Improving River Water Quality Using Ceramic Membranes from Clay and Zeolites

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Abstract. This study aims to determine the effect of the composition of the material & size of clay and zeolite which has been active as the formation of ceramic membranes against the values of TDS, Turbidity, Fe & Mn, pH and Flux. Then this study determines the optimum results of water treatment membranes from these variations. This study uses a treatment method on membrane size and analyses river water samples. Data analysis used a Complete Randomized Block Design (RAKL) and focused on a simple water filtration process. Variations in the size of raw materials of natural zeolite 50/60, 60/80 and 80/100 mesh which have been activated with Sulphate Acid Concentration of 1 N. Water samples originated from the Krueng Pasee river in North Aceh. Total membrane weight of 700 grams. Variations in this study clay mass: natural zeolite 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40%, & 50%: 50%. The results for pH parameters with membrane filtration obtained pH in accordance with the standard qualifications of drinking water group A, after filtering has increased. For the TDS, Turbidity, Fe & Mn parameters, the analyzed concentration decreases. The best comparison is 50% TL: 50% ZA & size 50/60 mesh for the flux test.

1. Introduction

Indonesia is one of the countries with the highest population growth in Asia, where half of the population lives in urban areas and it is estimated that by 2025 more than 70% of the total population will live in cities, it is a challenge for the Government to provide its population settlements. As a global agenda for sustainable development, the National Long-Term Development Plan (RPJPN) 2005-2025, is committed to ensuring the availability of safe water access. The importance of drinking water in an undeniable life requires all parties to care about water. Sectoral development improvements for lifestyle demands that reduce water quality (WEPA program article, 2008). Coupled with the development of industrial and economic technology in the community and what is known in North Aceh, the Industrial Zone is being revitalized into the Special Economic Zone (KEK) of Arun [1]. The scarcity of raw water sources and the high cost of water treatment technology require people to jointly save on water use and care about the environment. Because human behavior towards the environment will also affect the quantity and quality of raw water sources that should be utilized optimally for human welfare. Reflecting on developing and well-known countries as Wastewater Countries [2] such as Cambodia has implemented clean water treatment for health, namely making a membrane. This membrane as a filter media, the membrane is a ceramic filter. The Cambodian
community has made new innovations and even this ceramic membrane has commercial value [3]. Ceramic membranes are made from clay based or commonly called clay. Clay or clay which has pores, active site on its surface and composed of Hydrous Silicate Aluminum (Al2O3.2SiO2.3H2O), [4].

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2. Methods

2.1. Location
This research was carried out at the Medan Regional Health Laboratory, Wendy’s Ro Laboratory and Water & Waste Treatment Laboratory, Chemical Engineering Department Polteknik Negeri Lhokseumawe, in February-June.

2.2. Apparatus and Substances

Apparatus
1. Digital Scales
2. Turbid meter
3. TDS meter
4. pH meter
5. Sieve (test sieve) sizes 50, 60, 80 and 100 mesh
6. Container and closing
7. Paint Brush
8. Measured glass 1000 ml
9. Spatula
10. Beaker Glass 250 ml

Substances
1. River water samples
2. Natural Zeolites
3. Weight of clay
4. Aquades
5. Activated zeolite with H2SO4 1 N concentration
6. Filtering time is 900 minutes
7. The volume of river water per membrane is 500 mL.
2) Free Variables:
1. The Mass of Clay: Natural Zeolite
   a. 90%: 10%
   b. 80%: 20%
   c. 70%: 30%
   d. 60%: 40%
   e. 50%: 50%
2. Variation in Clay: Natural Zeolite
   a. 50/60 mesh
   b. 60/80 mesh
   c. 80/100 mesh
3) Bound Variables:
1. Fe & Mn
2. Ph
3. Membrane Flow Rate (Membrane Flux)
4. SEM
5. TDS & Turbidity Removal Efficiency

2.2.2. Procedure
Making Ceramic Membrane
- Mixture of Clay and Natural Zeolite, which has known water content and has also been activated.
- Mixing of Clay and Natural Zeolite, with a ratio of Clay: Natural Zeolite namely (90%: 10%, 80%: 20%, 70%: 30%, 60%: 40%, 50%: 50%), added the water is then mixed evenly.
- Make ingredients like dough then form the mixture in the form of a pot. After the mixture is in the form of a pot then place it on a plastic sheet or tarpaulin that is not sticky.
- The printed material is dried at room temperature for 7 days.
- The printed material is burned at a temperature of 1000°C for about 10 hours, then dried naturally with the help of sunlight.

3. Results and Discussion
From the results of research conducted at the Polteknik Negeri Lhokseumawe, Water & Waste Laboratory and the location of membrane production, obtained observational data from the analysis of samples on water quality before and after passing through membranes with the composition of Clay and Active Zeolite namely TDS, Turbidity, Fe & Mn, pH, Flux Membrane and SEM.

3.1. Preliminary sample
The initial sample is river water analyzed first before passing through the membrane with test parameters as in Table 1.

| Sample             | TDS (mg/L) | pH  | Turbidity (NTU) | Fe²⁺ (mg/L) | Mn (mg/L) |
|--------------------|------------|-----|-----------------|-------------|-----------|
| Water of Krueng Pasee North Aceh | 610        | 5, 2 | 169             | 0,3         | 0,45      |

In the observation Table 2, observational data is displayed with the results of physical and chemical analysis. Where is physically done TDS and Turbidity while chemically, namely the content of metal ions in Fe²⁺, Mn and pH.
Table 2. Observation data

| No. | Measured variable Zeolite (No.Mesh) | Composition TL : ZA | Turbidity (NTU) | TDS (mg/L) | Ph | Fe (mg/L) | Mn (mg/L) |
|-----|-----------------------------------|---------------------|-----------------|------------|----|----------|----------|
|     |                                   | 90% : 10%           | 0.626           | 277.3      | 7.04 | 0        | 0        |
|     |                                   | 80% : 20%           | 0.500           | 216.4      | 7.04 | 0        | 0        |
|     |                                   | 70% : 30%           | 0.326           | 197.6      | 7.00 | 0        | 0        |
|     |                                   | 60% : 40%           | 0.123           | 188.6      | 7.00 | 0        | 0        |
|     |                                   | 50% : 50%           | 0.093           | 173.6      | 6.55 | 0        | 0        |
| 1   | 50/60                             | 90% : 10%           | 0.493           | 245.3      | 7.64 | 0        | 0        |
|     |                                   | 80% : 20%           | 0.246           | 245.3      | 6.83 | 0        | 0        |
|     |                                   | 70% : 30%           | 0.200           | 230.6      | 6.74 | 0        | 0        |
|     |                                   | 60% : 40%           | 0.133           | 222        | 6.60 | 0        | 0        |
|     |                                   | 50% : 50%           | 0.086           | 205        | 6.58 | 0        | 0        |
| 2   | 60/80                             | 90% : 10%           | 0.816           | 259        | 8.50 | 0        | 0        |
|     |                                   | 80% : 20%           | 0.536           | 252.3      | 8.00 | 0        | 0        |
|     |                                   | 70% : 30%           | 0.480           | 243.6      | 7.10 | 0        | 0        |
|     |                                   | 60% : 40%           | 0.463           | 221.6      | 7.00 | 0        | 0        |
|     |                                   | 50% : 50%           | 0.08            | 149        | 6.75 | 0        | 0        |
| 3   | 80/100                            | 90% : 10%           | 0.271           | 110        | 8.50 | 0        | 0        |
|     |                                   | 80% : 20%           | 0.308           | 125        | 8.00 | 0        | 0        |
|     |                                   | 70% : 30%           | 0.320           | 130        | 7.10 | 0        | 0        |
|     |                                   | 60% : 40%           | 0.370           | 150        | 7.00 | 0        | 0        |
|     |                                   | 50% : 50%           | 0.666           | 270        | 6.75 | 0        | 0        |

In Table 3, the observation displays observational data with the results of analysis for flux testing, where to find out the flux (Membrane Flow Rate) which must be observed filtering time, volume of breakdown, diameter and cross-sectional area. Filtering time and cross-sectional area are determined the same. This is to observe the volume of water that escapes during filtration with different ingredients.

Table 3. Experimental results to determine flux

| No | Zeolite Size Variations (No. mesh) | Composition TL : ZA | Volume of Water Solubility (mL) | Flux (L.jam⁻¹.m²⁻¹) |
|----|-----------------------------------|---------------------|---------------------------------|---------------------|
| 1  | 50/60                             | 90% : 10%           | 325                             | 0.814               |
|    |                                   | 80% : 20%           | 350                             | 0.851               |
|    |                                   | 70% : 30%           | 400                             | 1                   |
|    |                                   | 60% : 40%           | 400                             | 1                   |
|    |                                   | 50% : 50%           | 430                             | 1.074               |
| 2  | 60/80                             | 90% : 10%           | 210                             | 0.518               |
|    |                                   | 80% : 20%           | 250                             | 0.592               |
|    |                                   | 70% : 30%           | 275                             | 0.679               |
|    |                                   | 60% : 40%           | 275                             | 0.679               |
|    |                                   | 50% : 50%           | 300                             | 0.740               |
| 3  | 80/100                            | 90% : 10%           | 110                             | 0.271               |
|    |                                   | 80% : 20%           | 125                             | 0.308               |
|    |                                   | 70% : 30%           | 130                             | 0.320               |
|    |                                   | 60% : 40%           | 150                             | 0.370               |
|    |                                   | 50% : 50%           | 270                             | 0.666               |

3.2. Discussion

3.2.1. Activation process of natural Zeolite becomes active Zeolite. In this study, it begins with the activation process. Where this process is carried out the process of activation of natural zeolite into active zeolite by the addition of sulfuric acid (H₂SO₄) 1 N which has been diluted as much as 1000 mL. This aims to modify the properties of zeolite and improve zeolite character. This is because sulfuric acid can reduce levels of alkali metals, alkaline earth and iron (Na, K, Ca and Fe). In addition,
sulfuric acid can dissolve impurities that cover the pores so that the pores become wider and wider. According to [6], zeolite surface area.

3.2.2. Flux testing process. Obviously, the mass ratio of clay must be larger than zeolite because according to its function as an adhesive and in terms of its nature, namely the ability to be easily formed. Theoretically also states the greater the active zeolite mass, the greater porosity of the membrane. Active zeolites have greater porosity and good absorption. For this reason, before activation of 70 m²/g, after activation zeolite surface area becomes 96 m²/g.

The ability of sulfuric acid is also able to reduce the activator by about 25% [7]. The reason is because sulfuric acid is a strong acid that causes the amount of Al to dissolve so that many atoms that come out of the zeolite framework also aim to eliminate inorganic impurities. The treatment of activation of natural zeolite with acid makes the natural zeolite more hydrophobic and capable of adsorbing. Activated zeolite is used as a separation process by filtration and adsorption methods.

Characteristically membranes with 50/60 mesh numbers are better than the size numbers 60/80 mesh & 80/100 mesh. The best comparison is also found in 50% Clay (TL): 50% Active Zeolite (ZA). This is observed in the flux value of the composition ratio of the ingredients. The following is the curve of the effect of material composition on flux (membrane flow rate).

![Figure 1: Comparison curve between the composition of the membrane-making material to the flux](image)

Figure 1 explains the effect of the composition of the membrane-making material on the resulting flux. From the curve, it can be observed that in the size of 50/60 mesh with a composition of 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40% and 50%: 50% increase with the gradual flux value up, 0.814; 0.851; 1; 1 and 1.074 in L/hour.m². Then followed by a mesh size of 60/80 mesh, which is 0.518; 0.592; 0.679; 0.679 and 0.740 in L/hour.m². Finally, for the composition of materials with a size variation of 80/100 mesh, which is 0.271; 0.308; 0.320; 0.370 and 0.666 in L/hour.m².

From the image data.1 where more material (zeolite) is used, the resulting flux is greater. This is in accordance with the theory of filtration, namely the liquid that is inserted into the porous membrane, the smaller the pore of the membrane, the lower the water (filtrate) is also slower, on the contrary the larger the pore of the membrane, the faster the water drops. This is in accordance with [8], the larger the size of the membrane pores shows that the volume produced as a flux value is also large. During the filtration process using a membrane, there is fouling on the membrane. This layer of fouling (foulant) inhibits the filtration process. This foulant can be in the form of organic, inorganic and particulate deposits. Foulant accumulated on the surface of the membrane because it does not take part in the mass transfer process. As a result, this foulant reduced the performance of the membrane. To reduce or lift this foulant, a backwash system must be done. Where this system can reduce the occurrence of deposits during filtration.
3.2.3. *pH analysis*. The initial sample of river water before simple filtration was pH 5.2. Then after filtration and adsorption on river water, the pH increased from acid to a pH standard that was feasible to drink in accordance with the decree of the Minister of Health Regulation No. 492/Menkes/Per/IV/2010 where the drinking water standard for class A ranges from 6.5 - 8.5. For pH from the membrane it is able to change the atmosphere of the water so that it becomes feasible to drink. The degree of acidity increases in the material with a mesh size number of 50/60 mesh. The composition of the material is 90%: 10% is 6.55. Then in the composition of the material 80%: 20% and 70%: 30% is with a neutral pH 7. Then in the composition of the material 60%: 40% and 50%: 50% the result is 7.04.

Followed by an assessment with a number size of 60/80 mesh, the composition of ingredients 90%: 10% obtained results of 6.58. Then 80%: 20% obtained results of 6.6, for 70%: 30% and 60%: 40% of the results were 6.74 and 6.83. Finally, in the size of 60/80 with a composition of 50% ingredients: 50% obtained the results of 7.64. Then further analysis of pH parameters for 80/100 mesh material, with a composition of 90%: 10% is 6.75. Then for 3 ingredients composition 80%: 20%; 70%: 30% and 60%: 40%, namely 7; 7.1; and 7.

The last measurement of the membrane with a ratio of 50%: 50% is 8.5. So, it is clear that the degree of acidity (pH) when filtrated with ceramic membranes has increased, from the acidic atmosphere to neutral. It can also be said that between the pH and the composition of the material the acidity is unstable in terms of the pH obtained for the pH parameter of filtered river water including standard group A.

3.2.4. *TDS analysis*. On the effect of the composition of clay material and natural zeolite on TDS the results of a decrease in the water content were obtained, where the total solids dissolved for the initial sample were 610 mg/L. Then after filtration with various variations of the membrane, a decrease occurs. For numbers of mesh size 50/60 with composition of ingredients - 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40% and 50%: 50% respectively the result is 277.3 mg/L; 266.4 mg/L; 245 mg/L; 241.6 mg/L and 222 mg/L. Then testing for size numbers 60/80 mesh, respectively the composition of the material 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40%, 50%: 50% is 259 mg/L; 250 mg/L; 245 mg/L; 239 mg/L and 197.6 mg/L. Finally, for the size of the number 80/100 mesh, successively the size of the composition of the membrane material is 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40%, 50%: 50%.

Then if observed from figure.2 there is an increase. In the composition of the material 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40%, 50%: 50%, for optimum allowance obtained on the membrane with the composition of the three ingredients namely 50%:50% with membrane size 50/60 mesh & 60/80.
mesh the result is 63.61%. but at 80/100 mesh size the optimum result is 71.54%. From the curve, it can be concluded that the best percentage of allowance is obtained by a membrane with a composition of 50%: 50% with a mesh size of 80/100.

Then if observed in figure 3, the result shows that the percentage of efficiency in the allowance for Turbidity has increased. Where with the composition of ingredients: 90%:10%, 80%:20%, 70%:30%, 60%:40%, 50%:50% The result is optimum conditions found in all three membranes with a composition of 50%:50%. For the composition of materials measuring 50/60 mesh, the optimum result is 99.94%, then 245.3 mg/L; 245.3 mg/L; 230 mg/L; 197.6 mg/L and 177.6 mg/L. The following is the TDS removal efficiency curve.

3.2.5. Turbidity analysis. The next physical parameter tested is the effect of material composition on turbidity. The effect of the composition of the material on turbidity, the result has decreased. In the initial sample the test results were 169 NTU. Then after going through the filtration and adsorption process on the membrane, the results for the size numbers 50/60 are in the composition of the material 90%: 10%, 80%: 20%, 70%: 30%, 60%: 40% and 50%: 50% where the value is 0.093 NTU; 0.536 NTU; 0.480 NTU; 0.463 NTU and 0.086 NTU. Then for the size numbers 60/80 mesh, for the composition of the ingredients 90%: 10%; 80%: 20%; 70%: 30%; 60%: 40% and 50%: 50% is 0.816 NTU; 0.500 NTU; 0.326 NTU; 0.213 NTU and 0.026 NTU. It is continued for testing the mesh size number 80/100 where the composition is 90%: 10%; 80%: 20%; 70%: 30%; 60%: 40% and 50%: 50% is 0.493 NTU; 0.246 NTU; 0.163 NTU; 0.08 NTU.

3.2.6. Testing the characteristics of water content. Chemical testing of water characteristics is by testing Fe and Mn which results in the initial sample 0.3 mg / L for Fe and 0.45 mg / L for Mn. For Fe even though drinking water standards have been permitted with such results, but when tested the result is 0 which means that in the water sample put into the membrane when filtration the Fe content in the filtrate becomes zero (0), this is due to active zeolite This is not only as water filtration as an adsorbent and also as an ion exchanger, which is useful for exchanging ions by reducing the ion. This active zeolite also functions for cation exchangers or cation exchangers.

3.2.7. Testing the membrane morphological structure. Furthermore, the parameters tested were to determine the morphological structure of the membrane. This analysis is done by testing SEM (Scanning Electron Microscopy). The following is a SEM test image before the combustion process.

![Fig.4 ceramic membrane before combustion](image1)

![Figure 5 ceramic membrane after combustion](image2)

Scanning Electron Microscopy (SEM) testing in this study was conducted on samples with a composition of 50% clay material: 50% natural zeolite with the best mesh size number 50/60. The
reason for taking a sample of 50/60 mesh is because this sample has a rapid decrease in flux and from several physical and chemical parameters testing, the results are reasonable.

In this test, of course, if observed in both Figures (4 & 5) the results are inversely proportional to the theory of the sintering process. Where, the lower the ceramic membrane is placed, the longer it will also warm up at high temperatures, so the sintering process will occur easily and certainly can reduce pore size [9]. The temperature at the combustion process is uneven and the position of the membrane when burned also affects the maturity of the membrane. At the time of placement of combustion, the position of the membrane is at the top level compared to other ceramics, causing the combustion temperature to be uneven. When the water content is exhausted in the membrane makes the membrane become fractured when it is burned so that a fracture occurs.

Geologically the form of porosity is not only in the form of a round but also can be in various forms, one of which is fracture. The occurrence of these fractures is due to the unstable temperature which causes zeolite which is a type of soft material to become weak so that it experiences stretching and cracking. This retreat occurs because it contains rock compositions such as quartz / silica. In this case it is also called the Hydraulic Fracturing phenomenon, which means here is a secondary porosity with a method that drives production due to the effect of fractures and gaps in a formation that injects fluid into the material under pressure which exceeds the material pressure on the material reservoir. This phenomenon can increase the permeability of the formation. Then it can be seen in Figure 4.5, where there is a crack propagation area and fatigue area.

4. Conclusion

The greater the composition of the material and the size of the clay compared to zeolite, the greater the flux produced. The greater the composition of the clay material compared to zeolite, the better the parameters for Turbidity, TDS, Fe & Mn and increasing pH parameters. The smaller the size of clay compared to zeolite, the better the Turbidity, TDS, Fe & Mn parameters and pH. The optimum results for flux (Membrane Flow Rate) are on membranes of size 50/60 mesh with variations in size of 50% Clay: 50% Active Zeolite can result in flux 0.895 L/h -1m². Whereas for the decrease in Turbidity, TDS, Fe & Mn parameters and pH is the membrane size 80/100 mesh with a size variation of 50% Clay: 50% Active Zeolite with a pH value of 6.75; TDS 177.6 mg/L; Turbidity 0.080 NTU; and for Fe & Mn is 0.

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