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Flat sheet membrane composite for desalination applications based on Bacterial Nanocellulose (BNC) from banana peel waste, cellulose, and silica

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Abstract

This research reports the making of flat sheet membrane composite for desalination applications based on Bacterial Nanocellulose (BNC) from banana peel waste, wood cellulose, and silica. Silica synthesized using the sol-gel method resulted in particles range 189–227 nm in size. Characterization with FTIR further confirms the silica cluster produced from the synthesis. The membrane was successfully made in the form of flexible paper sheets in three compositions: T1 (BNC 60%, microcellulose 20%, and silica 20%), T2 (BNC 50%, micro cellulose 20%, and silica 30%), and T3 (BNC 40%, microcellulose 20%, and silica 40%). The SEM characterization shows the constituent elements, BNC, microcellulose, and silica, were evenly spread on the resulting flexible membrane sheet and shows matrix of BNC and microcellulose while the space between them are filled in by silica particles. EDS characterization are carried out to observe morphology and dominant element on the membrane. Performance test of the membrane was done at pressure 4 bar. The T3 membrane had the largest maximum flux value of 4.412 × 10^3 Lm⁻² h⁻¹. The T2 membrane had the highest salt rejection value of 4.89% in the first minute, but the value was lower than T1 at the end of five minutes. The salt flux and rejection values of the entire membrane tend to decrease with time due to clogging on the membrane surface.

1. Introduction

Desalination is a process used to obtain highly purified water, or clean water, from water with high salinity content, such as seawater. Desalination is carried out by removing excessive salt content in a liquid, such as seawater, brackish water, or wastewater. The desalination process is generally used to process seawater into mineral-free water that is fit for human consumption (El-Dessouky and Attourney 2002). The desalination method which is currently being developed uses membranes. Physical water treatment that allows the purification of wastewater containing contaminants that are very small to ionic size (<5 nm) can be carried out with desalination membrane technologies such as reverse osmosis and nano filtration (Lee et al 2016). The development of materials science has greatly influenced the advances in membrane-based technology such as reverse osmosis, nano filtration, ultra filtration and micro filtration. Recent evolutions in materials science offer a broad spectrum of raw materials in membrane fabrication. Polymeric membranes are currently dominated for water and wastewater treatment markets (Le and Nunes 2016, Tshikovhi et al 2020), however, membranes can also be developed from inorganic materials (ceramic and carbonaceous) and inorganic-organic hybrid materials. Polymer membranes are susceptible to fouling due to surface hydrophobicity, resulting in significant reductions in separation efficiency, flux, and membrane life in the treatment of highly polluted water sources (Tshikovhi et al 2020). Meanwhile, the use of inorganic membranes is not only limited
by its brittleness but also high operating costs. In this regard, the selection of the raw material or filler used in preparation and modification is rather important to construct suitable membranes for different processing purposes. In pursuit of sustainable materials, cellulose-based materials have caught the attention of membrane researchers. The ideas of using cellulose, cellulose derivatives, or nanocellulose either wholly or partly in membrane fabrication are indicated for biocompatibility, non-toxicity, high availability, and renewal (Shaghaleh et al 2018, Tshikovhi et al 2020).

However, currently available inorganic membranes have several shortcomings which include high production costs and high-pressure requirements during operation. In addition, rigid membrane designs are inflexible and brittle. For practical applications, it is necessary to develop more resistant membranes that not only have high permeance and selectivity but also better mechanical stability (Setiawan et al 2017). Such shortcomings can be addressed by utilizing nanocellulose material which has many advantages.

Nanocellulose is an environment-friendly material that can form biocomposite films that have high strength and hardness, but low density (Belbekhouche et al 2013). Nanocellulose can be obtained from banana peel waste through a simple, relatively inexpensive, and environmental-friendly process using fermented Gluconacetobacter xylinus bacteria (Figueiredo et al 2015). Bananas are a popular fruit that grows in many tropical countries, such as Indonesia. The banana peel has a biomass that is rich in cellulose. The increased interest in utilizing this biomass, besides aiming to reduce environmental impact, is adding value to cellulosic byproducts (Pellisari et al 2014). Synthesis and characterization of bacterial nanocellulose (BNC) from banana peels (Musa sp L.) was carried out to determine the potential utilization of banana peel waste at the optimal condition for synthesis (Sijabat et al 2020). Cellulose produced from banana peel synthesis is called Bacterial Nanocellulose BNC. BNC is produced by bacteria when the organic substrate (sugar, fructose, glycerol) is polymerized during cultivation (Phanthong et al 2018, Shak et al 2018). The resulting BNC has the highest purity among various types of nanocellulose because it only contains cellulose without any components in other lignocellulosic biomass such as hemicellulose, lignin and pectin. BNC appears in the form of a twisted band with diameters ranging between 20 nm and 100 nm and a micrometer length. Although BNC has the same chemical composition as other types of nanocellulose, BNC exhibits higher purity, water holding capacity and crystallinity, which leads to excellent thermal and mechanical strength (Shak et al 2018, Tshikovhi et al 2020).

Membranes using chitosan Silica are now commonly produced by the deposition of colloidal silica particles on the substrate (support), which is synthesized bottom-up first, using the sol-gel method to obtain the desired pore characteristics. This method is relatively easy to do at low temperatures (<30 °C) to produce a controlled material morphology (Muthia et al, 2012). The basic material sources (precursors) used are in the form of alkoxide metal solutions which undergo hydrolysis to become colloids (sol) and are then condensed (gelation) into a solid phase (gel). This study uses basic material in the form of tetra-ethyl-ortho-silicate (TEOS) (Ladewig et al, 2011) as the resulting pore size is 3–5 Å and has high-quality salt rejection.

In this research, chitosan is used as the coupling agent to bind silica, which is a non-organic material, with cellulose, which is organic. Chitosan is a biopolysaccharide derived from the deacetylation of chitin, which is the process of removing acetyl groups (Pillai et al 2019). Chitin can also be degraded naturally and is biodegradable, non-toxic, and antibacterial. These properties allow chitin to be used in the food industry as a hydrating agent in cosmetics, a pharmaceutical agent in biomedical preparation, and an antimicrobial agent in clinical applications. Chitosan is also used for drug delivery, as a catalyst, and as a flavouring agent for organic and inorganic contaminants (Sandeep et al 2013).

2. Research methods

2.1. Materials
The materials and chemicals used in this research were: ethanol; Aqua Dest; ammonia (NH₃); TEOs; Natrium Hydroxide (NaOH) 98% flakes; chitosan; BNC from Kepok banana peels (Musa paradisiaca L.) from the province of Kalimantan.

2.2. Experimental procedure

2.2.1. Silica synthesis
The synthesis of silica particles starts with mixing water and ethanol in a beaker. The mixing process is then continued for five minutes, using a magnetic stirrer. After that, 25% Ammonia (NH₃) solution is added and stirred for 10 min. Finally, TEOs is added to the sol and stirred for 120 min at a temperature between 50 and 60 °C. The silica is isolated from the solution which was obtained after high-speed centrifugation for 30 min. The resulting sediment is then washed three times with Aqua Dest, with each washing followed by centrifugation for 10 min. Next, the sediment obtained is dried in an oven at 100 °C for two hours. The resulting crystal is then pounded fine to obtain silica powder.
2.2.2. Making flat sheet membrane

The resulting flat sheet membrane is made up of nanocellulose, microcellulose, and silica composites with the composites consisting of T1 (BNC 60%, microcellulose 20%, and silica 20%), T2 (BNC 50%, microcellulose 20%, and silica 30%), and T3 (BNC 40%, microcellulose 20%, and silica 40%), respectively. The silica is first mixed with a 1% chitosan solution as a coupling agent. The membrane is made in sheet form according to the specifications of the TAPPI Standard (TAPPI 2006) and hand sheets are formed for the physical pulp tests (Reaffirmation of T 205 sp-02). The diameter of the hand sheet is 25 cm.

2.2.3. Characterization of membrane using scanning electron microscopy (SEM)

SEM characterization was carried out using equipment type Hitachi SU3500 to determine the microstructure of the membrane, size, and shape of material BNC particle, micro cellulose, and silica particles that form the membrane.

2.2.4. Characterization of membrane using energy dispersive x-ray spectroscopy (EDS)

EDS mapping was carried out using equipment type Hitachi SU3500 to see the distribution of constituent elements on the flat sheet membrane produced.

2.2.5. Desalination tests

As shown in figure 1, desalination test samples are placed in a membrane housing and the machine is prepared. Artificial salt water (3% NaCl solution) was used as feed water in this test. When the desalination machine starts, the feed water flows to the membrane in dead-end system. Working pressure is set at the 4-bar level. At that moment, the output water (permeate) from the end of the membrane housing is collected. The permeate is taken in a one-minute period.

A. Calculating Membrane Flux

Membrane Flux: \( F = \frac{V}{A \times t} \).

Where: \( V \) = Permeated volume
\( A \) = Membrane area
\( t \) = Measurement time

B. Calculating Salt Rejection

Salt rejection: \( % R = \frac{s_p - s_f}{s_p} \times 100\% \).

Where: \( s_p \): Feed water salinity
\( s_f \): Permeated salinity

Figure 1. Desalination engine with a dead-end system.
3. Results and discussion

3.1. Silica synthesis
Silica was successfully synthesized using the sol-gel method. With a SEM of 40,000 times magnification, it can be seen that the silica obtained is perfectly round with particle sizes in the range of 189–277 nm, as shown in figure 2.

Figure 3 shows the result of the silica characterisation by FTIR which can be identified by the presence of silanol (Si–OH) and siloxane (Si–O–Si) clusters. From the spectrum, it can be seen that the absorption peak occurs at 1.605 cm⁻¹ wavelength. These peak numbers indicate the presence of O–H groups from the water molecules. The emergence of this peak indicates the absorption of water during the silica synthesis process. The peak at 3.428 cm⁻¹ indicates the O–H bonding of the Si–OH cluster. In addition to the two absorption peak numbers, the absorption peak also occurred at numbers 1.078 cm⁻¹ and 781 cm⁻¹ wavelengths. This number indicates the Si–O asymmetric bond of the Si–O–Si cluster. The absorption peaks at wavelengths 459 cm⁻¹ and 691 cm⁻¹ indicate the presence of Si–O bonds from the Si–O–Si cluster.

3.2. Making flat sheet membranes
Membranes were successfully made in the form of flexible paper sheets with a diameter of 25 cm for the three compositions: T1, T2, and T3. From these sheets, a small membrane with a diameter of 6 cm was made, as shown in figure 4. This was then tested using desalination test equipment, as shown in figure 1. Visually, all three membranes look similar.
3.3. Characterisation of SEM and EDS membranes

In the previous research (Sijabat et al. 2018) reports that the banana peel BNC microstructure is a 3D random, interwoven network formed by cellulose fiber and has the shape of a nanofibril of 30–50 nm in diameter. In manufacturing membrane filters, the banana peel BNC is expected to form a binding network with other materials of a certain porosity. This can be seen in figure 5.

From observation of the membrane morphology made by using SEM with a magnification of 10,000 ×, as seen in figure 6, it is obvious that the membrane consists of BNC particles in the shape of elongated fibrils. The space between the empty fibrils is filled with silica particles with chitosan as a coupling agent. From figure 6, it
can be seen the uniformity of the three components (BNC, micro cellulose and silica) that make up the membrane.

In the membranes, BNC and microcellulose act as the matrix. This matrix determines the membrane’s strength, pore size, and the flux of water that flows through the membrane. The larger the particle size and the membrane pore, the smaller the flow of flux produced. Silica particles act as an active agent; i.e. the agent that plays an active role in separating salt molecules from the water flow. Silica also acts as a catalyst in separating salt particles. Chitosan is used as a binder, which is a mixer between one particle and another. Chitosan also acts as an anti-bacterial agent in the membrane. Membrane morphology shows that the pores formed on the membranes are used to create a flow of water.

In this research, microcellulose was added to the membrane. Cellulose was added to provide gaps or pores so that water particles could pass through the membrane at low pressure (4-bar). The addition of cellulose enlarges the membrane pores so that the water flux that passes through the membrane becomes bigger.

The EDS characterization was carried out on membranes for quantitative composition analysis of the membrane constituent elements. Moreover, the EDS characterization was carried out to identify the mapping of the constituent elements of the membranes. The EDS characterization was carried out on one of the membranes: T2 membrane. The composition of the membrane constituents can be observed in the spectrum seen in figure 7.

Based on figure 7, it can be seen that the dominant constituent elements of the membrane are: Oxygen (O) and Carbon (C) with a composition of 51.39% and 46.13% of the known element mass. The elements C and O are derived from cellulose, which is the main constituent element of the membrane. The O element is also derived from silica and chitosan which are used to make the membrane. The silicon element (Si) is detected as 0.44%. This element is derived from silica which is used for synthesis. Furthermore, the Sodium (Na) element is detected as 1.86%. Na is derived from the BNC immersion process using NaOH during the BNC synthesis.
The EDS characterization was also carried out to determine the distribution of the membrane constituent elements as well as to learn whether the mixture of the elements on the membrane was homogeneous. The distribution of the elements in the membrane can be determined by observing the colours produced by EDS-Mapping. Each element has a certain energy level. The elements contained in a material can be analysed based on their energy levels. The energy levels are represented by colourful patterns as shown in figures 8 and 9.

From figures 7 and 8, it can be seen that the main constituent elements of the membrane; namely, O, C, and Si, are evenly distributed on the membrane. This indicates that the mixing process of the BNC, microcellulose, silica, and chitosan was successful in producing a membrane with a homogeneous composition.

3.4. Desalination test

Figure 10 shows that the T3 membrane had the largest maximum flux value at $4.412 \times 10^3$ l m$^{-2}$ h which was obtained at the first-minute measurement and continued to decrease until it reached $1.018 \times 10^3$ l m$^{-2}$ h at the fifth-minute measurement. The T2 membrane had the largest flux value at $3.648 \times 10^3$ l m$^{-2}$ h in the first-minute measurement and the smallest decrease in flux value at $636.4$ l m$^{-2}$ h in the fifth-minute measurement. The T1 membrane had the largest flux value in the first-minute measurement, which is equal to $2.137 \times 10^3$ l m$^{-2}$ h. In the first minute, the T1 flux value was smaller than that of the T3 and T2 membranes. However, the T1 smallest flux value was larger than that of the T2 membrane; namely, $975.8$ l m$^{-2}$ h in the fifth minute. The T3 membrane had the largest flux because the membrane layer morphology was coarsest compared to other samples. This means that the pore size formed by silica particles in the membrane layer is larger and allows water to flow more smoothly. Decreased membrane flux with time indicates the clogging phenomenon, which is the compression of the flow caused by the accumulation of salt particles on the membrane surface which can reduce membrane pore size, decrease membrane porosity, and form a fouling layer that decreases membrane permeability. The fouling layer can result because of several factors, such as hydrophobic nature,
pore size, concentration of other compounds in the water, temperature, water flow rate, and water turbulence. Fouling can also damage the membrane when decreasing the membrane permeate flow.

Figure 11 shows that the salt rejection value for all variations tends to decrease with increased time. T2 membrane has the largest salt rejection value of 4.89% at the first-minute measurement. The T2 membrane salt rejection value continued to decrease until it reached 2.28% at the fifth-minute measurement. The T2 membrane has a maximum salt rejection value of 4.56% at the first-minute measurement. The salt rejection value continued to decline until it reached a value of 2.61% at the fifth-minute measurement. The T3 membrane has the smallest salt rejection value compared to the T1 and T2 membranes; namely, 3.26% at the first-minute measurement which continued to decrease to 1.95% at the fifth-minute measurement. The T1 membrane had the highest average salt rejection value (3.774%) than T2 and T3 membrane. This is due to the smooth and homogeneous surface of the T1 membrane compared to the T2 and T3 membranes because the composition of the amount of BNC used is the largest. Where the size of the BNC 30–50 nm is smaller than the 189–277 nm silica particles. This condition provides an advantage in the pore shrinkage process by the pile of salt and increases the rejection value. Silica acts as a molecular sieve on the membranes as well as a selective barrier between water molecules and hydrated salt ions. Silica also contributes to the salt rejection value which tends to decrease as the test time increases. Silica has an amorphous weakness which is indicated when silica comes in contact with water. The silica structure then tends to undergo structural degradation and densification, which can certainly affect the selectivity ability of the membrane. A decrease in salt rejection can also be caused by the rapid build-up of salt on the membrane and the desalination system flow pattern where the feed water that has flowed into the filtering system flows back into the feed water tank, thus increasing the salt level of the feed water.
4. Conclusion

Silica synthesised using the sol-gel method resulted in particles between 189–227 nm in size. Characterisation with FTIR further confirms the silica cluster produced from the synthesis. The membrane constituent elements, BNC, microcellulose, and silica, are evenly distributed on the resulting flexible membrane sheet. The SEM characterisation shows matrix of BNC and micro cellulose while the space between them are filled in by silica particles and it can be seen that the three components are uniform. The EDC characterisation shows that the dominant element of membrane are Oxygen (O) at 51.39% and Carbon (C) at 46.13%. The T3 membrane (BNC 40%, microcellulose 20%, and silica 40%) has the largest maximum flux value of $4.412 \times 10^3$ $\text{lm}^{-2} \text{h}$. The T2 membrane (BNC 50%, microcellulose 20%, and silica 30%) has the highest salt rejection value at 4.89% in the first minute, which was lower than the T1 membrane (BNC 60%, microcellulose 20%, and silica 20%) at the end of five minutes. Performance test of the membrane was done at pressure 4 bar. The salt flux and rejection values of the entire membrane tend to decrease with time due to clogging on the membrane surface. Therefore, modifications in the desalination system are needed to reduce the speed of clogging on the membrane in order for the membrane to function optimally in the desalination process.

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