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Characterization Study of Inorganic Hybrid Membrane of Mixed Activated Zeolite and Clay with PVA Adhesives using Sintering Method for colourless Peat Water

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Abstract. The manufacture of inorganic hybrid membranes from the ingredients of activated zeolite (Z), clay (CL), white Portland cement (CW) and PVA adhesive has been carried out on various M1, M2 and M2 material compositions (Z: CL: CW: PVA = 25%: 50%: 20: 5%), (Z: CL: CW: PVA = 50%: 25%: 20: 5%), (Z: CL: CW: PVA = 75%: 0%: 20: 5%) respectively. 100 mesh zeolites are activated using 2M HCL. The membrane is printed in a cylindrical shape with a specification of 69,83x250mm and is burned at a sintering temperature of 500-700OC. This study aims to determine the classification of produced membranes and determine the effect of temperature on the characterization of an inorganic hybrid produced membranes based on permeability, density, porosity and membrane morphology test using Scanning Electron Microscopy (SEM). The results showed that the temperature influences membrane characterization. The higher is the temperature, the lower is the membrane density. The membrane pore size decreases and porosity increase. The results of the study obtained an inorganic hybrid membrane (MHA-ZC) classified as microfiltration membrane (MF) with a pore size of 1,2–6,302µm, porosity 45%, density 0,811 gr/cm³, and flux permeability 313,57 L/m².jam. The M1 membrane test has been able to remove the colour of the 90.59% peat water from 170 PtCu to 16 PtCu, and the pH of the peat water is successfully neutral at 6.5-7.5.

1. Introduction

Membrane technology has become a trending topic in recent years in the water treatment industry development. Membranes are defined as a selective barrier between two fluid phases [1]. In the process, the membrane acts as a very specific filter, since it separates the material based on the size and shape of the molecule, whereas only certain sizes of molecules can pass through the membrane and the rest is stuck on the membrane surface. Therefore, the process of separation with the membrane uses a pull force in the form of compressive strength, electric field, and different concentration. The weakness of the membrane process showed the difference that is inversely proportional between flux and selectivity,

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the higher the flux results, the lower the selectivity. While the expected process for membrane performance is to increase flux and selectivity [2].

Inorganic membranes are one of the synthetic membranes that made from inorganic compounds, such as ZrO_2 , $\gamma\text{-Al}_2\text{O}_3$, and SiO_2 [3]. Natural ingredients that contain lots of compounds $\gamma\text{-Al}_2\text{O}_3$, and SiO_2 are zeolites and clay soils [4].

Zeolite is the right material for making membranes since in the water it does not expand and easily forms a suspension into a membrane product [5]. Zeolite is widely used because of its porous structure [6]. Nature-derived zeolites still contain a lot of impurities so that natural zeolite activity tends to be low, therefore it is necessary to activate it [7]. The zeolite activation process can be done physically and chemically. Physical activation can be done with size reduction and heating at high temperatures. While chemical activation can be done by soaking with acid so that the cation is exchanged with H^+ [8]. Zeolite activation using 1%-HCl concentration for 8 hours was able to reduce 78.99% levels of Ca in groundwater [9].

Clay soil contains aluminosilicate, has very fine grains, the structure is known to be porous, has porosity properties that can absorb water molecules so that it is suitable as a ceramic membrane material [10]. Ceramic membranes from clay and organic additive-mixtures are reported to produce a membrane pore with the size of 11 μm and 43% porosity after the combustion process. The process of maturation of clay to ceramic soil occurs through the combustion process with a temperature exceeding 600°C, since it causes the clay to experience the change of the ceramic into a solid, hard and permanent mineral. Burning below 800°C free silica minerals (such as carbonate minerals) also change as well. This is a result of the calcination process [11].

Previous studies [12] reported the activation of natural zeolites from the Blang Pidie area of Southwest Aceh District using 0.05M-HCl and calcined 350°C for 2hours-tested due to improving the ability of zeolites to absorb the ions of copper. Microfiltration membranes were made from a mixture of Lampung natural zeolite with white Portland cement in a mixture ratio of 66.67: 33.33% as Z2S was able to reduce Fe^{2+} ion concentration to 99.4% and Mg^{2+} ions to 86.2% [13]. The ceramic membrane is made of 50x5 mm from a mixture of zeolite and white Portland cement at a ratio of 50: 50. Membrane morphology test results have the least uniformly and pore at 2 μm , density 0.86 gr/cm^3 , porosity 35.93%. Permeability test is carried out by giving the gravity thrust to the membrane and permeability is obtained 8428.15 L/m^2 . Hours. Brittle membrane texture [14]. Zeolite membrane (ZSM-5/ γ -Alumina) is characterized by morphological tests with SEM, structural tests with XRD and analysis with EDX with $\text{Si/Al} = 19$, and ZSM-5/ γ -Alumina membrane performance is very good in the oil separation process and water [15].

Hybrid is a combination of two or more different materials to get specific goals. The advantage of this material is to produce a good combination with different properties that have an original component. The membrane manufacturing process aims to modify the raw material used to form a membrane structure with the morphology needed for the filtration process. In a hierarchical manner, the material limits the techniques that can be used, the morphology produced, and the applied filtration principle. This means that not all types of membranes can be made from available materials.

The making membranes method varies depending on the type of material and the morphological purpose of the produced membrane. Some methods of making membranes are sintering, stretching, track-etching, phase inversion, sol-gel process, vapour deposition, and solution coating.

This study uses a mixture of activated zeolite minerals and clay soil into inorganic hybrids as the basic material of inorganic membranes using white Portland cement adhesive and polyvinyl-alcohol (PVA) to be applied to the removal of peat water. This study also uses sintering membrane-making method that aims to obtain the morphology and structure of the membrane type of microfiltration.

Based on the structure and the principle of separation, the membrane is classified into three different types namely porous, non-porous, and liquid membrane. Sintering is a simple method for making porous membranes from organic and inorganic materials such as metals, ceramics (aluminium-oxide, zirconium-oxide) graphite (carbon) and silica. This method involves compressing powder in the form of particles of a certain size that is heated at a certain temperature. As a result of heating, the contacting

side forms a hollow structure. The resulting pore size depends on the particle size of the powder and the particle size distribution. The more uniform the particle size, the more uniform the pore is obtained. This method generally produces a pore in the range of 0.1-10 μm . This technique method also produces a membrane type of microfiltration. Figure 1 shows an illustration of the membrane structure and its separation principle.

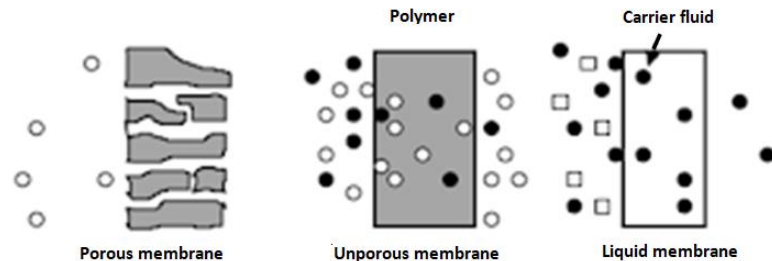


Figure 1. Illustration of membrane structure

Based on the operating system, it is divided into dead-end and crossflow systems. In this study, the membrane operation process uses a crossflow system. An overview of the dead-end and crossflow systems can be seen in Figure 2.

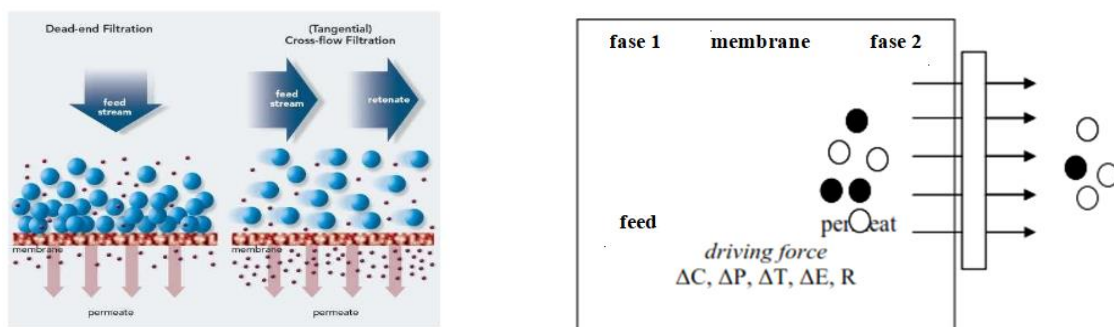


Figure 2. Membrane operating system scheme

Based on the pressure used as a force, membranes can be classified into several types, namely microfiltration (MF), ultrafiltration (UF), Nano-filtration (NF) and reverse osmosis (RO). The microfiltration membrane has a pore size of 0.05-10 μm , operates at a pressure of 0.1-2 bar and its permeability is greater than 50 L/m². h. Ultrafiltration has a pore size of 1-100 nm operating at 1–5 bar pressure and its permeability is 10-50 L/m². h. Nano-filtration has a pore size of < 2nm operating at a pressure of 5-20 bar and its permeability reaches 1.4-12 L/m². h. Reserve Osmosis has a pore size of < 2 nm operating at pressures ranging from 10-100 bar and its permeability reaches 0.005-1.4 L/m². h.

This study aims to determine the classification of the produced membranes and the effect of temperature on the characterization of inorganic hybrid membranes (MHA-ZC) generated based on permeability, density, porosity and membrane morphology tests using Scanning Electron Microscope (SEM). Membrane selectivity is obtained based on the percent color rejection of the produced peat water after processing using a MHA-ZC membrane on various pressure.

2. Method

The tools that have been used; analytic scales, crushers, 100 mesh sieves, SEM, UV-Vis, AAS, pH meters, ovens, furnaces, mixers/mixers, shear runners, module molding. The materials used include

natural zeolite, clay soil, white Portland cement, PVA, chloride acid, distilled water, peat water, colour analysis reagent, Fe analysis reagent.

2.1. Natural zeolite activation preparation

The zeolite is grounded with a 100-mesh fine crusher. 750g of fine zeolite is put into a beaker glass and added with 500ml of 2M-HCl, stirred and soaked for 2 hours, then filtered and washed with distilled water until the filtrate pH is 6-7. The residue is dried in an oven for 2 hours at a temperature of 700°C. Active zeolite is ready for use.

2.2. Inorganic Membrane Synthesis

2.2.1. Membrane Module

The membrane module is made of stainless steel, dimensions of $t \times d = 50 \times 5$ mm (module-1, density, and porosity test) and 69.83x250 mm (module-2, hollow, at 27.5 mm). Membrane molds are made as well as possible according to module 1 and module 2 specifications in accordance with the following Figure 3 and 4.

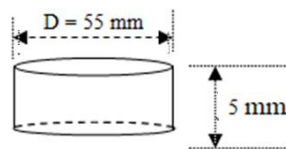


Figure 3. The Module-1 of inorganic membranes with specification 55x5mm

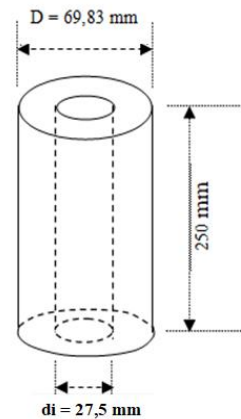


Figure 4. The Module-2 of hollow membranes MHA-ZC with specification 69,83x250 mm

2.2.2. MHA-ZC Inorganic Membrane Synthesis

A total of 1000 grams of mixture of natural zeolite (Z), clay (CL), white Portland cement (CW), and PVA are made according to the composition Z: CL: CW: PVA = M1 (25%: 50%: 20: 5%), M2 (50%: 25%: 20: 5%), and M3 (75%: 0%: 20: 5%). Then each dough is put into a container and add water little by little (2/3 parts) to form a paste. Paste dough is included in the 1-module and 2-module membrane molds and dried at room temperature (29°C) for 3 x 24 hours. The resulting MHA-ZC inorganic membrane was rinsed with water until the pH was neutral, and continued drying in a 70°C oven for 6 hours. Furthermore, it is sintered (burning) at a temperature of 500°C, 600°C, and 700°C for 6 hours in the furnace. Membrane characteristics test was carried out on membrane density, membrane porosity, morphological test with SEM. Membrane performance was tested based on membrane permeability, and membrane selectivity.

2.3. Inorganic Membrane Characteristic

2.3.1. Density Test

The MHA-ZC membrane from module 1 is placed back with the mold. Measure the membrane diameter and membrane thickness using a caliper or measuring instrument. Calculate the membrane volume of the diameter and thickness of the MHA-ZC membrane. Weigh the MHA-ZC membrane and record it as the mass of the membrane. Calculation of membrane density using the following equation:

$$\text{Membrane density} = \frac{\text{membrane mass (gr)}}{\text{membrane volume (cm}^3\text{)}} \quad (1)$$

2.3.2. Porosity Test

A total of 100 ml of distilled water was prepared into a 500-ml glass beaker. Insert the module 1 MHA-ZC membrane into the glass beaker. Let the membrane soak for 1x24 hours. Then the membrane is removed and weighed in wet conditions and then record the results as the weight of the wet membrane.

$$\text{Membrane porosity} = \frac{\text{wet weight} - \text{dry weight (gr)}}{\text{membrane weight (gr)}} \times 100\% \quad (2)$$

2.3.3. Morphological Test

MHA-ZC membrane morphology test was performed using an SEM tool. Membrane morphology test is intended to obtain a membrane pore size that affects the performance of the membrane in the filtration process.

2.4. Membrane Performance

2.4.1. Permeability Test

Membrane permeability is tested by measuring the flux of pure water passing through the membrane. Flux is the amount of permeate volume that passes through a unit of surface area of the membrane with a certain time in the presence of a thrust force, in this case in the form of pressure.

$$J = \frac{V}{A \cdot t} \quad (3)$$

where is J (flux, L / m².hr), V (volume of peer meat, L), A (surface area of the membrane, m²), and t (time, hour)

2.4.2. Selectivity Test

Membrane selectivity was measured based on the rejection coefficient (R) on the ability of the MHA-ZC membrane to clear the color of peat water. The color concentration of peat water in the bait and permeate is measured at all times at constant pressure. The coefficient of rejection is stated in equation 4.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (4)$$

where is R (rejection coefficient, %), the colour concentration of peat water on permeate, PtCu (C_p), the colour concentration of feed peat water in PtCu (C_f)

2.4.3. Scheme of Permeability and Selectivity Tests

The permeability and the selectivity tests of the MHA-ZC membrane are carried out according to the following set of equipment in Figure 5.

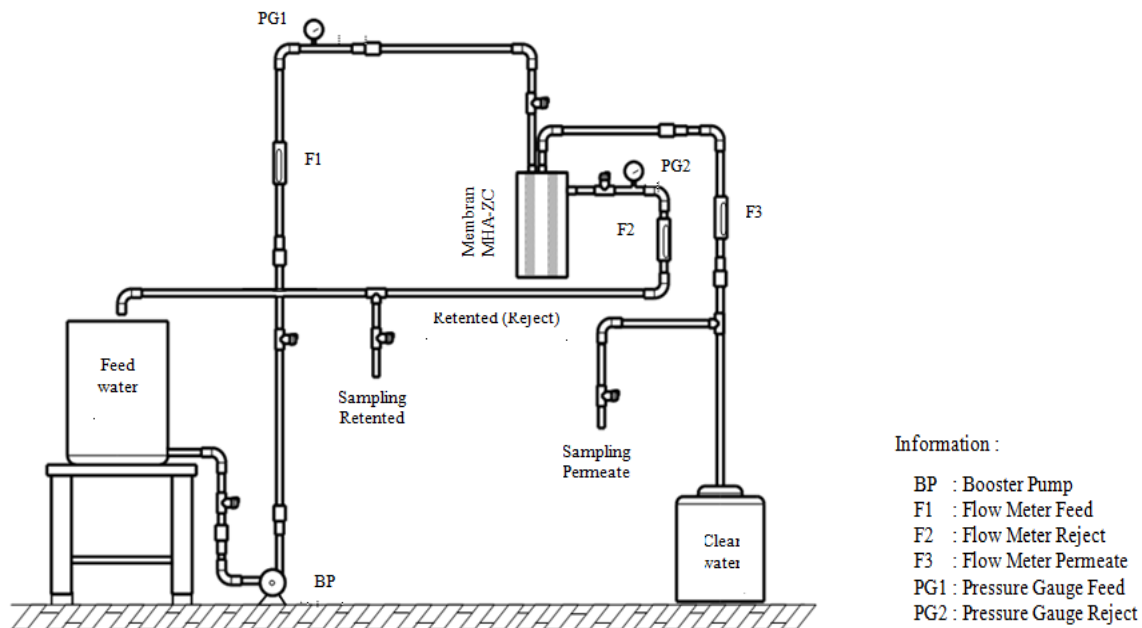


Figure 5. The Prototype for permeability test and selectivity test of membrane MHA-ZC

3. Results and Discussion

In this study, the manufacture of MHA-ZC inorganic membranes in the hollow form of a mixture of 250-750g-activated zeolite and 500-250g-clay soil using 200g-white Portland cement adhesive and 50g of PVA as an organic binder. The Sintering temperature was varied at 500°C-700°C with a burning time of 6 hours. The results of the MHA-ZC membrane characteristics obtained are presented in Table 1.

Table 1. Characteristics of MHA-ZC membrane test results on various compositions and sintering temperatures

Temperature (°C)	Composes Z:CL: CW: PVA	ρ (gr/cm ³)	ϕ (%)	Pori membrane μ m
500	M1	1,258	34,08	2,483
	M2	1,585	11,26	3,146
	M3	1,443	11,22	6,203
600	M1	1,025	41,60	1,477
	M2	1,555	18,59	2,783
	M3	1,226	20,19	3,146
700	M1	0,811	45,00	1,200
	M2	1,419	27,59	1,517
	M3	1,14	30,09	2,783

3.1. Effect of temperature on the density and porosity of the MHA-ZC membrane

The characteristic test results of the MHA-ZC produced membrane on density and porosity values obtained at various sintering temperatures can be seen in the graph in Figure 6.

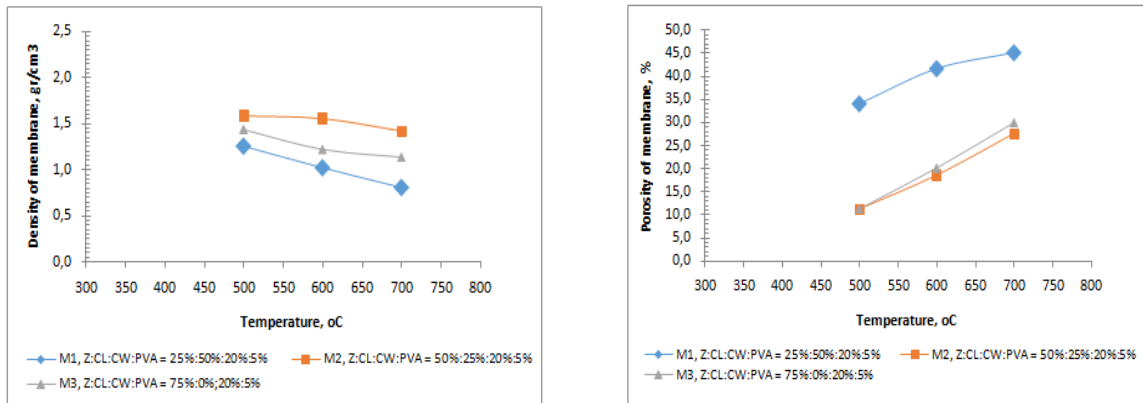


Figure 6. Temperature Effect on the density and porosity values of MHA-ZC membranes

From the graph that illustrated in Figure 6 the higher the sintering temperature, the lower the density and porosity increases. This is due to heating causing the contact side to form a hollow structure. So that the weight of the MHA-ZC membrane decreases at a fixed volume and the density of the membrane decreases and the porosity increases.

The sintering temperature of 700°C has the lowest density of 0.811 gr/cm³ and the porosity is at most 45%, namely the composition of M1. It can be concluded that the smaller the composition of the zeolite and the greater the composition of the clay soil, the better the characteristics of the MHA-ZC membrane. This is due to the heat load to release dirt in the zeolite cavity is reduced and at a temperature of 700°C clay soil has reached the point of maturity into ceramics.

3.2. Effect of temperature on MHA-ZC membrane morphology

MHA-ZC produced membrane morphology was tested using SEM to determine the size of the obtained size of membrane pore. The effect of sintering temperature on the pore size of the MHA-ZC membrane obtained is illustrated in the following Figure 7.

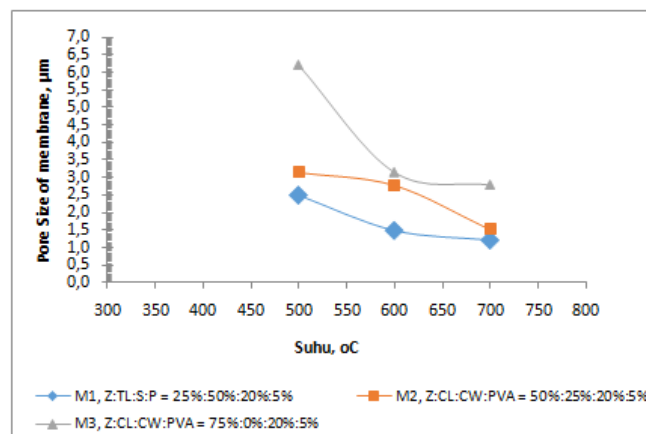


Figure 7. 3.2. Effect of temperature on membrane pore of MHA-ZC

From the graph in Figure 7 the higher the sintering temperature the pore size, the smaller the membrane become. The smaller the zeolite composition and the greater the clay soil composition, the smaller the membrane pore, the best in the composition of M1. For all variations in the composition of M1, M2 and M3 at a temperature variation of 500-700°C, the pore size was obtained from 1.2 to

6.203 μm . Based on the MHA-ZC membrane morphology test from the pore size obtained, it can be concluded that the MHA-ZC membrane showed a porous membrane classification with the type of microfiltration. MHA-ZC membrane morphology test results on M1 composition from various temperature variations are shown in Figure 8.

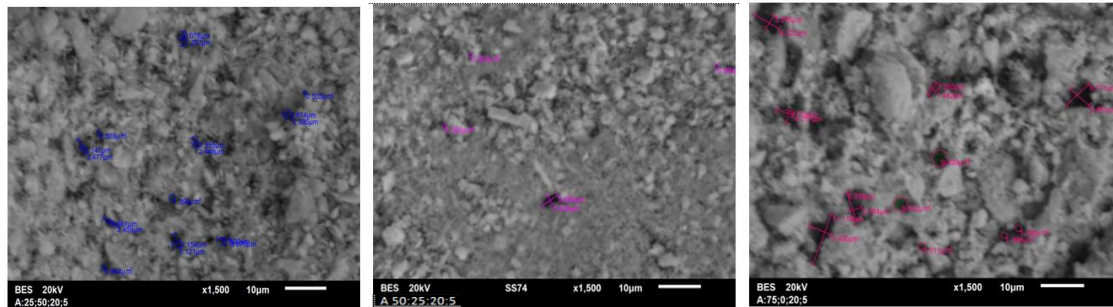


Figure 8. The Morphology of inorganic Membrane using SEM method

3.3. Membrane performance based on permeability and selectivity of MHA-ZC membranes

The performance of a membrane is determined by two parameters, flux, and selectivity. Volume flux is the amount of permeate volume obtained in the membrane operation of the time and unit membrane surface area with a pressure gradient as a driver. Permeability will determine the price of flux which is the permeate volume that passes through each unit of membrane surface area per unit of time. While selectivity shows the ability of the membrane to retain solute that passes through the membrane.

Ceramic membrane flux is directly related to porosity, where a good ceramic membrane is a membrane with high porosity but does not reduce the mechanical strength of the membrane. Factors that affect permeability are the number and size of the pore, the interaction between the membrane and the feed solution, and the pressure from the outside. The larger the membrane pore, the smaller the porosity, the greater the permeability and the smaller the membrane selectivity. The smaller the membrane pore, the greater the porosity, the smaller the permeability and the greater the selectivity of the membrane. The smaller the pressure applied to the operation of the membrane, the smaller the permeability and the greater the selectivity. So that the membrane performance is very dependent on the pore size and the pressure that can be given to the membrane to be able to withstand the solute (rejection) does not participate in the permeate expressed by membrane selectivity.

In this study, membrane permeability testing was carried out on membranes with the M1 composition for various sintering temperature variations. This is due to the composition of M1 having the smallest pore size and the largest porosity. Permeability testing is carried out by passing water free of solutes into the MHA-ZC membrane with the pressure of 1-2 bar. Calculation of the time required to get a specified amount of permeate volume is carried out. The results obtained are shown in Figure 9 (a). To determine the effect of operating time on fluxes, permeate volume measurements for 7 minutes were measured at 1 bar pressure. The results obtained are shown in Figure 9 (b).

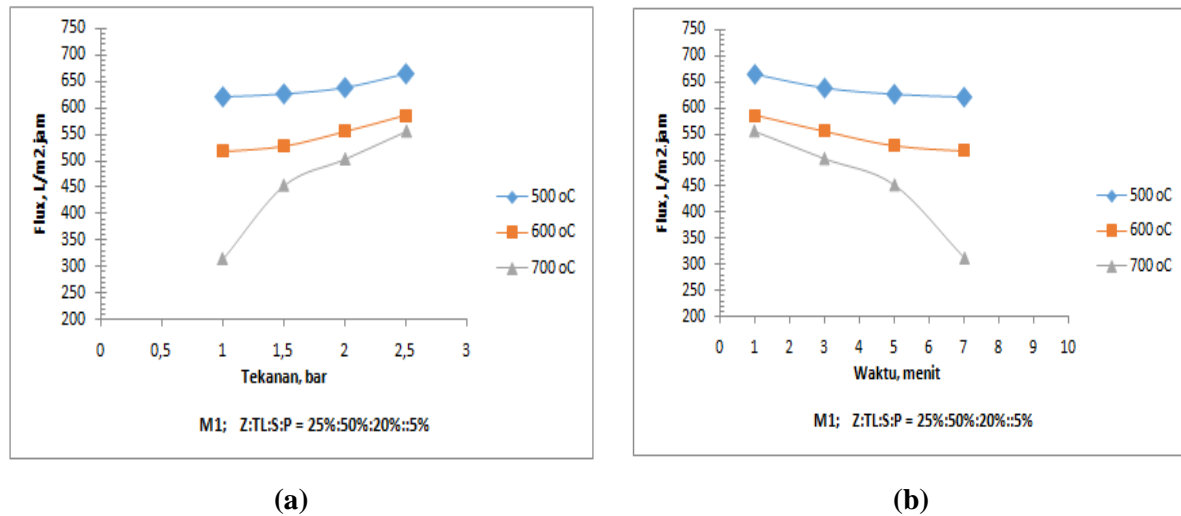


Figure 9. Performance of membrane MHA-ZC based on flux permeability; (a) the effect of pressure (b) the effect of flux permeability times on 1 bar

In Figure 8, the greater the pressure applied, the greater the membrane permeability obtained. This states that the external pressure applied to the membrane can push water particles through the membrane pore. The greater the pressure, the greater the thrust force of water passing through the membrane pore, the greater the permeate volume at a given time, the greater the membrane permeability.

The selectivity test of the MHA-ZC membrane was done by observing the changes in the color concentration of peat water at any time from the variation of pressure applied to peat water through the MHA-ZC membrane. The test uses a prototype circuit according to Figure 4. The results obtained are illustrated in the following Figure 10.

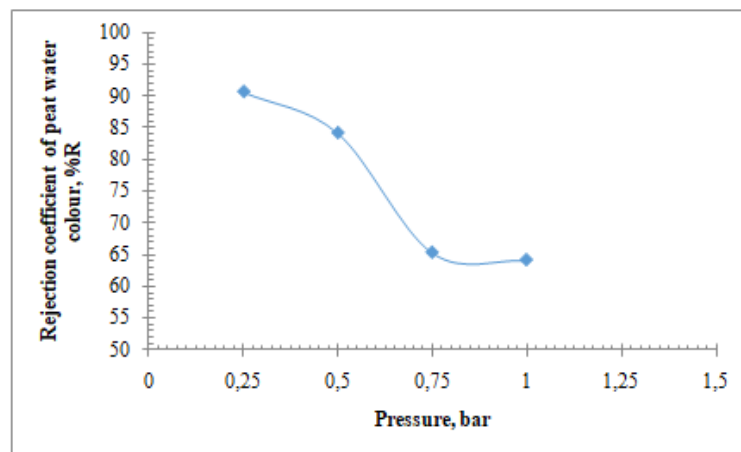


Figure 10. The effect of pressure on the colour rejection coefficient of peat water

From the graph in Figure 9 the greater the pressure, the smaller the rejection coefficient of the MHA-ZC membrane so that the membrane selectivity decreases. This is due to the greater pressure the greater the thrust force so that the pressure can push the dissolved peat water causing the color to break through the membrane pore. The greater the pressure the amount of solute retained on the membrane surface is

so small that the membrane selectivity becomes small with the amount of membrane permeability. It can be concluded that a pressure of 0.25 bar is able to provide a coefficient of (R) rejection of the color of peat water by 90.59%. The results of the analysis with spectrophotometer showed the color quality of peat water after being passed on the MHA-ZC membrane was able to drop from 170 PtCu to 16 PtCu with the pH of the resulting water reaching neutral.

4. Conclusion

The inorganic hybrid membrane is a mixture of activated zeolite (Z), clay (CL), white Portland cement (CW), and PVA named MHA-ZC membrane. Sintering temperature affects the characteristics of the MHA-ZC membrane. The higher the sintering temperature, the smaller the density, the greater the porosity of the membrane, and the smaller the pore size of the membrane. The composition (in percentage) of zeolite activation mixture, clay soil, white Portland cement, and the best PVA is Z:CL: CW:PVA = 25:50:20:5 with a pore size of 1.2 μ m, density of 0.811 gr/cm³, porosity 45%, membrane permeability 313.57 L/m². h, rejection coefficient of 90.59% colour of peat water. Based on the pore size, porosity and permeability of membranes obtained, the MHA-ZC membrane was classified as porous membrane type microfiltration.

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References

- [1] A. F. A. F. A. F. A. F. Ismail, N. Ridzuan, and S. A. S. A. S. A. S. A. Rahman, "Latest development on the membrane formation for gas separation," *Membr. Sci. Technol.*, vol. 24, no. April 2003, pp. 1025–1043, 2002.
- [2] R. W. Baker, "Third edition," in *Membrane Technology and Applications*, Third Edit., Menlo Park, California: John Wiley & Sons, Ltd, 2004.
- [3] M. Mulder, "Basic Principles of Membrane Technology, 2nd EdKluwer Academic Publishers," *Boston, MA*, 1996.
- [4] S. Arief and D. Nasmiati, "Studi Membran Anorganik Berbahan Dasar dari Alam serta Potensinya sebagai Filter," 2013, pp. 401–406.
- [5] T. M. Davis *et al.*, "Mechanistic principles of nanoparticle evolution to zeolite crystals," *Nat. Mater.*, vol. 5, no. 5, p. 400, 2006.
- [6] A. Damayanti, T. K. Sari, A. S. Afifah, Sutikno, L. T. Sunarno, and E. S. Soedjono, "The Performance Operation of Zeolite as Membrane with using Laundry Waste The Performance Operation of Zeolite as Membrane with using Laundry Waste Water," *J. Membr. Sci. Technol.*, vol. Volume 6 •, no. October, pp. 1–4, 2016.
- [7] G. Busca, "Acidity and basicity of zeolites: A fundamental approach," *Microporous Mesoporous Mater.*, vol. 254, pp. 3–16, 2017.
- [8] S. Nasir, T. Budi, and I. Silvatiy, "Aplikasi Filter Keramik Berbasis Tanah Liat Alam Dan Zeolit Pada Pengolahan Air Limbah Hasil Proses Laundry," *J. Bumi Lestari*, vol. 13, no. 1, pp. 45–51, 2013.
- [9] N. N. Aidha, "AKTIVASI ZEOLIT SECARA FISIKA DAN KIMIA UNTUK MENURUNKAN KADAR KESADAHAN (Ca dan Mg) DALAM AIR TANAH (ACTIVATION OF ZEOLITE BY PHYSICAL AND CHEMICAL METHODS," vol. 35, no. 1, pp. 58–64, 2013.
- [10] S. Sarkar, E. Guibal, F. Quignard, and A. K. SenGupta, "Polymer-supported metals and metal

- oxide nanoparticles_ synthesis, characterization, and applications _ SpringerLink,” *J. Nanoparticle Res.*, 2012.
- [11] N. Saffaj, M. Persin, S. A. Younsi, A. Albizane, M. Cretin, and A. Larbot, “Elaboration and characterization of microfiltration and ultrafiltration membranes deposited on raw support prepared from natural Moroccan clay: Application to filtration of solution containing dyes and salts,” *Appl. Clay Sci.*, vol. 31, no. 1, pp. 110–119, 2006.
- [12] Yulianis, Mahidin, and S. Muhammad, “Adsorption of Copper Ions Using Activated Nano Natural Zeolite,” *J. Litbang Ind.*, vol. 7, no. 1, pp. 61–69, 2017.
- [13] M. A. L. I. Akbar, “Dengan Penambahan Semen Portland Putih Program Studi Kimia Universitas Islam Negeri Syarif Hidayatullah 2010 M / 1431 H,” 2010.
- [14] Elfiana, A. Fuadi, and S. Diana, “Effectiveness of inorganic membrane mixture of natural zeolite and portland white cement in purifying of peat water based on turbidity parameter,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 345, no. 1, 2018.
- [15] J. R. Scheibler, E. R. F. Santos, A. S. Barbosa, and M. G. F. Rodrigues, “Performance of zeolite membrane (ZSM-5/ γ -Alumina) in the oil/water separation process,” *Desalin. Water Treat.*, vol. 56, no. 13, pp. 3561–3567, 2015.