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Effect of Dolomite Addition on Fly Ash Based Ceramic Membrane to Reduce COD and BOD of Liquid Waste

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Abstract

Ceramic membrane technology plays an essential role in separation fields such as wastewater treatment. Fly ash as a membrane material has proven to be very effective for many separation processes, including water and air purification, as well as industrial and environmental resource recovery. This study aims to develop a microfiltration ceramic membrane based on fly ash with the addition of dolomite. The synthesized ceramic membranes were then characterized using XRD, SEM, and TGA. Ceramic membranes are used to reduce COD and BOD levels in tofu industrial wastewater. The results showed that the value of membrane porosity tends to increase with the addition of dolomite 0% (D_0) to 30% (D_{30}). The increase in the porosity value in the membrane was followed by a decrease in the average pore size, namely 1.6994 m at D_0 and 1.1730 m at D_{30}. The membrane with 30% dolomite composition has the best mechanical properties with a compressive strength of 35.29 MPa and superior thermal resistance. This is very beneficial for the use of membranes in the long term. Meanwhile, the membrane filtration ability and the ability of the membrane to reduce COD and BOD levels of waste increased with the addition of dolomite from 0% to 30%. However, the decrease in COD and BOD was smaller in the membrane with 45% dolomite. D_{30} membrane can reduce COD 80% and BOD up to 71.44%. D_{30} membrane is the most effective fly ash and dolomite composition in forming pores on the membrane with the best COD and BOD reduction performance.

1. Introduction

Inorganic membranes, commonly called ceramic membranes, have been widely used in various industrial fields [1]. Ceramic membrane technology is a very competitive choice compared to traditional separation technologies or organic separation membranes because it has the advantages of excellent chemical and thermal stability and has strong pressure resistance [1]. In one of its applications, ceramic membranes can be used in wastewater treatment. Liquid waste is a by-product of the activities of every industry, one of which is the tofu industry. Tofu liquid waste still has potential as an environmental pollutant due to its smell, color, high BOD and COD values, and high suspended solids content [2]. However, the application of ceramic membranes is severely limited by the high cost of production from the starting material to the sintering process [3]. In recent years, many researchers have focused on developing new models of inorganic membranes, such as carbon membranes [4], zeolite membranes [5], and natural mineral-based ceramic membranes [6, 7, 8, 9].

On the other hand, fly ash production in Indonesia reaches 5.4 million tons/year. A broader application of fly ash needs to be further developed to use solid waste resources better. The main chemical components of fly ash, namely silica, and alumina are similar to clays and kaolin, used as starting materials for making porous ceramic membranes [10]. Therefore, fly ash can be considered a potential material to be applied in preparing porous ceramic membranes. As the main ingredient of membrane technology, fly ash has proven to be very effective for many separation processes, including water and air purification, as well as resource recovery in industry and the environment [11]. In previous studies, coal fly ash was used as raw material to make mullite membranes ($3Al_2O_3{\cdot}2SiO_2$) [12, 13], cordierite membranes ($2MgO_2Al_2O_3{\cdot}5SiO_2$) [14] and anorthite membranes ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) [15]. These studies focused on the physical properties of ceramic membranes through controlling the phase assemblage and pore structure. Meanwhile, the brittle nature of ceramic membranes, which can inhibit large-scale production and application [11], has not received much attention.

In this study, to improve the structure and mechanical properties of the membrane, dolomite was used as a support for a porous ceramic membrane. Dolomite ($CaMg(CO_3)_2$) is a natural mineral with abundant reserves throughout the world, including Indonesia. The thermal decomposition of dolomite follows two stages: $CaMg(CO_3)2$ first decomposes to $CaCO_3$, MgO, and CO_2, which is then converted to $CaCO_3$ to CaO and CO_2 [16]. The addition of dolomite to the support of the porous ceramic membrane is intended to increase the porosity and permeability as well as to provide biaxial flexural strength to the membrane [15] by developing using a co-sintering or coating-sintering reaction. The effect of dolomite on the structure and properties of porous ceramic membranes is discussed in detail based on the distribution of porosity and pore size, and microstructure. This article discusses the expansion of fly ash waste to developing inexpensive microfiltration ceramic membranes with the addition of dolomite, which is intended to improve the mechanical quality of the membrane used to reduce COD and BOD levels in liquid tofu waste. This research is significant to expand applications in waste treatment and is expected to help reduce environmental pollution.

2. Methodology

2.1. Tools and Materials

The tools used in this research were glassware, hot plate, magnetic stirrer, mortar and pestle, analytical balance, furnace, stopwatch, hydraulic press with 4 cm diameter mold, X-Ray Fluorescence (XRF) EQUA Powder Mylar, A set of membrane mechanical properties test equipment (Pearson Panke Equipment Ltd.), Scanning Electron Microscope (SEM) Quanta 650, X-Ray Diffraction (XRD) Panalytical Type Empyrean, and Thermogravimetric Analysis (TGA) NetzscR STA449F3A00. The materials used to prepare the microfiltration ceramic membrane were distilled water, coal fly ash from PT. PJB PLTU UBJO&M Rembang, Mineral Dolomite, Polyethylene Glycol (PEG) 1000, Polyvinyl Alcohol (PVA) Technical with Mw 13,000-23,000, and HNO_3 p.a (65% = 1.39 Kg/L, Merck). While the materials used for testing the levels of COD and BOD in wastewater were standard solution $K_2Cr_2O_7$ 0.05 N (Mr = 294.216 g/mol; E. Merck), silver sulfate-sulfuric acid ($Ag_2SO_4.H_2SO_4$) reagent, indicator ferroin, FAS standard solution ($Fe(NH_4)_2(SO_4)_2$) 0.1 N (Mr = 390.00 g/mol; E.Merck), 0.025 N $Na_2S_2O_3$ solution (Mr = 248.21 g/mol; E . Merck), $MnSO_4$ solution, Mercury sulfate ($HgSO_4$) powder or crystals, KOH-KI solution, H_2SO_4 pa, starch indicator, Tofu liquid waste produced from the tofu industry in Sumur Jurang Village, Gunungpati District, Semarang City.

2.2. Preparation

Fly ash was prepared by calcining at 700°C for 2 hours and then sieved with 200 mesh. A total of 6 g of PVA was mixed with 10 mL of 1 M HNO_3 and 190 mL of distilled water. The mixture was stirred with a magnetic stirrer for 1 hour at 80°C. Heating was given to accelerate the dissolution of PVA [17].

2.3. Solid membrane preparation

0.1 g of PEG was added with 2.26 g of PVA solution and 10 g of coal fly ash. Then the mixture was dry pressed by pressing indirectly into cylindrical pellets (40 mm in diameter and 2-3 mm thick) at 3700 Psi. The pressing results were calcined in a furnace at a temperature of 1100°C for 2 hours with a heating rate of 10°C/minute (Heating for 2 hours starts when the temperature reaches 1100°C).

2.4. Membrane Coating Process

A mixture of fly ash and a mixture of dolomite 0%(D_0), 15%(D_{15}), 30%(D_{30}), and 45%(D_{45}) was made into a liquid slurry with the addition of PEG and PVA. Then the mixture was stirred until homogeneous. This mixture was then coated onto fly ash by the dip-coating method. After coating, the membrane was dried at room temperature for 24 hours. It was then heated using a furnace at a temperature of 700°C for 2 hours with a heating rate of 10°C/minute (Heating for 2 hours starts when the temperature reaches 700°C). Four types of membranes that had been made were then tested for water flux, mechanical testing, and analyzed using a Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), and Thermogravimetric Analysis (TGA) to examine the characteristics of the membrane.

2.5. Membrane Thermal Resistance Analysis Using Thermogravimetric Analysis (TGA)

The thermal resistance of the membrane was evaluated by thermogravimetric analysis (TGA). This method can characterize a material or sample based on how much the sample loses its mass or the occurrence of decomposition, oxidation, or dehydration. The membrane sample was cut and weighed 10-20 mg. TGA analysis was carried out using argon as carrier gas and heating rate of 10°C/min from ambient temperature to sintering temperature.

2.6. Application of Microfiltration Ceramic Membrane for Lowering COD and BOD of Liquid Waste

The membrane was put in a vacuum filtration device connected to a vacuum pump. Then 100 mL of liquid waste flowed through the membrane with a vacuum pump pressure of 0.5 bar. The liquid that had passed through the membrane was collected and analyzed for its COD and BOD levels. In addition, before passing the liquid waste on the membrane, the levels of COD and BOD were measured first.

2.6.1. Chemical Oxygen Demand Analysis of Liquid Waste

5 mL of sample was put into a 250 mL Erlenmeyer, then 0.2 grams of $HgSO_4$ powder was added. Furthermore, 5 mL of 0.05 N potassium dichromate solution and 15 mL of sulfuric acid – silver sulfate reagent were added slowly while cooled in cooling water. Then the mixture was heated using a hotplate for 2 hours at 150°C. The mixture was cooled to room temperature, added 2 to 3 drops of ferroin indicator, titrated with 0.1 N FAS (Ferro Ammonium Sulfate) solution until a brownish-red color, and noted the need for FAS solution. Furthermore, the same steps were carried out for distilled water as a blank. FAS solution requirement (SNI 06-6989.15-2004) was recorded

2.6.2. Biological Oxygen Demand Analysis of Liquid Waste

Eight bottles of BOD were prepared, then put the sample solution, namely liquid waste, into eight bottles until they were full, then the bottles were tightly closed to avoid the formation of air bubbles. A total of 4 sample bottles were incubated for five days while the rest were not (D_0 and D_5). 5 mL of liquid waste was prepared in an Erlenmeyer, then 1 mL of $MnSO_4$ and 1 mL of KOH-KI were added and shaken until a brownish white precipitate was formed. Then, 1 mL of concentrated H_2SO_4 was added, shaken, and allowed to stand until a brown color was formed. The sample was then titrated with 0.025 N sodium thiosulfate to form a pale-yellow solution. The solution was then added with five drops of starch indicator and titrated again with 0.025 N sodium thiosulfate to form a colorless solution. The volume of sodium thiosulfate used is equal to the final DO value (SNI 6989-72.2009).

3. Results and Discussion

3.1. Characteristics of Starting Materials

The results of the crystallinity test of the starting material and the membrane are presented in Figure 1. Figure 1 (a) shows that the diffraction peaks from the fly ash analysis show the main content of minerals (Q) quartz (SiO_2) and (M) Mullite ($3Al_2O_3.2SiO_2$), which are primarily amorphous phases. The main mineral Quartz is shown by sharp diffraction peaks at $2\theta = 22°$ and $26°$, while Mulite at $2\theta = 29°$, $35°$, and $42°$ is of low intensity. These results are in agreement with previously reported studies [15].

The dolomite diffractogram used in the preparation of the ceramic membrane presented in Figure 1(b) reveals that the purity of the dolomite sample is very high at $2\theta = 30°$ and is in accordance with previously reported [18].

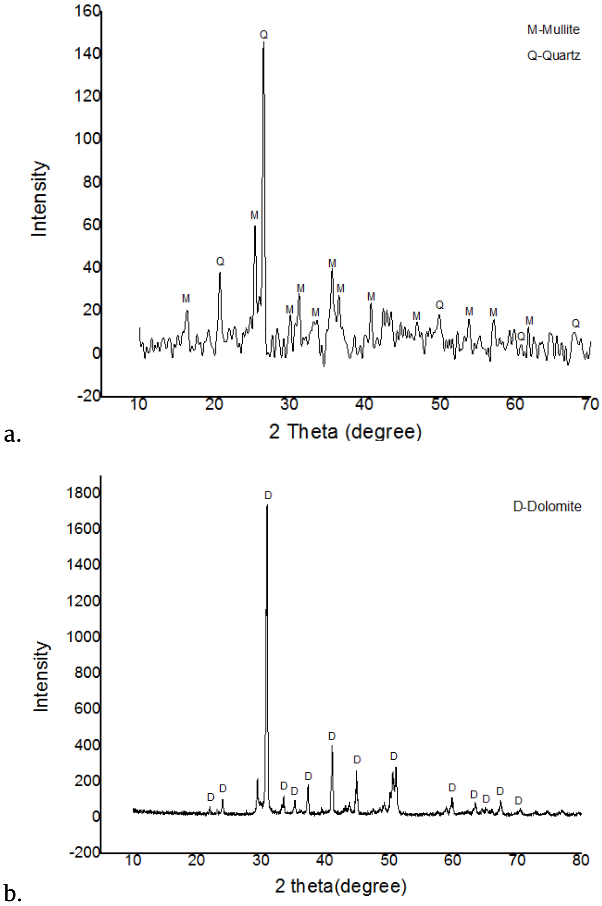

Figure 1. XRD pattern (a) fly ash (b) dolomite

3.2. Mineral Composition and Phase

Characterization using XRD was carried out to determine the composition and analyze the mineral phase of the ceramic membrane. Samples were analyzed with Cu radiation at 30.0 mA 30.0 kV. The diffraction peaks resulting from the analysis are then matched with the search and match method with reference journals. The composition and mineral phase of the membrane with various variations of the addition of dolomite can be known. XRD diffractograms of various membranes are presented in Figure 2.

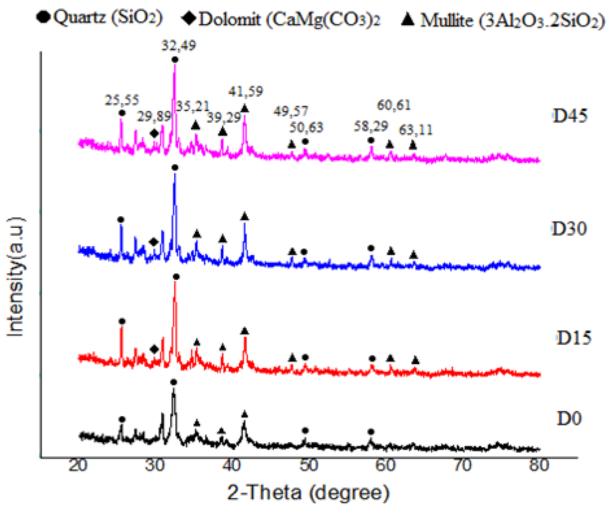

Figure 2. Diffractogram of membranes with variations in dolomite content

Ceramic membranes with various dolomite compositions showed different intensities at each diffraction peak of quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$) minerals. Low intensity and broad humps formed between 2θ = 20° and 2θ = 40°, indicating the characteristics of an amorphous gel. SiO_2 peaks appear as quartz at 2θ = 25° and 32° and as mullite ($3Al_2O_3.2SiO_2$) at 2θ = 35°, 39°, 49°, and 60° with low intensity. This is following the results of studies that have been reported [9, 15, 19, 20]. The dolomite peak is seen at 2θ = 30° according to the literature [15].

3.3. Membrane Morphology

The use of SEM in this study is a direct method to determine the character of the membrane. This method can be used to see membrane morphology which includes pore structure and membrane pore size. The SEM micrograph of the membrane with the addition of dolomite is presented in Figure 3. It can be seen that the membrane sample has % porosity which tends to increase with the average pore size decreasing with the addition of 0% to 30% dolomite (D_0 to D_{30}). The results of the pore size analysis using the Image J program are presented in Table 1.

The more dolomite is added, the more dolomite decomposes into more CO_2. The more CO_2 resulted in the resulting membrane being more porous and increasing the porosity of the membrane with relatively small pore size. Meanwhile, the addition of more than 30% dolomite decreased the porosity of the membrane, with an average pore size of 1.8472 µm. Dolomite effectively inhibits fly ash densification so that the addition of too much dolomite makes the membrane porosity decrease, with the pore size tending to be large. This indicates that the fly ash is not well densified. SEM on D_{45} showed the presence of microgram grains of fly ash that were not densified, the same as the membrane at the addition of 0% dolomite (D_0).

Table 1. Data on % porosity and average pore membranes, which were analyzed using the Image J . program

Membrane	Porosity	Average pore diameter
D_0	54.77%	1.6994 µm
D_{15}	41.42%	1.2621 µm
D_{30}	65.56%	1.1730 µm
D_{45}	39.50%	1.8472 µm

3.4. Thermal Resistance of Membrane

Thermal analysis is used to determine the stability of the ceramic membrane against heat so that it can be seen whether the membrane still functions well even at high-temperature conditions. The membrane TGA curve presented in Figure 4 shows that transformation occurs through membrane phase decomposition.

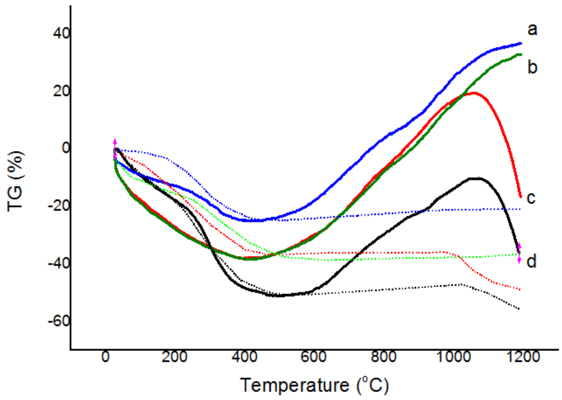

Figure 4. TGA curves of membranes a) D_{30}, b) D_{45}, c) D_0, d) D_{15}

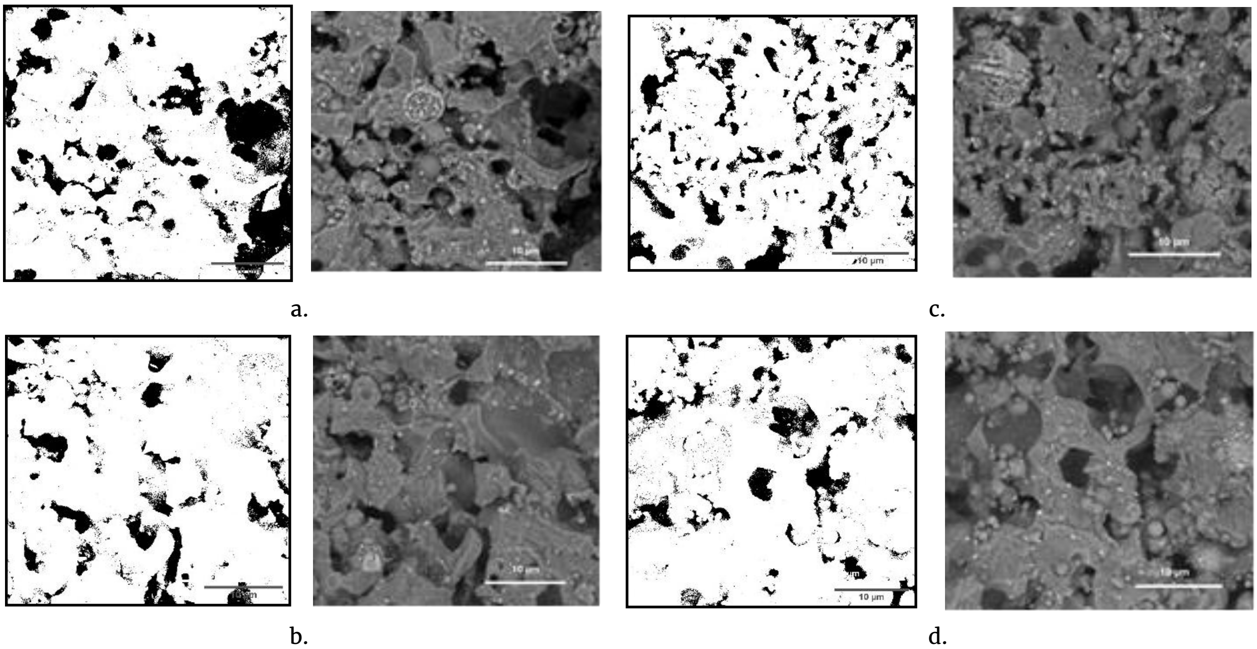

Figure 3. SEM images of membranes with dolomite variation. On the left is the appearance of the membrane pore threshold obtained using Image J software. Meanwhile, on the right is the original appearance of the membrane with a bar scale of 10 m, with a) membrane D_0, b) membrane D_{15}, c) membrane D_{30}, d) membrane D_{45}.

Weight loss regularly occurs at a temperature of 100°C to 200°C, a water release process [21]. The TGA results showed that the continuous weight loss from low temperature was associated with dehydration and dehydroxylation of amorphous aluminum hydroxide. Then the kaolinite disappears after dynamic heating above 500°C [22]. The weight reduction observed in the temperature range of 300°C, and 500°C was associated with the decomposition of uncarbonated brucite and dehydroxylation of hydromagnesite. The weight reduction in the temperature range of 500-800°C was mainly associated with the decomposition of calsate and decarbonization of HMC (Hygroscopic Moisture Content), which was hydromagnesite and nesquehonite on dolomite [23].

From the comparison of various samples, it can be seen that the membrane with the addition of 30% dolomite (D_{30}) has a higher temperature resistance than other variations. It can be seen that the decomposition that occurs is only about 0.396% for a temperature of 409°C. This value is relatively small compared to that which occurs in other variations. This is in accordance with SEM analysis that the D_{30} membrane has the smallest average pore size, which is 1.1730 µm. The pore structure formed on the membrane affects the properties of the membrane, including its thermal resistance and mechanical properties [24]. The D_{30} membrane, in addition to having the best thermal resistance, also has the highest compressive strength. Meanwhile, the D_0 and D_{45} membranes have almost the same thermal stability. The same properties were also shown in the SEM test data, which showed that the pore formation of the two membranes was similar.

3.5. Compression Strength

The compressive strength test was carried out to determine the strength of the ceramic membrane produced against a given pressure. The sample is made with a thickness of 15 cm and a diameter of 4 cm to be pressed. The compressive strength test of ceramic membranes with variations in the addition of dolomite can be seen in Figure 5.

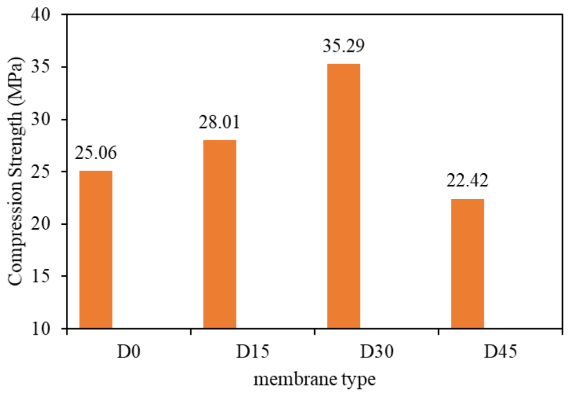

Figure 5. Compressive strength of ceramic membranes

Figure 5 shows the compressive strength of the membranes after the addition of dolomite. At the addition of 0% to 30% dolomite (D_0 to D_{30}), the compressive strength increased from 25.06 MPa to 35.29 MPa and decreased with the addition of 45% dolomite. This decrease in the physical strength of the membrane is associated with the analysis of the average pore size formed, which affects the physical strength of the membrane. The results of SEM analysis showed that the addition of dolomite 0% to 30% caused the pore size to be smaller and more evenly distributed, which is 1.6994 µm at D_0 and 1.1730 µm at D_{30}. With the addition of 45% dolomite, the membrane formed the larger pore size was 1.8472 µm. This is following the physical test results on the compressive strength of membranes which weakened with the addition of 45% dolomite. The addition of dolomite concentration further impairs the formation of the membrane due to the phase transition of the dolomite material leading to the release of gas, thus forming a macropore structure and resulting in a weakening of the physical strength of the membrane [25].

3.6. Membrane Filtration Capability

The flow rate or flux is an important parameter to determine the efficiency of membrane separation. These parameters are influenced by membrane composition, structure, distribution, and pore size. Flux is the flow rate that indicates the amount of water that moves through the membrane with the help of a driving force; pressure. The membrane water flux test was carried out on distilled water by applying a pressure of 0.5 bar. The volume of water that comes out is accommodated using a measuring cup and collected every 10 minutes. Measurements were carried out for up to 10 minutes to 4 or for 40 minutes. The results of the membrane flux measurement are shown in Figure 6.

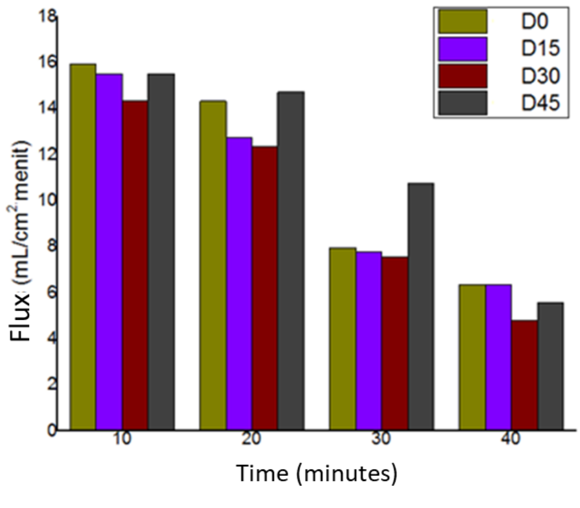

Figure 6. Water flux of various membranes

The flux value is related to the separation efficiency in the membrane filtration process. The membrane structure influences the flux value, such as pore size distribution, pore shape, and porosity. Figure 6 shows that the longer the filtration time, the smaller the flux produced. The decrease in flux value is due to the blockage of the membrane pores by micro particulates and the denser the membrane structure [26].

The addition of dolomite in the membrane composition affects the flux value. The flux value with the addition of 0% to 30% dolomite decreased, while the addition of 45% dolomite caused the flux value to increase. This is because adding 0% to 30% dolomite causes the best composition to be achieved, which functions to form denser membrane pores, resulting in decreased flux. The addition of dolomite concentration further impairs the formation of the membrane due to the dominance of the brittle nature of dolomite so that the pores become larger and result in an increase in the flux value. This is following the results of the SEM analysis, which shows the smaller the pore size of the membrane until the addition of 30% dolomite.

With the addition of more dolomite, the porosity increases up to the addition of 30% dolomite. The addition of dolomite up to 45% reduced porosity significantly. However, it was not matched by data on water flux (ease of water passing through the membrane pores) and average pore size. The calculation of membrane porosity (%), analyzed with the Image J program using membrane SEM images.

3.7. Ceramic Membrane to lower COD and BOD

The reduction of COD and BOD levels was carried out by flowing liquid tofu waste through a membrane arranged in such away. The membrane ability test in reducing COD and BOD levels was carried out with a vacuum pressure of 0.5 bar. Then the liquid waste after filtration was analyzed for COD and BOD using the titration method. The physical appearance of the solution before and after it is passed on the membrane is seen from the difference in the color intensity of the liquid waste before and after passing through the membrane. It can be seen directly that organic compounds are retained on the membrane so that the COD and BOD levels of wastewater that have passed through the membrane decrease, as shown in Figure 7. The membrane filters or blocks organic compounds in liquid tofu waste whose molecular size is larger than the membrane's pore size.

(a) (b)

Figure 7. Photo of liquid tofu waste (a) before filtration (b) after filtration

The sample of liquid waste used is liquid waste from the tofu industry, which comes from Sumur Jurang Village, Gunungpati District, Semarang City, Central Java. Before being treated with the filtration method, the liquid tofu waste was analyzed for COD and BOD to determine the quality of the waste. The results of the analysis of liquid tofu waste before and after filtration are presented in Table 2.

Table 2. Analysis of COD and BOD content of liquid waste from tofu production in Sumur Jurang Village

Treatment	COD (mg/L)	BOD (mg/L)
Before filtration	1224	408.16
D0	571.2	174.88
D15	326.4	155.5
D30	244.8	116.56
D45	408	174.96

The initial characteristics of tofu factory effluent before filtration application showed that the COD and BOD values exceeded the specified quality standards. The COD and BOD values for tofu wastewater were 1224 mg/L and 408.16 mg/L, respectively. Meanwhile, the quality standards for soybean processing industrial waste are 300 mg/L and 150 mg/L, respectively (Ministry of Environment Regulation, 2014). Tofu liquid waste in Sumur Jurang Village is not suitable to be disposed of directly into the waters because its COD and BOD exceed the quality standard of wastewater. The waste needs to be treated before being discharged into the waters.

Table 2 shows that the decrease in COD and BOD levels using ceramic membranes with the addition of dolomite from 0% to 30% has a greater decrease with dolomite. However, the decrease in COD and BOD was smaller in the membrane with 45% dolomite. This is in accordance with the results of SEM analysis which shows that the pore size and porosity of the membrane are getting better with the addition of 0% to 30% dolomite because many organic compounds are retained by the pores on the membrane surface and cause a decrease in COD and BOD.

The physical waste treatment process (filtration) affects the decrease in BOD and COD concentrations caused by the adsorption of waste pollutants into the membrane. The particles accumulate and form a layer on the surface and pores in the membrane, which helps to reduce the concentration of COD and BOD [27]. In addition, the decrease in COD and BOD can also occur due to adsorption events on the surface of the fly ash contained in the membrane. The process that occurs is a combination of filtration and physical adsorption by a ceramic membrane. The smaller the membrane pores lead to an increase in the membrane's selectivity so that it is more difficult for organic matter to escape from the membrane pores. The adsorption of organic substances by the membrane can result in reduced organic compounds contained in wastewater so that the amount of oxygen needed to oxidize organic substances becomes less [28]. Meanwhile, the increase in the concentration of dolomite further enlarges the pores because the dominance of the dolomite composition changes the membrane structure to become brittle. This causes the selectivity to COD and BOD to decrease [21]. The composition of the D_{30} membrane is the most effective composition of fly ash and dolomite in forming pores on the membrane so that the resulting membrane has the best COD and BOD reduction performance.

The appearance of the membrane after using membrane filtration shows that the membrane pores tend to look clean. The pore diameter analysis results using the Image J program also did not show much difference between the membranes before and after filtration was used. This indicates that the membrane is not clogged and can be used again. The accumulation of retained organic matter is only on the upper surface of the membrane.

4. Conclusion

From this study, it can be concluded that the addition of dolomite to ceramic membranes tends to increase the porosity of the membrane, with the average pore size decreasing with the addition of 0% to 30% dolomite (D0 to D30). The D30 membrane has the best thermal stability and has the highest compressive strength. Ceramic membranes with the addition of dolomite from 0% to 30% had a higher COD and BOD reduction but lower COD and BOD reduction in membranes with 45% dolomite addition. D30 membrane is the most effective fly ash and dolomite composition in forming pores on the membrane with the best COD and BOD reduction performance, namely 80% for COD and 71.44% for BOD.

References

[1] Sareh Rezaei Hosein Abadi, Mohammad Reza Sebzari, Mahmood Hemati, Fatemeh Rekabdar, Toraj Mohammadi, Ceramic membrane performance in microfiltration of oily wastewater, *Desalination*, 265, 1, (2011), 222-228 https://doi.org/10.1016/j.desal.2010.07.055

[2] Wa Atima, BOD dan COD sebagai parameter pencemaran air dan baku mutu air limbah, *Biosel: Biology Science and Education*, 4, 1, (2015), 83-93 http://dx.doi.org/10.33477/bs.v4i1.532

[3] Chengwen Song, Tonghua Wang, Yanqiu Pan, Jieshan Qiu, Preparation of coal-based microfiltration carbon membrane and application in oily wastewater treatment, *Separation and Purification Technology*, 51, 1, (2006), 80-84 https://doi.org/10.1016/j.seppur.2005.12.026

[4] Yingchao Dong, Jian-er Zhou, Bin Lin, Yongqing Wang, Songlin Wang, Lifeng Miao, Ying Lang, Xingqin Liu, Guangyao Meng, Reaction-sintered porous mineral-based mullite ceramic membrane supports made from recycled materials, *Journal of Hazardous Materials*, 172, 1, (2009), 180-186 https://doi.org/10.1016/j.jhazmat.2009.06.148

[5] Jiaoying Cui, Xiongfu Zhang, Haiou Liu, Shuqin Liu, King Lun Yeung, Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water, *Journal of Membrane Science*, 325, 1, (2008), 420-426 https://doi.org/10.1016/j.memsci.2008.08.015

[6] S. Khemakhem, R. Ben Amar, A. Larbot, Synthesis and characterization of a new inorganic ultrafiltration membrane composed entirely of Tunisian natural illite clay, *Desalination*, 206, 1, (2007), 210-214 https://doi.org/10.1016/j.desal.2006.03.567

[7] L. Palacio, Y. Bouzerdi, M. Ouammou, A. Albizane, J. Bennazha, A. Hernández, J. I. Calvo, Ceramic membranes from Moroccan natural clay and phosphate for industrial water treatment, *Desalination*, 245, 1, (2009), 501-507 https://doi.org/10.1016/j.desal.2009.02.014

[8] M. R. Weir, E. Rutinduka, C. Detellier, C. Y. Feng, Q. Wang, T. Matsuura, R. Le Van Mao, Fabrication, characterization and preliminary testing of all-inorganic ultrafiltration membranes composed entirely of a naturally occurring sepiolite clay mineral, *Journal of Membrane Science*, 182, 1, (2001), 41-50 https://doi.org/10.1016/S0376-7388(00)00547-0

[9] Jing Fang, Guotong Qin, Wei Wei, Xinqing Zhao, Preparation and characterization of tubular supported ceramic microfiltration membranes from fly ash, *Separation and Purification Technology*, 80, 3, (2011), 585-591 https://doi.org/10.1016/j.seppur.2011.06.014

[10] Abdelhamid Harabi, Fahima Zenikheri, Boukhemis Boudaira, Ferhat Bouzerara, Abdelkrim Guechi, Lazhar Foughali, A new and economic approach to fabricate resistant porous membrane supports using kaolin and CaCO3, *Journal of the European Ceramic Society*, 34, 5, (2014), 1329-1340 https://doi.org/10.1016/j.jeurceramsoc.2013.11.007

[11] Yi-Lan Elaine Fung, Huanting Wang, Nickel aluminate spinel reinforced ceramic hollow fibre membrane, *Journal of Membrane Science*, 450, (2014), 418-424 https://doi.org/10.1016/j.memsci.2013.09.036

[12] Jingjie Cao, Xinfa Dong, Lingling Li, Yingchao Dong, Stuart Hampshire, Recycling of waste fly ash for production of porous mullite ceramic membrane supports with increased porosity, *Journal of the European Ceramic Society*, 34, 13, (2014), 3181-3194 https://doi.org/10.1016/j.jeurceramsoc.2014.04.011

[13] Li Zhu, Yingchao Dong, Stuart Hampshire, Sophie Cerneaux, Louis Winnubst, Waste-to-resource preparation of a porous ceramic membrane support featuring elongated mullite whiskers with enhanced porosity and permeance, *Journal of the European Ceramic Society*, 35, 2, (2015), 711-721 https://doi.org/10.1016/j.jeurceramsoc.2014.09.016

[14] Yingchao Dong, Xingqin Liu, Qianli Ma, Guangyao Meng, Preparation of cordierite-based porous ceramic micro-filtration membranes using waste fly ash as the main raw materials, *Journal of Membrane Science*, 285, 1, (2006), 173-181 https://doi.org/10.1016/j.memsci.2006.08.032

[15] Jing Liu, Yingchao Dong, Xinfa Dong, Stuart Hampshire, Li Zhu, Zhiwen Zhu, Lingling Li, Feasible recycling of industrial waste coal fly ash for preparation of anorthite-cordierite based porous ceramic membrane supports with addition of dolomite, *Journal of the European Ceramic Society*, 36, 4, (2016), 1059-1071 https://doi.org/10.1016/j.jeurceramsoc.2015.11.012

[16] Keiko Sasaki, Xinhong Qiu, Yukiho Hosomomi, Sayo Moriyama, Tsuyoshi Hirajima, Effect of natural dolomite calcination temperature on sorption of borate onto calcined products, *Microporous and Mesoporous Materials*, 171, (2013), 1-8 https://doi.org/10.1016/j.micromeso.2012.12.029

[17] Eka Suprihatin, Titin Anita Zaharah, Nelly Wahyuni, Pembuatan Membran Silika dari Fly Ash

dan Aplikasinya untuk Menurunkan Kadar COD dan BOD Limbah Cair Kelapa Sawit, *Jurnal Kimia Khatulistiwa*, 4, 3, (2015), 48-53

[18] Yanfei Chen, Qiming Feng, Guofan Zhang, Dezhi Liu, Runzhe Liu, Effect of Sodium Pyrophosphate on the Reverse Flotation of Dolomite from Apatite, *Minerals*, 8, 7, (2018), 278 https://doi.org/10.3390/min8070278

[19] Dong Zou, Minghui Qiu, Xianfu Chen, Enrico Drioli, Yiqun Fan, One step co-sintering process for low-cost fly ash based ceramic microfiltration membrane in oil-in-water emulsion treatment, *Separation and Purification Technology*, 210, (2019), 511-520 https://doi.org/10.1016/j.seppur.2018.08.040

[20] Devagi Kanakaraju, Muhamad Hazim bin Ya, Ying-Chin Lim, Andrea Pace, Combined Adsorption/Photocatalytic dye removal by copper-titania-fly ash composite, *Surfaces and Interfaces*, 19, (2020), 100534 https://doi.org/10.1016/j.surfin.2020.100534

[21] Songxue Wang, Jiayu Tian, Qiao Wang, Zhiwei Zhao, Fuyi Cui, Guibai Li, Low-temperature sintered high-strength CuO doped ceramic hollow fiber membrane: Preparation, characterization and catalytic activity, *Journal of Membrane Science*, 570-571, (2019), 333-342 https://doi.org/10.1016/j.memsci.2018.10.078

[22] José Pascual, José Zapatero, María C. Jiménez de Haro, Ignacio Varona, Angel Justo, José L. Pérez-Rodríguez, Pedro J. Sánchez-Soto, Porous mullite and mullite-based composites by chemical processing of kaolinite and aluminium metal wastes, *Journal of Materials Chemistry*, 10, 6, (2000), 1409-1141 http://dx.doi.org/10.1039/A909380J

[23] Shaoqin Ruan, Jiawei Liu, En-Hua Yang, Cise Unluer, Performance and Microstructure of Calcined Dolomite and Reactive Magnesia-Based Concrete Samples, *Journal of Materials in Civil Engineering*, 29, 12, (2017), 04017236 https://doi.org/10.1061/(ASCE)MT.1943-5533.0002103

[24] Syukri Arief, Defina Nasmiati, Studi Membran Anorganik Berbahan Dasar dari Alam serta Potensinya sebagai Filter, *Prosiding SEMIRATA FMIPA Universitas Lampung*, 1, 1, (2013), 401-405

[25] Lidiane Pereira Bessa, Natália Mazzarioli Terra, Vicelma Luiz Cardoso, Miria Hespanhol Miranda Reis, Macro-porous dolomite hollow fibers sintered at different temperatures toward widened applications, *Ceramics International*, 43, 18, (2017), 16283-16291 https://doi.org/10.1016/j.ceramint.2017.08.214

[26] Mahmud Mahmud, Penurunan Warna Dan Zat Organik pada Pengolahan Air Gambut Menggunakan Membran Ultrafiltrasi, *Info-Teknik*, 4, 2, (2003), 72-80

[27] Subriyer Nasir, Teguh Budi, Idha Silviaty, Aplikasi Filter Keramik Berbasis Tanah Liat Alam Dan Zeolit Pada Pengolahan Air Limbah Hasil Proses Laundry, *Bumi Lestari*, 13, 1, (2013), 45-51

[28] Ghufran H. Faisal, Ali J. Jaeel, Thaar S. Al-Gasham, BOD and COD reduction using porous concrete pavements, *Case Studies in Construction Materials*, 13, (2020), e00396 https://doi.org/10.1016/j.cscm.2020.e00396