0.5 wt %) were added into the above solution. After being blended with a mechanical stirrer at 30 °C and 120 r/min for 6 h, the homogenous dope solution was obtained. Table 1 shows nine dope formulations of ultrafiltration (UF) membranes to be fabricated. The dope solution was cast to a thin layer on the glass plate using a glass rod with 200 µm diameter. The glass plate was then immersed into the coagulation bath (distilled water) to form the composite membrane at room temperature. After 2 min, the PSF-Kenaf Cellulose (PSF-KC) prepared membrane was dipped in distilled water for 24 h until further used.

Table 1
Formulations of dope solution

Composite	PSF (wt. %)	NMP	PVP	Kenaf Cellulose	Total
1	20.5	78	0.5	1	100
2	20.5	77	0.5	2	100
3	20.5	76	0.5	3	100
4	20.5	75	0.5	4	100
5	20.5	74	0.5	5	100
6	20.5	73	0.5	6	100
7	20.5	72	0.5	7	100
8	20.5	71	0.5	8	100
9	20.5	70	0.5	9	100

2.4 Membrane Hydrophilicity

The degree of hydrophilicity can be determined using the contact angles. Using sessile technique, the contact angle of the membrane was investigated. It was carried out on a synthetic membrane sample that had been air dried in a chamber mounted to a contact angle goniometer (DSA 10, KRuSS). The equilibrium value was determined to be the average between the left and right side. About 4uL of deionized water was applied to the membrane surface using a tiny syringe to measure the contact angle. After 3s, the water contact angle value was recorded. The contact angles were produced by averaging at least five measurements made at various points on the membrane surface sample.

2.5 Fourier Transforms Infrared (FTIR) Spectroscopy

The fabricated membranes were also analyzed for FTIR. Fourier transform infrared spectrometry (FT-IR) analyses were carried out on the FTIR-1650 spectrophotometer (Shimadzu, Japan) in the range of 400–4000 cm^{-1}. Chemical bond types in the phases that make up synthesized materials, semiconductors, and new materials (liquid or solid) are identified by FTIR. By shining an IR light through a sample, the infrared (IR) spectrum of the sample is captured. The amount of energy absorbed at each wavelength is revealed by analyzing the transmitted or reflected light. One can analyse the absorption characteristics that disclose information about the sample's molecular structure from a transmittance or absorbance spectrum.

2.6 Scanning Electron Microscopic (SEM)

The Scanning Electron Microscopic (SEM) apparatus was used to examine the top surface and the structure of the membrane. The Hitachi TM-3000 scanning electron microscope has a distance range of 6 to 10 mm and a 15 kV acceleration. Using two resolutions, 500x and 1500x, the SEM was used to examine two components: the membrane's pore size and its cross section. In order to obtain a clean cross-section of the membrane, membrane samples were submerged in liquid nitrogen, fractured, and then coated with gold in a sputter coater. After that, using a scanning electron microscope with potentials of 15kV to achieve magnification ranging from 250x to 5000x, the samples were scanned and captured on camera.

2.7 Ultrafiltration Properties of Composite Membrane

An ultrafiltration procedure was used to quantify the pure water flux and rejection, as illustrated in Figure 1. The tests were conducted at room temperature with a working pressure of 0.1 MPa. Using the apparatus depicted in Figure 1, the following approach was utilised to assess the ultrafiltration capabilities of composite membranes. Pure water was poured into the apparatus through the feeding hole once the ultrafiltration membrane had been installed. The test started after the rotor was turned on and the steel bottle was attached to the nitrogen (N_2) supply to maintain a pressure of 0.1 MPa. The pure water flux [J ($L \cdot m^{-2} \cdot h^{-1}$)] was calculated with the following equation.

$$J = \frac{V}{A \times t} \tag{1}$$

where V is the volume of filtered water (m^3), A is the membrane area (m^2), and t is the working time (h). The rejection was tested by filtrating salt (NaCl) solution (1 g/L), and the salinity was measured with a conductivity meter. Then the rejection was calculated using Eq. (2);

$$R = \left(1 - \frac{Cp}{Cf}\right) x100\% \tag{2}$$

where Cf and Cp are the salt concentrations (mg/L) in the feed and permeate, respectively.

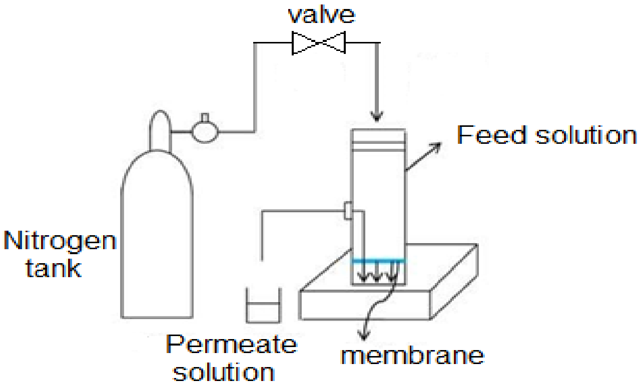

Fig. 1. Schematic diagram of the membrane filtration rig

3. Results

3.1 Hydrophilic Properties of Composite Membrane

The hydrophilicity of a polymer material can be evaluated by its contact angle (θ) with water. In general, a membrane's surface hydrophilicity increases as its contact angle decreases. Figure 2 depicts the contact angle and surface energy of composite membranes with various concentrations of kenaf cellulose fibrils as well as pure PSF membranes. The contact angles of the composite membranes decreased gradually from 62.4° to 45.2° compared to the pure PSF membrane, while surface energies rose with increasing cellulose content from 120 mN/m^2 to 175 mN/m^2. This finding suggests that hydroxyl group-containing hydrophilic cellulose fibrils were exposed on the membrane surface.

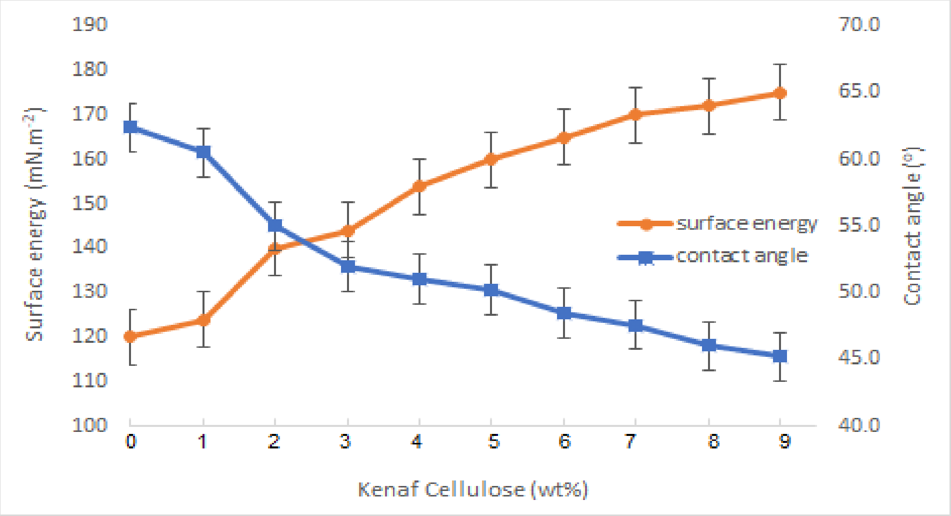

Fig. 2. Effect on hydrophilic angle (a) And surface energy (b) Of composite membrane with different cellulose fibrils contents

3.2 Infrared Spectroscopy Analysis

Specific absorption peaks can be identified for particular groups in FTIR. Figure 3 shows the spectra of kenaf cellulose fibrils (a), pure PSF membrane (b), and composite PSF-KC membrane (c). From spectrum a, it was observed that the hydrogen bond O-H stretching at 3347 cm^{-1}, the C-H stretching at 2903 cm^{-1}, the -CH_2 bending at 1429 cm^{-1}, and the C-H bending at 1370 cm^{-1} represented characteristic peaks of cellulose. The peak at 1058 cm^{-1} was related to the CO stretching. The CH bending and CH_2 stretching at 899 cm^{-1} indicated the amorphous structure of cellulose fibrils. In addition, the peak at 1635 cm^{-1} was detected as the O-H bending of adsorbed water, because water adsorbed in the cellulose molecules was too difficult to extract. Spectrum b shows characteristic peaks of PSF molecular structure. The PSF structure includes a benzene ring, an ether bond, and a sulphone structure. The C-H stretching peak of the benzene ring was situated at 3097 cm^{-1}. Three peaks between 1600 cm^{-1} and 1400 cm^{-1} were attributed to aromatic skeletal vibration. The C-O-C stretching peaks were located at 1324 cm^{-1} and 1239 cm^{-1}. The S=O stretching peaks were present at 1151 cm^{-1} and 1105 cm^{-1}.

From spectra b and c, the OH stretching peak became apparently wide and strong in the range between 3200 cm^{-1} and 3700 cm^{-1} regions. This indicated that hydrogen bonds were formed between OH groups of cellulose molecular and oxygen atoms in ether and sulphone groups of PSF. The characteristic peaks of cellulose fibrils were also present in the spectrum c. It was the evidence that cellulose fibrils were kept in the composite membrane. However, C-O-C and C-O stretching peaks were not observed, since they might be covered by other strong peaks of PSF absorption bands. Upon comparison of spectra b and c, characteristic peaks of pure PSF membrane were displayed in spectrum c. For instance, benzene ring skeletal vibration peaks were displayed at 1579 cm^{-1}, 1475 cm^{-1}, and 1411 cm^{-1}. The C-O-C and S=O stretching peaks were present at their original locations. No new peaks appeared in the spectra of composite membrane. This could be explained as evidence that cellulose fibrils and PSF did not produce new function groups during the preparation of composite membrane. Also, cellulose and PSF were interacting together at a molecular level. The wave numbers of absorption bands in composite membrane fluctuated to some extent.

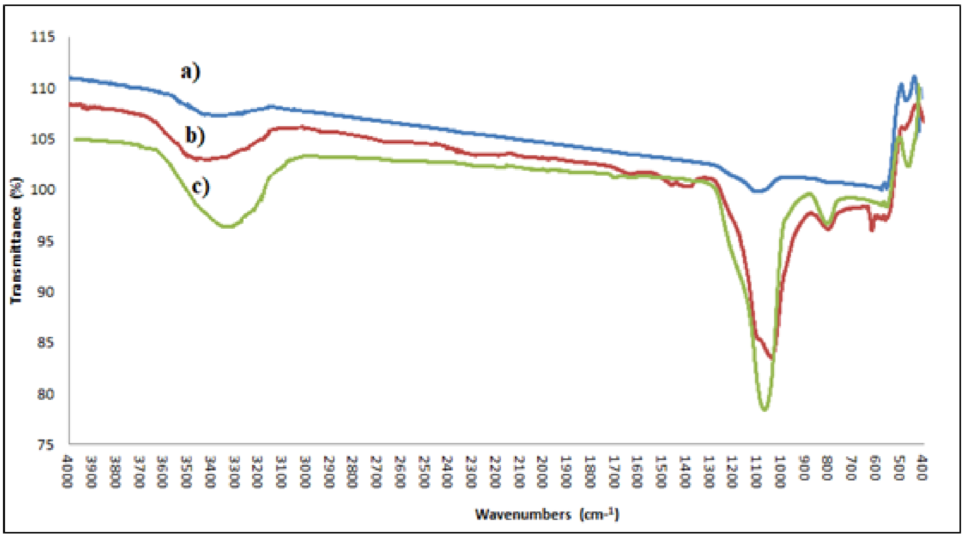

Fig. 3. a) FTIR of cellulose fibrils b) Pure PSF membrane c) Composite membrane

3.3 Morphology of Composite Membrane

Figure 4 shows the surface morphology of PSF and PSF-KC membrane respectively. Both membranes exhibited the dense layer of membrane pores on thin layer surface morphology. This is due to the addition of KC on the membrane surface enhanced the pore formation and distribution. The cross-section area of the PSF-KC membrane shows a longer finger-like structure than the pure PSF membrane as shown in Figure 5. These results indicated that the KC was able to improve the morphological structure of the membrane cross section hence leading to highest pure water flux. Therefore, the newly fabricate membrane of PSF-KC and PSF membrane are porous and asymmetric which has a dense top layer and a porous sub-layer. KC is also known as a pore forming agent hence larger pore size is observed in PSF-KC membrane. This is due to the fact that KC accelerated the velocity of water diffusion during the casting process. It is also shown that KC can increase membrane porosity with good connectivity. Previous study by Fernandes *et al.,* [13] also shows the SEM image with the increase in pore distribution and filterability tests indicate an increasing permeability with an increasing additive (silica) content.

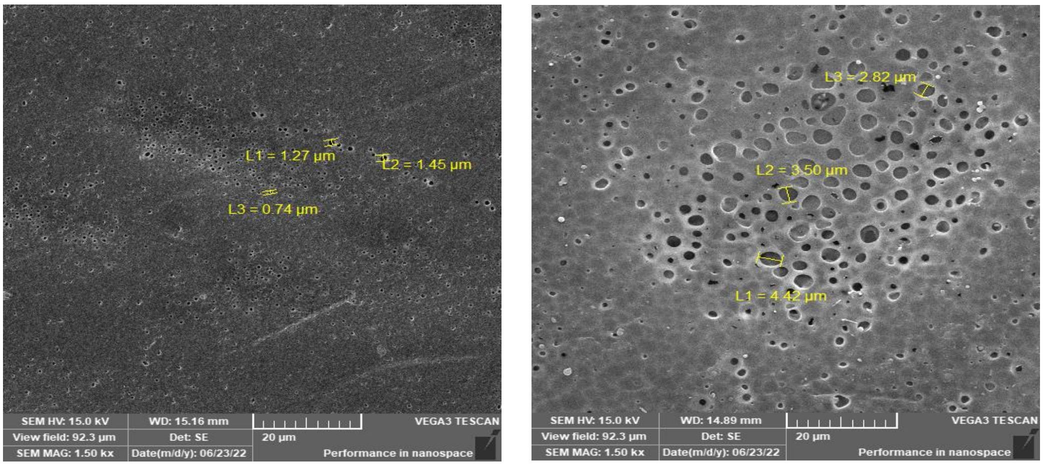

Fig. 4. SEM images for surface layer of pure PSF and composite PSF-KC membrane

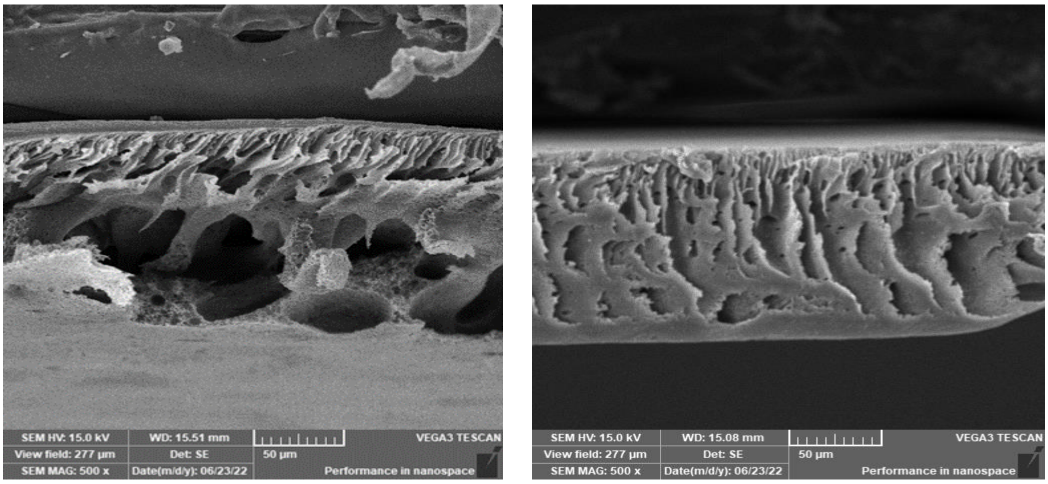

Fig. 5. SEM images for cross-section of pure PSF and composite PSF-KC membrane

3.4 Effects of Cellulose on Ultrafiltration Performance

Figure 6 shows pure water flux and salts rejection results for the pure PES membrane and composite membranes with different contents of cellulose fibrils. The operating pressure and temperature were 0.1 MPa and 25 °C, respectively. The pure water flux of composite membrane increased with increasing the content of cellulose fibrils. At the same time, salt rejections of composite membranes decreased from approximately 68% to 35%. In comparison with pure PSF membrane, the salt rejection and pure water flux of the composite membrane at 3 wt.% of cellulose improved 56.8 % and 68.9 L/m^{2}hr, respectively.

This change could be attributed to the fact that cellulose fibrils were better dispersed in PSF casting solution, which relatively decreased the content of organic solvent, NMP. The components of the casting solution were changed owing to the existence of cellulose fibrils at the phase separation process. In addition, the multi-exchange rate between NMP and water was accelerated by the strong hydrophilicity of cellulose fibrils. Also, the high multi-exchange rate facilitated phase separation and growth of a polymer-poor phase. These processes were beneficial for the formation of a composite membrane with higher salt rejection and smaller mean pore size. However, cellulose fibrils might also have blocked pores of the composite membrane to a significant extent when the content of cellulose fibrils was more than 1 %.

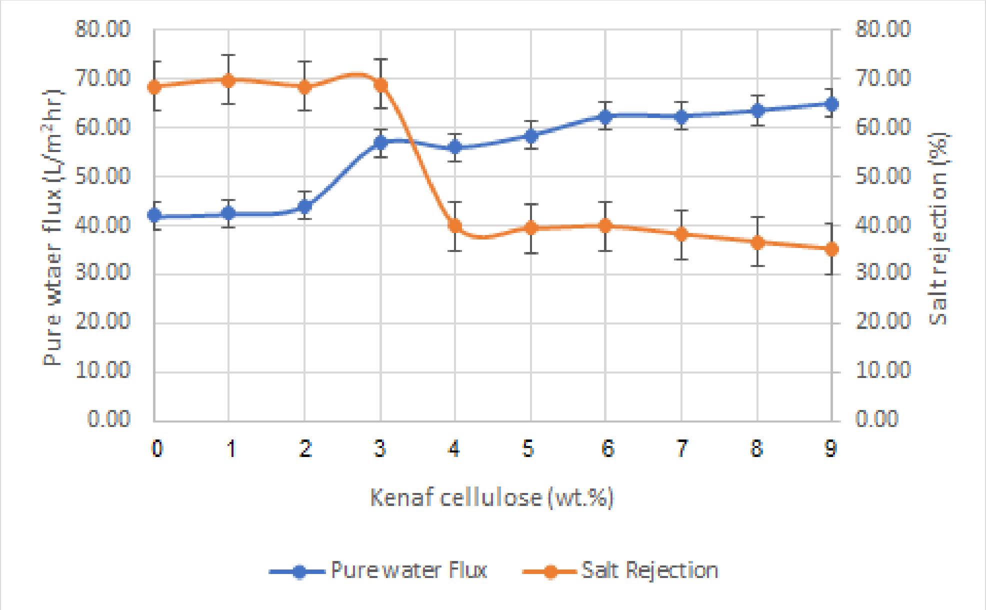

Fig. 6. Effect on pure water flux and rejection of composite membrane with different kenaf cellulose fibrils contents

4. Conclusions

A composite membrane of PSF blended with cellulose fibrils by ultrasonic treatment, was prepared by the phase inversion process. The contact angle decreased and surface energy increased with increasing content of cellulose fibrils. FT-IR analysis showed that a suitable level of molecular compatibility was achieved, which was based on the existence of inter-molecular hydrogen bonds between PSF and cellulose fibrils. The surface layer of the composite membrane material was dense, and the support layer of the composite membrane had larger size pores than that of a pure PSF membrane. The cellulose fibrils changed both properties and structures of the composite membrane. The pure water flux of composite membrane increased with increasing the content of cellulose fibril. At the same time, salt rejections of composite membranes remained at a higher level. The pure water flux of the composite membrane reached a maximum value of 68.9 L/m^{2}h when the content of cellulose fibrils was 3 wt. % of the casting solution.

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