Aluminium copper pillared clay membrane: application for dyestuff filtration

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Abstract. Membrane production from Al-Cu pillared clay has been carried out. Al-Cu pillared clay was made by mixing Al-Cu pillared solution in clay suspension with Al³⁺ and Cu²⁺ molar ratio of 8:2 while molar ratio of [OH]/[Cu²⁺+ Al³⁺] was 2.2. The clay suspension was dried at 60°C for 5 hours to remove water molecules in the clay structure and then calcined for 4 hours at 200°C, 300°C and 400°C with a heating rate of 1°C/minute. The pillared clay obtai

1. Introduction
Membrane is a selective barrier that allows the transport of smaller species and holds larger species. Judging from its constituent material, the membrane can be classified as organic membranes, inorganic membranes and hybrid membranes consisting of a combination of organic and inorganic materials. In general, the inorganic membrane was made in layers, where the thinnest layer that become the filter is placed on the surface of the supporting solids which have larger pores called a membrane support. Therefore the inorganic membrane is generally arranged asymmetrically [1, 2]. This ceramic membrane has many advantages, including efficient separation, good thermal and chemical stability, resistance to high pressure, long term usage and easy to clean [3, 4].

Membrane support serves to provide mechanical strength so that the thin membrane above it can be held and at the same time also produce good flow for the species to be separated [4]. A good membrane support should have a good mechanical strength and a high pore volume hence it can flow the species well and have a narrow pore size distribution hence it is selective for the product to be separated [2]. In general, the material often used in the manufacture of membrane support is alumina. Alumina has several advantages including having good durability, high temperature stability, chemical resistance [5], high permeability, good bending strength and good resistance to acid/alkali [2]. Nevertheless, alumina...
also has limitations, such as brittleness similar to other dense ceramics. This shortcoming restricted the alumina application and also shorten the time of use [5]. In addition, alumina requires very high sintering or calcination temperatures up to 1700°C or more to obtain adequate mechanical strength for its use as a membrane support [2].

On the other hand, clay is an important component in soil that acts as a natural pollutant catcher that flows along with water. The clay conducts various molecule adsorption and ion exchange processes which produce clean waters. With the vital role that clay can play, and its abundance in nature, it makes sense that natural clay is functioned as an inexpensive adsorbent with a high ion exchange capacity [6]. Yet, the clay when mixed with water will swell like a pasta and when heated will deflate [7]. These characters cause the pores in the clay unstable. Therefore, to overcome these limitations, researchers [8-11] has conducted researches regarding the pillared clay synthesis. The pillarisation process serves to improve the thermal stability of clays, increase pore volume, specific surface area, narrow the pore distribution and increase the acidity of the clay surface. Pillarization is carried out by inserting polycations from hydroxy metal cations into clay interlayer. Furthermore, the calcination process converts the cations into rigid metal oxide groups which inhibits the inter-layer space collapse [12-14]. Seeing the weakness of alumina and the opportunity to produce porous material from pillared clays, the research tried to make membrane support from pillared clay.

Pillarisation using Al cation and cations that has greater radii than that of Al cation as pillars will give different ionic radii which then will cause the increase of pillared clay basal spacing compared to the use of Al cation only [10]. Kim and Lee [8] showed that Al-Cu pillared clay which was calcined at 400°C had a surface area about 140 m²/g with a basal spacing of 18 Å [15]. Previous researches [15-17] revealed that the Al-Cu pillared clay could be used as a catalyst. Based on the above descriptions in this research, the membranes from Al-Cu pillared clays were manufactured and their characters and performances in methylene blue filtration were examined. The test for methylene blue filtration is expected to provide an overview of the opportunity to use pillared clay as a membrane for large molecules or membrane support in place of alumina.

2. Methodology

Research on Al-Cu pillared clay membrane manufacture and characterization were conducted in several stages, i.e. the manufacture and characterization of Al-Cu pillared clays, the manufacture and characterization of membrane along with membrane performance testing.

2.1. Synthesis and characterization of Al-Cu pillared clays

The natural clay was washed, dried, crushed and sieved to 170 mesh size to get smaller and uniform particles. The molar ratio [Al³⁺] and [Cu²⁺] was 8:2. The molar ratio between [OH⁻]/[metal] = 2.2 in accordance with Tabak et al. [18]. The addition of NaOH solution was conducted carefully to avoid precipitation of Al(OH)₃. Pillaring solution was stirred for 24 hours and aged at 60°C in an oven for 24 hours. Al-Cu pillaring solution was then mixed to the 10% clay suspension and stirred for 24 hours at room temperature. Then the intercalated clays were washed until they were free of Cl⁻. Afterwards, the intercalated clays were dried and calcined for 4 hours at 200°C, 300°C and 400°C with a heating rate of 1°C/min. The Al/Cu pillared clays were analysed by X-Ray Diffraction (XRD).

2.2. Al/Cu pillared clays membrane preparation

Uncalcined Al/Cu pillared clay was crushed and added with PEG-400 and water with a weight ratio Al/Cu pillared clay; PEG-400: water of 8; 5; 1.5 (w/w). The mixture was then put on a press tool with 50 kg/cm² in pressure for 10 minutes. Al/Cu pillared clay was dried for 12 hours at 70°C and calcined for 10 hours at 600°C with a ramp rate of 1°C/minute. The natural clay underwent the same treatment with Al-Cu pillared clay to compare the character of the resulting membrane. Natural clay membrane and Al-Cu pillared clay membrane were characterized by Gas Sorption Analyser (GSA).
2.3. Membrane performance test

Performance test of Al-Cu pillared clays membrane was tested on the filtration of methylene blue dye. Methylene blue dye solution was made with a variety of concentration of 10 ppm, 20 ppm, 40 ppm and 80 ppm. The filtration equipment designed is presented in Fig. 1 and the method used in the filtration process was crossflow.

Figure 1. Schematic of methylene blue filtration apparatus

Membrane filtration performances are presented in the form of flux to measure the production capabilities and rejection to determine the efficiency. The flux and rejection were obtained from the following equation:

\[
\text{Rejection} = \left(\frac{\text{Initial absorbance} - \text{final absorbance}}{\text{Initial absorbance}}\right) \times 100\%
\]

\[
\text{Flux} = \frac{\text{flowrate}}{\text{surface} \times \text{pressure}}
\]

3. Results and Discussion

3.1. X-ray Diffraction

The clay used in this study was the clay from the village of Banyusri, District Wonosegoro, Boyolali. Fig. 2 shows the physical appearance of grayish clay while the diffractogram of natural clay and Al-Cu pillared clay is shown in Fig.3.

Figure 2. Boyolali natural clay
Fig. 3(i) shows that the natural clay peak found at 2θ is 5.86°, derived from the reflection of basal spacing (d_{001}) that obtained a distance of 15.08 Å. Although the XRD diffractograms were not completely measured until 2θ = 90°, the existence of peak 2θ <10° could possibly be the basal spacing of montmorillonite mineral. This result is supported by a research of Suarya [19] which stated that the basal spacing of montmorillonite clay was 15.43 Å (2θ = 5.72°).

The XRD results also show that the intercalation process using Aluminium and copper shifts the peaks to smaller 2θ value or increases the basal spacing (d_{001}). In the calcination process, metal polycations incorporated into the clay interlayer underwent dehydration (removal of water molecules) and dehydroxylation of polycation structure forming metal oxide clusters which kept the interlayer space permanently. The basal spacing calculation results are displayed in Table 1.

From the data in Table 1, the increase in basal spacing (d_{001}) occurred on all the Al-Cu pillared clay calcination temperature variations. This indicates the accomplishment of the Al-Cu intercalation process in the clay interlayers. Urruchurto et al. [20] compared a conventional calcination process with a drying calcination spray. The result revealed that the Al-Cu pillared clay that were conventionally calcined produced a basal spacing of 16 Å [20].
Table 1. XRD Data on natural clay and Al-Cu pillared clays

| Samples                     | 2θ  | Basal spacing (d_{001}) |
|-----------------------------|-----|-------------------------|
| Natural clay                | 5.86°| 15.08 Å                 |
| Al-Cu pillared clay (60°C)  | 5.09°| 17.34 Å                 |
| Al-Cu pillared clay (200°C) | 5.5° | 16.05 Å                 |
| Al-Cu pillared clay (300°C) | 5.39°| 16.37 Å                 |
| Al-Cu pillared clay (400°C) | 5.65°| 15.62 Å                 |

The XRD diffractogram results also showed that with by increasing in calcination temperature, the crystallinity of Al-Cu pillared clay was decreased which was characterized by low intensity and wide peak of XRD diffractogram. Samples that have low and wide intensity show a low level of crystallinity [21].

3.2. Al-Cu pillared clay membrane

The pillared clays were then moulded into the flat membrane as presented by Fig. 4. Fig. 4 displays a change in colour of the membrane. This was caused by the evaporation of solvent and transformation of Al³⁺ and Cu²⁺ ions becoming Al₂O₃ and CuO. According to Masturi et al. [22] during calcination, there is an evaporation of free water, decomposition of the PEG and the formation of pores. Furthermore, clay particles hardened and bounded generating strong porous membrane. Calcination also caused the shrinkage of the pore [22].

![Figure 4. Al-Cu pillared clay membrane (i) prior to calcination (ii) after calcination](image)

Adsorption-desorption isotherms of natural clay and Al-Cu pillared clay membrane is presented in Fig. 5. The nitrogen adsorption is a physical adsorption used in BET method for determining solid total surface area and pore structure [23]. It is observed that the N₂ adsorption isotherms of Al-Cu pillared clay membrane shows a similar pattern with natural clay where there is a slow increase in relatively low pressure (P/P₀) then escalates slowly in the middle and rises rapidly when P/P₀ approaches one. The first increase occurred, caused the adsorbed gas molecules interacting with the solid surfaces which in this stage, a monolayer formed. In the middle area of P/P₀, the accretion of gas molecules occurs on the surface of the layer that has been occupied by the gas molecules. These gas molecules have previously formed a monolayer which at this stage, the accretion formed a multilayer. At the end, there is a condensation of adsorbed gas molecules [24].

This isotherm is a type IV. Type IV isotherm is a kind of adsorption of mesoporous solids which has a pore size of 20-500 Å [25]. It can be concluded that the Al-Cu pillared clay has a mesoporous size.
addition, there is a presence of hysteresis loops H3 which shows the characteristic for the adsorption isotherm on montmorillonite clays [26]. The H3 loop shape is also related to the non-rigid nature of the adsorbent and the characteristic shoulder position in line with condensate destabilization on the limiting P/P₀ value [27]. This meso pore type is expected to produce a membrane with higher flux because meso pores only hold large molecules while small molecules are easy to pass. Pore and surface morphological data of the natural clay and Al-Cu pillared clay membrane are displayed on Table 2.

**Table 2.** Pore and surface morphological data of the natural clay and Al-Cu pillared clay membrane

| Samples               | Pore diameter (Å) | Pore volume (cc/g) | Surface area (m²/g) |
|-----------------------|-------------------|--------------------|---------------------|
| Natural clay          | 34                | 0.137              | 52.45               |
| Al-Cu pillared clay   | 38                | 0.155              | 50.48               |

Table 2 shows the diameter and pore volume of the Al-Cu pillared clay membrane is higher than the natural clay membrane. This indicates that the process of intercalation of the clays can enlarge the pore size. Pillar contained in the clay can prevent the membrane pores to not shrink when heated at high temperatures. Pore enlargement can also be observed from the difference between the basal spacing of the Al-Cu pillared clay with natural clay. Al-Cu pillared clay basal spacing is higher than the natural clay. Hence, when Al-Cu pillared clay was used as a base material for membrane manufacture, it produced a bigger pore diameter because there were pillars that sustained the size of the pore. However, Al-Cu pillared clay surface area was slightly smaller than the membrane of natural clay.

Fig. 6 shows the difference in the pore distribution on the natural clay membrane and Al-Cu pillared clay membrane. In the natural clay membrane, the pore distribution declines and there is no escalation with the increasing of pore diameter. This indicates that there is no dominant pore in the natural clay. Whilst, the Al-Cu pillared clay membrane displays a small increase in pore diameter around 38 Å and 65 Å. This suggests that Al-Cu pillared clay membrane has more uniform pores.
Figure 6. Pore distribution of the natural clay membrane and Al-Cu pillared clay membrane

Nonuniformed pore size distribution was probably caused by less homogenous mixing between Al-Cu pillared clays and PEG that therefore produced small and large pore simultaneously. Most probably, there was a coagulation of PEG particles during the mixing process that caused the formation of very large pore size during calcination process, as hypothesized in Fig. 7.

Figure 7. Pore model formed on the Al-Cu pillared clay membrane

3.3. Al-Cu pillared clay membrane performance test
Tests on the Al-Cu pillared clay membrane was conducted to determine the performance of Al-Cu pillared clay membrane that was made through the filtration of methylene blue. The methylene blue concentration was varied (10 ppm, 20 ppm, 40 ppm and 80 ppm). The filtration result was then measured to determine the rejection and flux. We did not test using natural clay because it has become common knowledge that clay which calcined at high temperature will become dense. So comparing the porous material with the dense material for dye filtration is certainly not appropriate.

Fig. 8 demonstrates there is a significant difference in dyestuff before and after filtration which entire filtration results exhibit the solution was clear by visual observation.
Figure 8. Methylene blue before and after filtration on some variation of concentration

Fig. 9. presents the flux and rejection values obtained from the filtration of methylene blue. Initial and final absorbance were measured by UV-Vis spectrophotometer at a maximum wavelength of methylene blue of 664.5 nm. The entire filtration process gives tremendous results with a rejection value more than 99%. Although it is small, the value of rejection increases with increase of methylene blue concentrations. The rejection increase is probably due to fouling which occurred in Al-Cu pillared clay membrane.

Figure 9. Flux and rejection of Al-Cu pillared clay membrane

Fouling of the membrane is divided into two, i.e. the fouling on the surface and internal fouling. In this case, the occurred fouling was on the surface. Particle precipitations occurred on the surface was assumed to actually increase the selectivity of Al-Cu pillared clay membrane. The more particles settled on the surface, then large pores on the surface would be covered. Thus, increasing the ability of Al-Cu pillared clay membrane to filter the methylene blue. However, the membrane flux decreased with the increase of methylene blue concentration. This reinforces the hypothesis that membrane fouling on the surface occurred.

The filtration process generally occurs because the membrane pore size is smaller than the particle size that is needed to be filtered. Therefore, the particles cannot pass through the pores so the water molecules can be separated from the dissolved material. However, Al-Cu pillared clay membrane pore diameter was 38 Å which was bigger than the diameter of methylene blue molecule which is 15-25 Å [28]. The explanations why Al-Cu pillared clay membrane could filter methylene blue well was due to the thickness of the Al-Cu pillared clay membrane. Since Al-Cu pillared clay has a thickness of 0.3 cm,
it caused the inside pores to pile onto one another or stratified. This build-up caused the pore size to become smaller. Illustration of pore build-up is presented in Fig. 10.

Figure 10. Illustration of stratified pores in Al-Cu pillared clay membrane

The presence of multilevel pores causes a reduction in channel diameter because the interlocking pores which have implications for the separation of water molecules from dissolved materials can occur.

4. Conclusion
The manufacture of Al-Cu pillared clay membrane using a simple mixing method to filter methylene blue dye has been conducted. The X-Ray Diffraction (XRD) showed that the basal spacing of the Al-Cu pillared clay was higher than natural clay. Pore volume and pore diameter of the Al-Cu pillared clay were greater than the natural clay yet the surface was smaller. The methylene blue filtration results showed clear and colourless liquid at all concentrations of methylene blue. Rejection value increases with the increase in concentration but the water flux values decreased.

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