Effectiveness of inorganic membrane mixture of natural zeolite and portland white cement in purifying of peat water based on turbidity parameter

Elfiana, A Fuadi and S Diana
Chemical Engineering Department, Politeknik Negeri Lhokseumawe, Aceh
E-mail: elfiana@pnl.ac.id

Abstract. Peat water is water surface that brownish red colour caused by the contained constituents. Solving the peat watercolor problem requires special attention considering the quantity of peat water and suitable to be used to meet the daily needs. This study aims to know the inorganic membrane capability of mix nature zeolite and white Portland cement to purifying the peat water based on turbidity parameter. The study was conducted by varying the composition of nature zeolite (Za) and white Portland cement (Sp) in the ratio of Za:Sp is (25%:75%; 50%:50%; 75%:25%) with zeolite condition activated using HCl 2M and nonactivated zeolite treatments. The result of the characteristic test on membrane morphology using SEM (Scanning Electron Microscope) showed that the pore surface size of the membrane is 2 μm that could classified in microfiltration membrane an organic type. The characteristic test showed also resulted in the density of 0.77 to 0.86 gr/cm 3, porosity 26.22% to 35.93%, and permeability 2736.19 to 8428.15. While the water retention capacity is in range of 30.64% to 46.46%, The result of inorganic membrane application on peat water showed turbidity of peat water decreased 94.17%, from 10.3 NTU to 0.6 NTU.

1. Introduction
Peat water is the surface water found in peatlands. Visually, reddish-brown peat water, acidic and smelly. The Geology Resource Centre review from the Department of Energy and Mineral Resources reported that until 2006 peatland resources in Indonesia covered 26 million hectares (ha) spread over Borneo Island (± 50%), Sumatera (± 40%) and the rest spread over Papua and other islands. And for this peatlands, Indonesia occupies the 4th largest position in the world after Canada, Russia and the United States. Based on these data, peat water in Indonesia can potentially be utilized as daily human water resources if it is managed properly, and it also needs to be considered an adequate peat water treatment technology to convert peat water into clean water.

Several methods of peat water treatment have been done in both laboratory and field scales, however, the result is not maximal yet. Several previous studies have suggested that laboratory conventional coagulation method using coagulant of clamshell and coral in peat water treatment area of Geuredong Pase is only able to set aside 5-58% iron concentration and does not give significant water color change either so that the processed peat water still looks colorful brownish yellow. Two Stage Coagulation method is able to reduce the peat organic compounds of Bangkinang area in Riau up to 88% using Alum coagulant at a dosage of 280-300 mg/L but not significant either to the decrease of iron concentration which is stable to organic. Peat water treatment using eggshells as adsorbent powders is able to eliminate 95% of organic compounds peat water at a pH of 4.01 [1]. Low degree of
acidity is not recommended for clean water. Therefore, the advanced process of peat water treatment using economical and reliable microfiltration membrane technology needs to be done.

Utilization of natural zeolite as a raw material for inorganic membrane production is considering. Aceh is one place whereas the plains contain natural zeolite could be found. In general, this natural zeolite has not been utilized optimally, especially in its utilization for membrane making. As it has been noticed that natural zeolites have the ability to perform a series of functions in various chemical processes such as catalysts, adsorbents and ion exchangers. Through-membrane technology, zeolites can be used as a medium for absorption and separation simultaneously [2].

Currently, the utilization of natural zeolite as an inorganic membrane is of much concern to the researchers because of its uniform porosity structure, stable to heat, good mechanical strength, and resistance to extreme chemical environment. Natural zeolite is a mineral that is sediment in nature, which is a compound of aluminosilicate that forms a three-dimensional structure framework between AlO4 and Tetrahedral SiO4. Natural zeolite is a suitable material for inorganic membrane fabrication because it is not easy to inflate in water and easily form a suspension to coat the membrane as support [3]. Natural zeolites have different characteristics than conventional membranes made from commonly used compounds such as Al2O3 or ZrO2 and others since natural zeolites form inter-particle active pores when sintered in a dry state. Zeolites have the ability to perform a series of functions in various chemical processes such as catalysts, adsorbents and ion exchangers. Through-membrane technology, zeolites can be used as a medium for absorption and separation simultaneously [2]. The advantages of using membranes as filter media are greater efficiency, simpler operation and smaller energy requirements [4]. According to Mourato (2002), one of the most commonly used membranes in a water treatment process is a microfilter membrane, suitable for holding suspensions and emulsions. In addition, the microfilter membrane price is cheaper and the required operating pressure smaller i.e. less than 2 bars.

Previous research has been done Akbar (2010) regarding the making of natural zeolite microfilter membrane with the addition of Portland cement. The study was conducted by varying the mixture of natural zeolite Lampung with white Portland cement to see the best mixture as a filter on the 50:50% mix ratio as Z1S, 66.67:33.33% as Z2S, and 75:25% as Z3S. From the results of this study obtained membrane separation efficiency of Fe2+ ion is 96.4%, 99.4% and 99.2%; for Mg2+ ions were 69.4%, 86.2% and 73.7%; as well as for Mn2+ ion obtained maximum results, i.e., up to 100%. While the efficiency of organic compounds separation and watercolor has not been tested. Previous research reported natural zeolite from Blang Pidie area of Southwest Aceh Regency that was chemically activated using 0.05 M HCl and calculated 3500°C for 2 hours has been tested to improve the performance of zeolites in the ability to absorb copper metal ions [2]. Buggraaf (1996) reports that an inorganic membrane needs to be tested for characteristics of the membrane pore diameter that is formed [5]. Baker (2004) concluded that most membrane materials are made of synthetic organic polymers, such as MF and UF membranes made from the same material but different formation conditions so that the pore size becomes different [6]. Scheibler (2015) shows the zeolite membrane (ZSM-5 / γ- Alumina) performs well in oil and water separation processes. The resulting zeolite membrane was tested for its characteristics based on a morphological test with SEM, structural test with XRD and analysis with EDX showed the material formed with Si / Al = 19 [7].

Therefore, the research was conducted to find out the inorganic membrane capability of natural zeolite mixture and white Portland cement in reducing the turbidity of peat water to meet the standard of clean water. Inorganic membrane synthesis is carried out in a variation on the ratio of natural zeolite mixture and white Portland cement from several compositions to the activated and non-activated zeolite state. Membrane characterization test was performed based on morphology test with SEM, structuring test with XRD, flux test, perm-selectivity, hardness, porosity, and density. Membrane performance can be known based on the efficiency of peat land TDS concentration decrease.
2. Research method

The used instruments include analytical scales, 80 mesh sieves, SEM (Scanning Electron Microscope), turbid meter, oven, beaker glass 1000 ml and 500 ml, 250 ml measuring flask, mixer, slipper, eraser mortar, module mold, picnometer. Materials used include peat water, natural zeolite; white Portland cement, chloride acid, aquades, and agent foam.

2.1 Preparation activation of natural zeolite

The zeolite is crushed and crushed with mortar until it is 80 meshes in size. Then 500 gr of fine zeolite was introduced into the Erlenmeyer and added with 300 ml of 2M HCl, heated while stirring until boiling for 1 hour, then cooled, filtered and washed with aquades until pH filtrate 6-7. The residue is dried for 5 hours at 70°C. Finally, the active zeolite is ready to use.

2.2 Inorganic membrane synthesis

2.2.1 Membrane module

The membrane module is made of stainless steel or PVC pipe, dimensions t x d = 5x5.5 cm (module 1, permeability test) and 25x6.5 cm (module 2, hollow fiber, at 3 cm). The membrane molds are best prepared according to the specifications of Module 1 and Module 2 according to the following Figure 1.

![Figure 1. The module of inorganic membranes where (a) 5x5.5 cm as module 1; (b) 25x6.5 cm as module 2](image)

2.2.2 Inorganic membrane synthesis of module 1 (permeability testing)

A total of 100 grams of natural zeolite mixture (Za) and white Portland cement (Sp) were prepared according to the composition Za1.2.3:Sp1.2.3 = 25%;75%; 50%;50%; and 75%;25%. Then each dough is put into a beaker glass and adds water little by little (ratio of zeolite:water = 1:10) to a paste. The paste dough is inserted in the module membrane mold 1 and dried at room temperature (29°C) for 3x24 hours. The resulting ZaSp inorganic membrane was rinsed with water to a neutral pH and continued by oven drying at 70°C for 6 hours. Membrane characteristic test was performed on membrane density, membrane permeability, water storage capacity and morphology test with SEM.

2.2.3 Inorganic membrane synthesis module 2 (membrane performance testing)

A total of 500 grams of natural zeolite mixture (Za) and white Portland cement (Sp) were prepared according to composition Za1.2.3:Sp1.2.3 = 125:375 gr; 250:250 gr, and 375:125 gr. Dough put in beaker glass and add water bit by bit (ratio of zeolite:water = 1:10) to form a paste. The paste dough is inserted in module 2, (hollow fiber) membrane mold, and dried at room temperature (29°C) for 3x24 hours, rinsed with water to neutral pH, dried oven at 70°C for 6 hours. Insert the ZaSp hollow membrane into the housing membrane and drain the peat water at normal pressure, test the quality of permeate clearance based on turbidity parameter. Membrane performance was measured by the percentage of turbidity removal before and after filtration with inorganic membrane ZaSp.
2.3 Inorganic membrane characteristics

2.3.1 Permeability test
The ZaSp membrane permeability test can be carried out according to the following set of equipment.

![Permeability Test Setup](image)

The ZaSp membrane module 1 is inserted into a feed cell, passed water with gravity flow velocity into the feed cell at normal pressure. Calculate the time obtained to accommodate the Permeate of 500 ml; the flux will be obtained according to the following equation:

\[ J = \frac{V}{A \times t} \]  

where: 
- \( J \) = Fluxs (l/m².hr)
- \( V \) = volume permeate (ml)
- \( A \) = Area of membrane (m²)
- \( t \) = time (hours)

2.3.2 Measurement of Membrane Density
Module 1 is the ZaSp inorganic membrane is retracted in the mold. If there is an excess volume or thickness of the membrane to the mold, then the erosion or smoothing using paper sandpapers. The membrane volume is calculated by measuring changes in membrane diameter and membrane thickness using the sliding term. ZaSp membranes are in a dry state prepared. Then weighed and recorded the result as a dry mass of membranes. Membrane density was calculated based on data of volume measurement and dry mass membrane using equation as follow:

\[ \text{Membrane Density} = \frac{\text{Mass Membrane (gr)}}{\text{Volume Membrane (cm²)}} \]  

2.3.3 Morphological test of inorganic membranes
ZaSp membrane morphological tests include the pore diameter and membrane surface structure performed using SEM equipment (Scanning Electron Microscope)
2.3.4 Measurement of water storage capacity
Determination of water storage capacity in the membrane (degree of swollen), done by using data of
measurement of the dry mass of membrane (m_d) and mass of water saturated membrane (m_s). The
calculation of the %Ds water storage capacity (degree of swollen) uses the following equation:

\[
\%Ds = \frac{m_s - m_d}{m_d} \times 100\%
\]  

2.4 ZaSp membrane performance testing procedures
Experiments testing the ability of the peat water treatment process using inorganic membrane hollow
fibber ZaSp done by passing peat water into the housing inorganic membrane hollow at normal
pressure. The turbidity of peat water before and after passing through the membrane is measured and
calculated its turbidity removal efficiency at any given time. The prototype of peat water treatment
with ZaSp inorganic membrane of hollow fiber type is shown in Figure 3.

Figure 3 illustrates the circulation of peat water fed into the filter cartridge 03μ - 01μ then
forwarded to the membrane ZaSp. Retinted is returned to the feed tank while permeate is collected and
analyzed for pH and turbidity parameters.

3. Results and discussion

3.1. Peat water characterization

| Parameters            | Units | Level | Boundary Condition |
|-----------------------|-------|-------|--------------------|
| pH                    | -     | 5,7   | 6,8-8,5            |
| TDS                   | mg/L  | 250   | 1.500              |
| Turbidity             | NTU   | 4,55  | 25                 |
| Ion Iron              | mg/L  | 16,18 | 1                  |
| Organic Compound (KMnO₄) | mg/L | 395   | 10                 |
3.2. The effect of zeolite weight on membrane permeability

Permeability or membrane flux is a measure of the velocity of a species across a broad union membrane and time with a pressure gradient as a driving force. Ceramic membrane flux is directly related to porosity, where the fine ceramic membrane is a high porosity membrane but does not decrease the mechanical strength of the membrane. Factors affecting permeability are the number and size of the pore, the interaction between the membrane and the feed solution, and the pressure from the outside. This measurement of the flow rate of the membrane is employed by the pressure of gravity based on the feed force which continues to decrease its pressure as it decreases the feed. Membrane permeability depends on the size of the pores on the membrane, so the larger the pores on the membrane then the resulting permeability will be large and vice versa on the small pore size will make the permeability on the membrane small or small.

In this research, the inorganic membrane production of zeolite mixture and white portland cement was prepared with several mixed compositions of natural Zeolite (Za) and white Portland cement (Sp) and given sample type Za1Sp1 (25%:75% = 125gr:375gr), Za1Sp2 (50%:50% = 250gr:250gr), and Za1Sp3 (75%:25% = 375gr:125gr). The results showed the largest permeability or flux membrane was 9577.32 kg/jam.m² in Za3Sp3 sample with Za activated. While the smallest permeability is 2736.19 kg/jam.m² obtained on sample Za1Sp1 with Za without activation. Permeability is influenced by pores on the membrane and sample size. The activated zeolite material has cleaner pores than impurities that make zeolite performance less than optimal. The larger the zeolite composition the greater the permeability of the membrane and the smaller the zeolite composition the smaller the permeability. The relationship of the mixture of zeolite and white portland cement to membrane permeability is shown graphically in Figure 4.

Figure 3. Prototype of peat waters treatment using hollow fiber type of inorganic membrane ZaSp.
Figure 4. The effect of zeolite composition Za:Sp on flux permeability of membrane.

From Figure 4 it can be seen, the larger the zeolite composition the greater the membrane permeability flux obtained. Activated zeolite gives effect to better permeability value for each composition of zeolite. It can be concluded that zeolite activation improves the permeability performance of inorganic membrane of natural zeolite mixture and white Portland cement.

3.3. The effect of zeolite weight on membrane density

The results showed the greater the composition of the zeolite the smaller the membrane density and vice versa. These results are shown graphically in Figure 5.

Figure 5. The effect of zeolite composition Za:Sp on membrane density.

The highest membrane density values were obtained in a sample of 250 gr of zeolite without activation (Za2Sp2) and the lowest density was in the 125 gr sample of activated zeolite (Za1Sp1). The magnitude of the membrane density values for zeolite conditions is not activated due to the release of
impurities attached to the zeolite pore so that in the same membrane volume larger with zeolite without activation.

3.4. The effect of zeolite weight on membrane porosity

The aforementioned porosity is a void space occupying an object per unit volume. The formation of membrane pores is closely related to the particle size of the material, especially the zeolite. Tan et al. (2001) states that zeolites with large pores will produce a large absorption as well; so the smaller the size of the zeolite grains will result in greater absorption rate.

The membrane cavities explain that the amount of empty space occupied by the air or water of the membrane and the results of the inorganic membrane construction of the active zeolite mixture and the white portland cement has the largest cavities or porosity in the Za3Sp3 sample of activation and the lowest porosity present in the Za1Sp1 activation sample. The data are shown graphically in Figure 6, in which density and porosity are related to each other can explain the greater the density of an object, the smaller the pore or cavity.

![Figure 6. The effect of zeolite composition Za:Sp on Porosity of Membrane](image)

3.5. The effect of zeolite weight on membrane capacity

The amount of water storage capacity in the membrane due to the number of cavities between the particles (void space) or porosity that is formed. At the time of membrane molding, the formation of fine bubbles due to zeolite particles that are filled with air by water and the addition of foam (foam) that makes the pores on the membrane more so that the membrane sample has large water storage cavities. The value of the membrane water storage capacity obtained is shown graphically in Figure 7. The highest membrane water storage capacity values obtained in the Za3Sp3 membrane sample with the activated zeolite and the lowest capacity were obtained in Za1Sp1 membrane samples with zeolite without activation.

From Figure 7, it can be seen that the water storage capacity is also associated with the resulting porosity, the larger the axis then the larger space or the cavity that can be occupied by water. Inactivated zeolites have the largest water storage capacity of zeolites without activation, with large cavities in the activation zeolite making uptake or storing water of great value.
3.6. Morphology of ZaSp inorganic membranes

Structure of the surface of a membrane or one way to know the morphology of a membrane is by SEM (Scanning Electron Microscope) test. SEM can also know the distribution of pores, pore geometry, pore size and porosity on the surface of the membrane, making it easier for us to know how membrane pore or pore membrane size. The results of membrane morphological testing with SEM test are shown in Figure 8.

From Figure 8 above it can be seen that the membrane surface has a size variation of 2μm-200μm. So it can be grouped that the resulting ZaSp inorganic membrane is a microfiltration membrane group with a pore size of 0.1μm -10μm. The smaller the pore size the smaller the permeability and the cleaner the water produced.

3.7. Performance of ZaSp inorganic membrane based on percentage reduction of turbidity of peat water

Based on the results of initial characteristics of peat water of Desa Ek Treun it is known that the turbidity level of peat water is 10.3 NTU. To find out the performance of ZaSp inorganic membrane in peat water processing is to make hollow type ZaSp membrane species as module 2 with 25 cm high dimension, outer diameter 6.5 cm and 3.5 cm inner diameter.
The experiment is carried out by draining the peat water at normal pressure to the inorganic membrane housing of ZaSp for a certain time, then the permeate is accommodated for its turbidity analysis while the retentate is returned to the feed tank. The results showed that the effectiveness of ZaSP inorganic membrane performance can decrease 95% turbidity of peat water from 10.3 NTU to 0.52 NTU on inorganic membrane Za1Sp1. The result of calculating the efficiency value of decreasing the turbidity with ZaSp inorganic membrane is shown graphically in Figure 9 below.

![Graph showing efficiency removal of peat water turbidity before and after treatment](image)

**Figure 9.** Performance inorganic membrane ZaSp based on efficiency removal of peat water turbidity before and after treatment

From Figure 9, it can be seen that the greater the composition of zeolites in the ZaSp membrane mixture, the efficiency of turbidity removal due to the smaller pore membrane the better the separation process of turbidity of peat water. The results showed the greatest turbidity decrease efficiency was 94.17% in Za3Sp3 with activation zeolite weight 375 gr.

4. Conclusion and recommendation

Based on the research that has been done can be concluded that activated natural zeolite can improve the inorganic membrane performance of the mixture of natural zeolite and white Portland cement. The greater the composition of the zeolite in the mixture, then the greater membrane permeability up to 9577.32 kg/hr.m². Performance of ZaSp inorganic membrane can be seen from the efficiency of turbidity reduction of peat water after treatment, with the largest value obtained is 94.17%. The results of the ZaSp membrane morphology test using SEM showed the inorganic membrane ZaSp grouped in the microfiltration membrane.

References

[1] M A Zulfikar and Henry S 2013 *Int. J. Chem. Tech. Res.* 5 1532-1540
[2] McLearly E E, Jansen J C and Kaptein F 2006 *Microporous Mesoporous Mater.* 90 198-220
[3] Davis T M 2006 *Nat. Mater.* 5 400-408
[4] Nandi B K, Uppalum R and Purkait M K 2008 *Appl. Clay Sci.* 42 102-110
[5] Burggraaf A J 1996 *Membrane Sci. Technol.* 4 21-34
[6] Guibert D, Rabie H, Cote P and Ben Aim R 2002 *Desalin.* 148 395-400
[7] Scheibler J R, Santos E R F and Barbosa A S 2015 *Desalin. Water Treat.* 56 3561-3567