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Research Article
Preparation and Characterization of Volcanic Ash-chitosan Composite Ceramic Membrane for Clean Water Production

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Abstract
Background and Aim: Volcanic ash is a material released by volcanic eruptions. It contains high composition of silica and alumina which can be used as ceramic membrane material for clean water production. Clean water is one of the most important natural resources for human life and health. The clean water production using volcanic ash based ceramic membrane is constrained by its low mechanical strength. To overcome the problem, in this research, ceramic membrane material from volcanic ash-chitosan composite is studied for obtaining stronger ceramic membrane. **Materials and Methods:** Volcanic ash consists of silica dioxide (SiO_2) 48.23%, aluminum oxide (Al_2O_3) 18.40%, ferro oxide (Fe_2O_3) 18.45%, calcium oxide (CaO) 4.51% and the other remaining compounds. The ceramic membranes were casted via molding and calcination process. The ceramic supports were then coated with various concentration of chitosan (1, 2, 3, 4 and 5%). The composite ceramic membranes were characterized by particle size distribution analysis, scanning electron microscope (SEM), X-ray diffraction (XRD). **Results:** Membrane characteristics were influenced by material composition and mixing homogeneity, the greater ash composition in the ceramic membrane matrix significantly increased the permeate flux and the membrane porosity was directly proportional to the thrust force which is given in the calcination process at 1100°C, **Conclusion:** This study produced composite ceramic membranes with chitosan which have excellent stability in water. This is indicated by the resulting membrane mechanical performance that is not damaged during application and the membranes have porosity, structure and mechanical integrity that can be applied for water treatment to produce clean water.

Key words: Ceramic membrane material, chitosan, clean water, composite membrane, volcanic ash

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Membrane characterization is a process which is performed to obtain informations about porous structure and membrane morphology. Membrane characteristics play an important role in membrane separation performance. Characterization is required to produce good and strong ceramic membrane as well as excellent separation efficiency which can be applied for clean water treatment[1]. The development of membrane technology is currently very rapid and widely used in membrane separation process. Performance for membrane separation process is usually expressed by permeate flux and separation factor (selectivity)[2]. The performance efficiency of the separation will increase with increasing selectivity on the other hand the increase in selectivity is generally inversely proportional to the permeate flux, therefore an optimization is required[3]. Clean water treatment using membrane technology is expected to help the community to solve the problem in terms of clean water[4]. Research on clean water treatment has been developed as an effort to overcome environmental pollution in water so that it can meet the quality standard and not endanger human health[5]. In this study, newly developed clean water treatment technology with membrane technology, membrane technology is an environmentally friendly clean technology[6]. It is expected that with the utilization of membrane technology for water treatment, the produced water can meet the standard of clean water quality established in Indonesia, in accordance with Ministerial Decree No. 907/MENKES/SK/VII/2002[7,8]. This membrane technology can reduce the organic and inorganic compounds that are found in water without any chemicals addition in their operation[9]. The clean water production in this research was performed using ceramic membrane technology made from volcanic ash of Kelud volcanic eruption on February 13, 2014. This volcanic ash is suitable to be used as raw material for making ceramic membrane because it contains high concentration of SiO_2 and Al_2O_3 compounds. Those compounds have the same pore structure (uniform), stable at high temperatures and have good mechanical strength[10]. This compound is found as an aluminosilicate compound that forms the AlO_4 and SiO_4 tetrahedral structural framework which is suitable for ceramic membrane fabrication[10,11]. The use of clay-based materials as ceramic membranes for water treatment can decrease the level of iron ions and arsect content in water up to 95% depends on the Fe/As ratio[9]. The typical compositions of volcanic ash from Kelud Vulcano Mountain are SiO_2 (48.23%), Al_2O_3 (18.40%), Ca^{2+} (4.51%) and Fe_2O_3 (18.45%). Based on the ash composition, it has the potential to be utilized as raw material in the ceramic membrane fabrication[10]. The main objective of this research is to make composite ceramic membrane of volcanic ash and chitosan for water treatment through calcination, molding and coating process. The membrane characterizations of SEM test, XRD test and permeation test were performed to obtain the information about membrane structure and morphology[12]. This is a novel concept in utilizing the vulcano ash as a ceramic membrane material for clean water production.

This study formulated the volcanic ash-chitosan composite membrane with various concentrations which is effective in cleaning the water without addition of any material. Thus this is first study of kind which formulated the membrane with volcanic ash-chitosan in obtaining composite ceramic membrane with good stability for clean water production. This study will be beneficial in water treatment technology. The volcanic ash that at the current condition is not utilized yet will be used for membrane preparation. The prepared will be used as water treatment to supply clean water to the community.

MATERIALS AND METHODS

Materials: Volcanic ash was obtained from Kelud mountain, Solo region of Central Java-Indonesia, Kaolin Clay, Carboxymethyl Cellulose (CMC), Sodium Citrate and Chitosan Deionized water were purchased from CV. Indrasari Semarang Indonesia, γ-Alumina (Al_2O_3) and Magnesium Sulfate ($MgSO_4.7H_2O$) were purchased from Merck kGaA Germany, Polyethylene Glicol (PEG) MW 400 was purchased from Sigma-Aldrich Co. USA. Clean water microfiltration and membrane casting equipment made by Binarendra research device Semarang Indonesia.

Membrane preparation: Ceramic composite membranes were prepared by sieving the volcanic ash using shaker to obtain homogenous ash with average particle distribution of 200 mesh. The membrane fabrication was performed by mixing the main support layer materials such as volcanic ash 14-22 wt-%, kaolin 30 wt-%, alumina 22%, deionized water and 10 wt-% additive mix of carboxymethyl cellulose, polyethylene glycol, sodium citrate and $MgSO_4$. Each of them corresponds to the prescribed composition, after which the main ingredient mixture and the additive mixture were mixed for 15 min. The mixture was pugged for 30 min to form a homogeneous and elastic paste. The ceramic paste was then left at room temperature and kept away from direct sunlight for 30 min (aging process). The ceramic paste was molded with certain pressure into circular disk shape (φ = 4.5 cm and thickness 2.5 mm). The ceramic disk were dried at 250°C for an hour to remove water and organics content.

Calcination process: In this study, the calcination process is done at 1100°C for 6 h. The calcination process is necessary because it serves to open the membrane pore, it needs high temperature. Prior to the calcination process, a drying process is carried out at a temperature of 200°C for an hour in order to eliminate its organic content.

Support layer coating using chitosan solution: Composite membranes were fabricated using dip-coating technique in chitosan solution. Chitosan solutions were prepared by dissolving various amount of chitosan (1, 2, 3, 4 and 5 wt-%), PEG 400 1 wt-% and Al $(OH)_3$ 1 wt-% in acetic acid. The Support layer (circular disk ceramic)was dipped in beaker glass containing chitosan solution. The membrane is then fed into the oven and heated to 40°C for 24 h.

Membrane characterization

Scanning electron microscope test (SEM): The SEM is used to determine the micro structure of a material in the form of membrane morphology, composition and particle surface crystallography information. The SEM test was conducted at University of Negeri Malang (SEM JEOL JSM 6510).

X-ray diffraction test (XRD): X-ray diffraction can be used to analyze the structure of the prepared membrane. The principle of X-ray diffractometer (XRD) is X-ray wave diffraction that undergoes scattering after collision with crystal atoms. The resulting diffraction pattern represents the crystal structure, the test was performed at the BPPT-Serpong Physics Laboratory (type Quartz HP 121-Syn 208).

Water treatment (permeation) test: The principle of water treatment using composite ceramic membrane microfiltration was utilizing the separation process of volatile compounds which was capable to be adsorbed by the membrane while non volatile compounds such as arsen were retained on the side of the feed (upstream). In this study, filtration process was carried out using a circular disk membrane flat module with average effective diameter of 42 mm and thickness of 2 mm with operating pressure 4-7 kg cm^{-2}.

RESULTS AND DISCUSSION

Permeability test result: Membrane permeability is a measure of the velocity representing the number of specified spaces that can pass through a membrane which can be expressed as a flux quantity defined as the amount of permeate volume passing through one unit of membrane area in a given time divided by the pressure used (L h^{-1} m^{-2})[13].

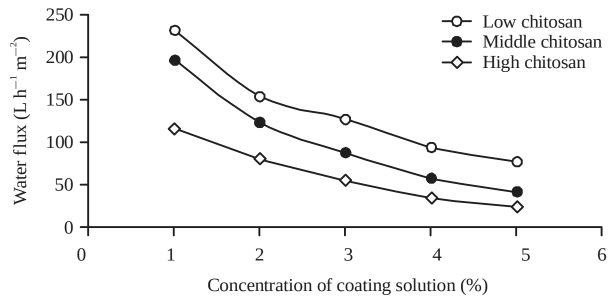

Fig. 1: Result of permeability test with effect of flux quantity with concentration of solution

Figure 1 illustrated the permeability obtained by the concentration of chitosan solution in acetic acid. The higher chitosan concentration declined the permeability of the film. This was due to the higher concentration of chitosan the higher the viscosity of the solution so that the resistance generated by the film was also higher and the water volumetric rate becomes smaller. At chitosan concentrations above 3%, chitosan can not be completely dissolved so that the film is not homogenous and porous. This will result in an increase of flow rate.

The permeation test result also showed that the molecular chain of chitosan also gave significant effect to the permeate flux. The higher chitosan molecular weight, the overall permeate flux decreased. This could be due to the higher molecular weight chitosan affected the active layer density.

Swelling test: Swelling test on the membrane aimed to predict the size of a substance that can diffuse into the membrane[14,15]. Swelling can also indicated that there was still a cavity between the bonds in the polymer, which can affect the mechanical properties of the polymer where the smaller cavity within polymer had better mechanical properties. Figure 2 showed that the higher concentration of chitosan in the membrane caused the percentage of swelling smaller, this was due to the higher concentration of chitosan inflicted on the distance between molecules in chitosan will be more dense and the pores formed on the membrane will be smaller so the water was difficult to diffuse into the membrane causing small expansion ability. Conversely, the lower concentration of chitosan in the membrane, the ability to expand was larger, this was due to in case of low concentration of chitosan, more amount of solvent was used (solute concentration was lower), larger pores in the membrane were formed. In general, membranes with concentrations of 1, 2, 3, 4 and 5% had good stability in water, this was indicated by the resulting membrane that was not destroyed or brittle during water treatment filtration process.

In case of low concentration of chitosan (1 wt-%) the swelling degrees were 15, 17 and 20% for high, middle and low molecular weight chitosan, respectively. There were more pores with higher gap between chitosan molecule, this resulted in the filling of water molecules between chitosan molecules during the water filtration process. thus the distance between chitosan molecules was larger which make the swelling degree higher. This will have an impact on the separation efficiency of components in the treated water. In addition, from Fig. 2, it can also be taken that the molecular weight of the chitosan was very influential on the swelling degree. the greater the molecular weight means the more tightly so there was no room for water, as a result the swelling degree smaller.

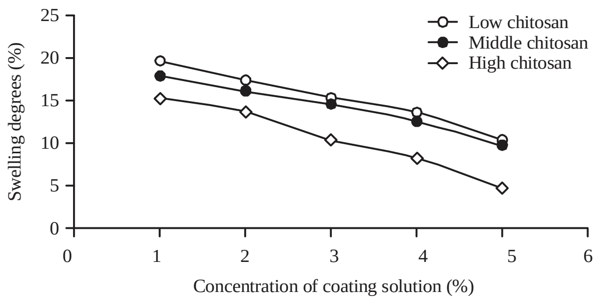

Fig. 2: Effect of swelling degree with concentration of coating solution

Scanning electron microscopy (SEM) test: The SEM analysis was performed to determine the microstructure of a material in the form of membrane morphology, composition and particle surface crystallography information[16].

Figure 3 showed the SEM images of membrane with composition 120 gr volcanic ash and 2.5% chitosan concentration. From Fig. 3 was found that the smaller particle

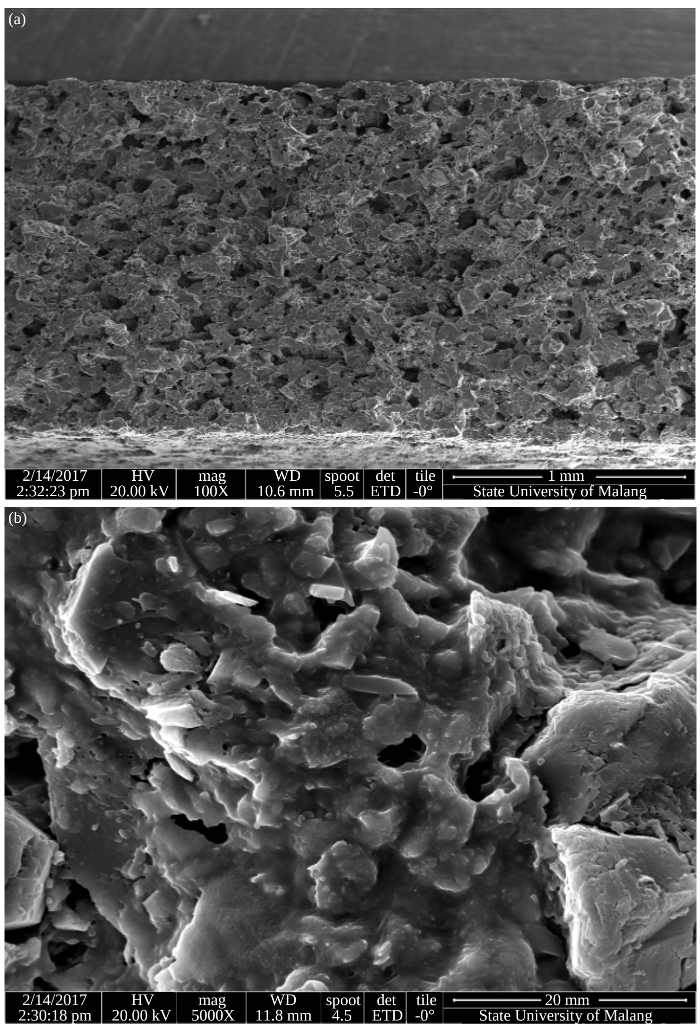

Fig. 3(a-b): SEM micrographs of the ceramic membrane with composition volcanic ash 120 g and chitosan concentration 2.5% and magnification at 5000x, (a) Cross-section and (b) Surface

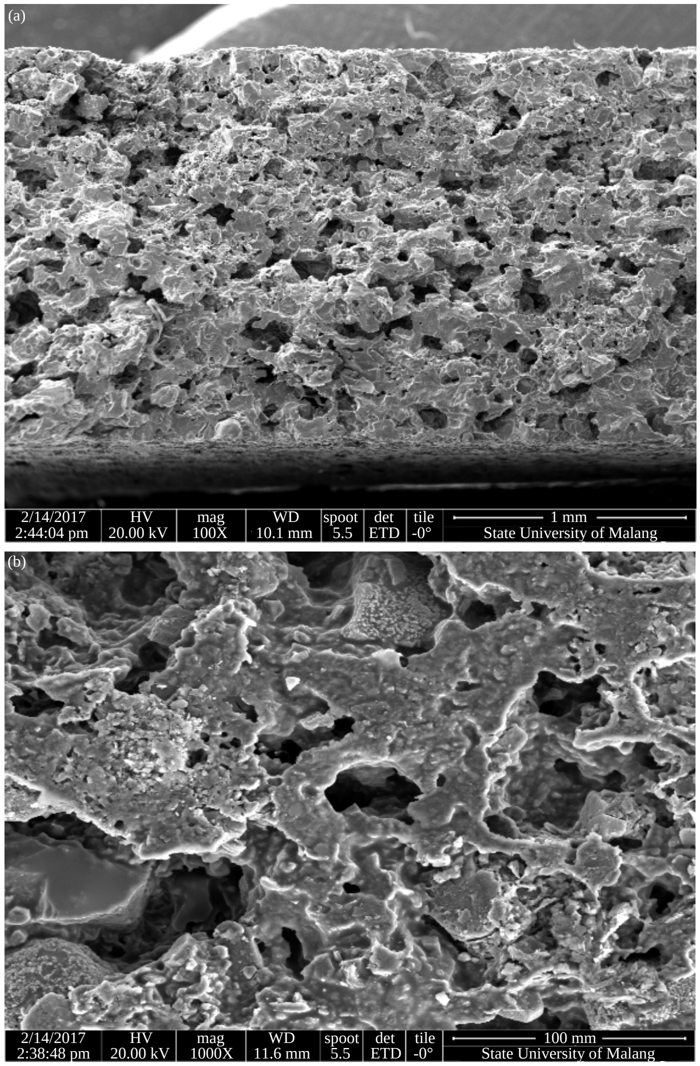

Fig. 4(a-b): SEM micrographs of the membrane with composition volcanic ash 140 g and 3% chitosan concentration and magnification of 5000X, (a) Cross-section and (b) Surface

size of particles in the ceramic membrane, permeate easier to pass the membrane pore barrier. At chitosan concentration of 2.5% the morphology of the porous membrane exhibited the best particle size position and indicated that the higher pressure applied during casting process, the larger pores size were formed in the membrane. This could be due to the release of some existing component during calcination process. This factor determined the flow rate because the ceramic membrane of volcanic ash-chitosan support which was produced had a good permeation rate making it easier in the process of filtration for water treatment.

Figure 4 showed the SEM images of higher composition of volcanic ash (140 g) and 3% chitosan concentration. Based on this SEM analysis, the higher concentration of ash in the membrane showed the crystallographic structure of Al/Si on the surface of ceramic membrane was getting smaller. The pore structures that were formed on the membrane support with the higher volcanic ash content produced a membrane with an increasingly tight porous structure. this kind of structure will inhibit the membrane permeation rate during the filtration process.

XRD (X-ray diffraction) test: Figure 5 showed the results of XRD analysis of ceramic membrane with molding pressure 20 kg cm^{-2} and various membrane composition (C1 = volcanic ash 140 g and 2.5% chitosan, C2 = volcanic ash 140 g and 3% chitosan) and the identification of the ceramic membrane structure at the calcination temperature of 1100°C. Figure 5 shows that the structure of the volcanic ash composition was dominated by SiO_2 in figure P20 C2 at 1.198 (PDF-4+2013 RDB), reaching a peak at 27.929 degrees. Analysis of volcanic ash was decreased in the formation of

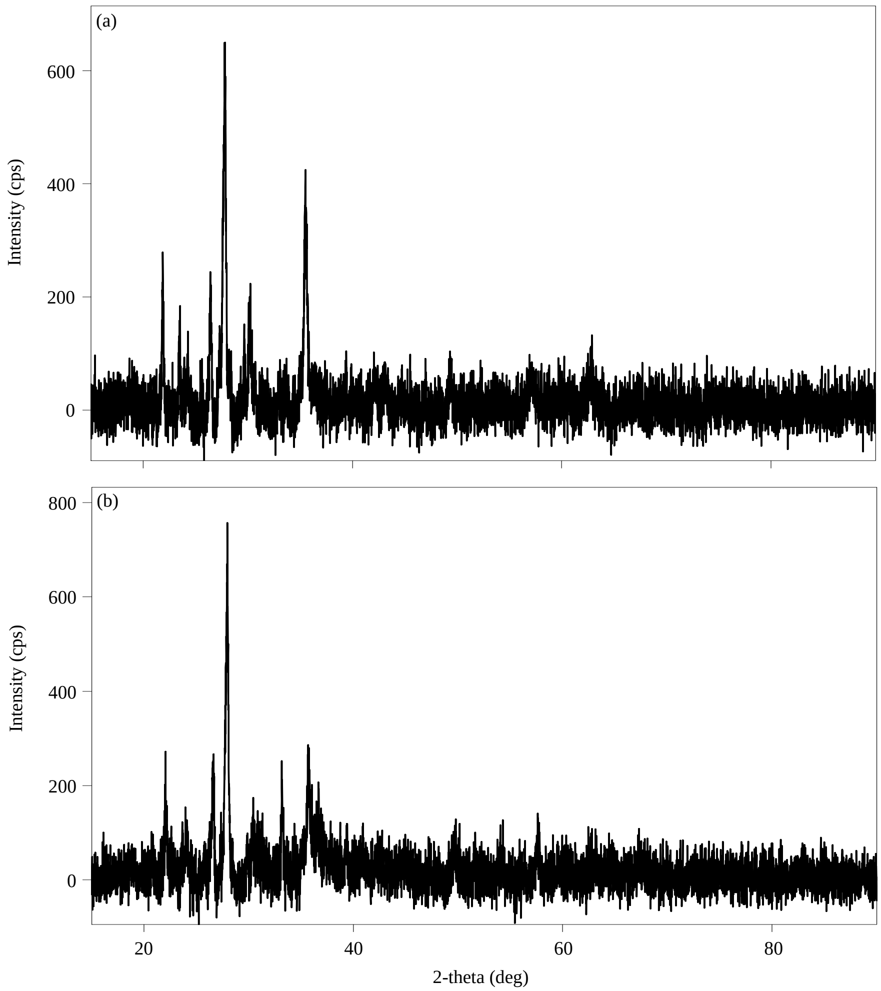

Fig. 5(a-b): XRD pattern of intensity of membrane support layer at pressure P = 20 kg cm^{-2}, various composition C and calcination temperature at 1100°C, (a) XRD spectra of C1 and (b) XRD spectra of C2

SiO_2. The decrease was caused by the formation of SiO_2 in Si instability making it easier to interact with other atoms. The results of this study indicated that the temperature of calcination and the resulting changes in the density of pressure casting, porosity and microstructure resulting in membrane, increasing the density will decrease the porosity and the microstructure formed then become easily homogeneous, so it could be used for purification. As the result, surface water is the alternative water sources. However, the surface water quality generally doesn't meet the clean water quality standard.

CONCLUSION

Volcanic ash-chitosan composite ceramic membranes were successfully fabricated via molding, calcination and chitosan dip-coating processes. The characteristics of prepared membranes were influenced by material composition and membrane molding pressures. The permeability test results show that higher chitosan concentration decrease the permeate water flux. The molecular weight of chitosan also serves significant effect on permeate flux and swelling degree. The analysis showed that the condition of P20 C2 with force 20 kg cm^{-2} and XRD test result showed intensity at SiO_2 = 750 cps. This resulted the changes in density, porosity and microstructure of the membrane. Due to the density increased, the micro-structure porosity decreased. The water tends to diffuse homogeneously in lower porous membrane, so the membrane can be used for water treatment. the experimental results show that the membrane is stable in therm of mechanical strength under pressurized water feed. By this study's result, it will be an alternative technology in supplying clean water from contaminated surface water, moreover the volcanic ash that continuously generated by Kawi mount in Indonesia can be utilized.

SIGNIFICANCE STATEMENT

In this study, the potential of volcanic ash to be utilized as a ceramic membrane for water treatment has been discovered. Indonesia has many volcanic mountains (ring of fire) and the volcanic ash is generated in large quantities. The benefits of this study are giving the scientific report about the utilization of volcanic ash as membrane material, treating the unused volcanic ash become more valuable, Indonesia's government have published about the regulation of deep ground water utilization, where the utilization of deep ground water was prohibited. By this invention, the water scarcity can be prevented. The new theory that will arrived by this research is the addition of chitosan on volcanic ash ceramic membrane significantly enhance the ceramic membrane properties.

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