Nano-ZnO impregnated – cellulose acetate hybrid membrane for increasing eugenol content in clove oil

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Abstract Clove oil is an essential oil that is obtained from cloves leaf. Indonesia is one of the largest producer of clove oil in the world. However, the quality of clove oil which is directly obtained from cloves leaf has low quality. This is due to the low concentration of eugenol in crude clove oil that is 60-80%. The purpose of this research is to increase the quality of clove oil by increasing the concentration of eugenol. In this research, clove oil is being purified by using Cellulose Acetate (CA)-ZnO nanofiltration membrane. The membranes were fabricated by dry-wet phase inversion method from dope polymer solution in acetone. The SEM results revealed the formation of nano-particles framework among the polymer matrix. The additions of 0.5 wt-% of nano-ZnO slightly increase the content of eugenol in permeate from 69% to 72%. However, the further addition of nano-ZnO decreases the content of eugenol drastically to 69% (no separation occurs) with the addition of 1.0 and 1.5 wt-%. The addition of high concentration of nano-ZnO (more than 0.5 wt-%) will produce large nano-particle cluster with macro-voids around the cluster which decreases the membrane selectivity.

Keyword: cellulose acetate, clove oil, essential oils, eugenol, hybrid membrane, nano-ZnO,

1. Introduction
Clove oil is an agricultural commodity with economics value. Clove oil itself is an essential oil produced from clove plants (Eugenia caryophyllata Thunb). This essential oil can be obtained from flowers, trunks, and leaves of clove plants. The quality of the oil is evaluated from the content of phenol, especially eugenol. The quality of clove oil is determined by eugenol [1,2]. Eugenol is one of the main components of essential oils isolated from cloves (Eugenia caryophyllata), which have been widely used as herbal remedies to treat dyspepsia, acute inflammation, and diarrhea [3]. Eugenol also has some potential for the industry, namely in the flavor industry and perfume industry [2]. While β-Caryophyllene is an impurity that must be removed due to its effect that decrease the purity of clove [4].

Membrane separation technology can be proposed as an alternative separation technology because it is now known as a low cost technology, low energy consumption, can be done in light operating conditions, and easy to scale up [5,6]. The process of fractionation distillation, involving evaporation and latent heat of vaporization that usually in a large amount, so this process requires a lot of energy. While one of the advantages of separation with the membrane itself is the cost of separation is low [7]. However, the membrane also has several weaknesses; easy fouling in the surface of membrane resulting in drastically lower productivity, incompatibility of membrane material with some chemicals that cause swelling,
dissolved, or weaken, and most membrane modules can not be operated at high temperatures [8,9]. The only literature to report on clove oil purification using membranes is reported by Nasution et al. at 2014. They used a cellulose-chitosan membrane to purify clove oil, the result obtained with 2.5 bars trans-membrane pressure showed a permeate flux of 0.239 L/m².sec with the highest eugenol level achieved was 58.21% [10].

Hybrid membrane, also known as mixed matrix membrane, is a membrane of a combination of polymeric (organic) and inorganic materials that are useful for maintaining good membrane permeability and selectivity. The matched combination of polymer and inorganic filler combinations has an effect on hybrid membrane development [11]. The ratio of hybrid membrane development resistance will determine the minimum performance of the membrane [12]. In this research, hybrid membrane will be developed by adding nano-ZnO material. The addition of this nano-material is expected to reduce the swelling problem in the membrane. Therefore, a nanofiltration nano hybrid membrane with Cellulose Acetate (CA)/nano-ZnO in purification of clove oil to obtain eugenol will be developed. The novelty of this research is the use of Cellulose Acetate (CA)/nano-ZnO membranes to purify crude clove oil and the way to overcome swelling problem.

2. Material and methods

Materials

Cellulose acetate with 53-56% acetic content was purchased from Alpha Chemika, India. Crude cloves leaf oil was obtained from clove farms in Semarang, Indonesia with the chemical characteristics as shown in Table 1. Nano-particles ZnO was supplied from Nano Center Indonesia, Indonesia. Industrial grade nitrogen gas with purity >99% was purchased from Aneka Gas, ltd., Indonesia.

| No.  | Chemical composition                                      | Percentage (%) |
|------|------------------------------------------------------------|----------------|
| 1.   | Phenol, 2-methoxy-4-(2-propenyl) (Eugenol)                | 69.51          |
| 2.   | Alpha-Cubebene                                            | 0.93           |
| 3.   | Trans-Caryophyllene                                        | 25.19          |
| 4.   | Alpha-Humulene                                             | 2.79           |
| 5.   | Hexadecanoic acid, 1-(Hydroxymethyl)-1,2-ethanediyl ester | 1.58           |
|      | Total                                                      | 100            |

Fabrication of membrane

In this study, two types of membrane were fabricated. Membrane fabrication was performed using dry-wet phase inversion technique [13,14]. The first type was neat CA membrane with polymer concentration of 17 wt-% and the second type was nano hybrid membrane with the same polymer concentration and nano-ZnO incorporation with 0.5, 1.0, 1.5 wt-% concentration in total solid. The membranes were fabricated by preparing dope solution consisting of CA polymer and acetone as solvent for first type membrane and CA polymer, acetone, nano-ZnO for second type of membrane. An appropriate amount of nano-ZnO membrane was filled to acetone in an Erlenmeyer flask then was sonicated for 60 min. the CA polymer was then added to the nano-ZnO solution and stirred for 24 h to obtain a homogeneous solution. Furthermore, the solution was allowed to stand for another 24 h to remove air bubbles. The membrane was casted on the clean glass
plate using casting equipment with a film thickness of 150 μm. The casted film was allowed for dry coagulation first for 30 seconds and subsequently the film on the glass plate was immersed in a solidification bath containing demineralized water for 24 h under room temperature (28-30°C). The membranes were dried in an oven with temperature of 40-50°C for 24 h.

**Membrane morphology characterization**

Surface morphology of the membrane was analyzed using scanning electron microscope (SEM). A piece of dried membrane sample was placed on sample holder and then it was coated with pure platinum (sputtering) that serves as a conductor [15]. The sample was observed under SEM JEOL series JSM-6510-LA, Japan with certain magnification.

**Membrane swelling measurement**

Membrane swelling was presented as the ratio of swollen membrane and initial membrane volume. It is hard to measure the volume of the membrane directly. Yi and Bae [16] proposed the gravimetric method to measure the volume of membrane. Membrane samples (5 cm x 5 cm) were dried at 50-60°C for 60 min then weighed as dry membrane weight (W₀). The membranes were then immersed in eugenol for 8 h and then wiped with filter paper before weighing as swollen membrane weight (Wᵢ). The degree of swelling was calculated as the ratio of volume change as expressed by the equation 1.

\[
\frac{V_i}{V_0} = \frac{(W_0/\rho_{mem}) \times [(W_i - W_0)/\rho_{eug}]}{W_0/\rho_0}
\]

(1)

Vᵢ and V₀ were the membrane volume of swollen and initial condition, respectively. ρ<sub>mem</sub> was the membrane density of swollen membrane without eugenol inside membrane. ρ₀ was the density of dry membrane, in this study the ρ<sub>mem</sub> and ρ₀ were assumed to be the same. ρ<sub>eug</sub> was the density of eugenol.

**Filtration test procedure**

Flux determination was performed with a dead-end filtration instrument. The simple schematic diagram of membrane cell filtration is shown in Figure 2.1. A piece of membrane with an effective area of 12.57 cm² was mounted on membrane holder. The cylinder was placed over the membrane holder and tightened. To the feed chamber which has been membrane installed inside was flowed a mixture of Clove Oil and n-Hexane 50% wt. The nitrogen gas was flowed on the membrane and the pressure was maintained at 5 bar. The permeate was collected for 1 h filtration process. Permeate flux was calculated using equation 2.2 [17].

\[
J = \frac{V}{A \cdot t \cdot \Delta P}
\]

(2)

With, J was a permeate Flux (L/m².bar.h), V was volume of permeate (L), A was an effective area of the membrane (m²), t was the operating time time in batch (h), ΔP was the trans-membrane pressure (bar).
3. Results and discussions

Surface morphology of membrane using SEM

Characteristic of membrane surface is important to be observed because it provides the separation properties of membrane. To obtain the detail structure image of membrane surface, the SEM analysis at 20,000x magnification has been performed. The SEM images of membrane surface were displayed in figure 2.

![Figure 2. SEM image of membrane surface (A) neat CA membrane, (B) CA-NanoZnO 1.0 wt-% hybrid membrane at 20,000x magnification.](image)

The effect of nanoZnO addition on the membrane surface structure was observed. As shown in Figure 2, the surface structure of both membranes are significantly different. The neat CA membrane as shown in sub Figure 2.A was dense and there is no unselective void was observed. Meanwhile, after impregnating the nanoZnO particles in CA dope solution, the macrovoids (unselective voids) were observed as shown in sub Figure 2.B. The formation of unselective void was formed due to the low affinity between particle surface and polymer matrix [18]. This insufficient attachment of nano particles in CA polymer was reported as result of low adhesiveness of the particle and irregular shape of the particles. The formation of unselective void is not beneficial for membrane development because it reduces the selective properties of the membrane. Particles agglomerates were also observed in the hybrid membrane, this is not beneficial for
membrane separation. Nano particle should spread evenly over the membrane surface. Agglomeration of nano particles was formed as a result of attraction force between nano particles itself. It has been also found that some other organic-inorganic hybrid membrane such as CA-nanoZnO exhibits the phenomenon of unselective pore-forming in polymer matrix system during phase inversion.

**Swelling degree of fabricated membranes**

One of the polymeric behavior when contact with eugenol is to swell. The swelling degree of membrane is the increase of membrane volume as a result of liquid penetration. Swelled membrane changes the separation properties of the membrane. As reported by Kusworo [19], the swelled membrane decreased the membrane separation efficiency up to 0% (no separation occurred). The addition of nano particles was intended to suppress the swelling degree of membrane. The effect of nano particle addition on the membrane swelling degree was shown in Figure 3.

NanoZnO addition in CA dope solution significantly affected the membrane swelling degree. As shown in Figure 3, the addition of nanoZnO decreased the swelling degree of the membrane. The neat CA membrane’s volume expanded its volume up to 25% after being immersed in eugenol for 8 h. The addition of 0.5 wt-% of nanoZnO decreased the swelling degree from 25% to 15%. The swelling degree decreased along with the addition of nanoZnO particles. The lowest swelling degree was observed in the hybrid CA membrane with 1.5 wt-% of nanoZnO impregnation. The membrane swelling was suppressed by the addition of inorganic particles because the particles restricted the movement of polymer chain. This restriction made the eugenol molecule couldn’t penetrate into polymer body. This becomes a contradictory where the addition of nanoZnO is able to overcome the swelling problem but on the other hand it increases the formation of unselective pores which decreases the membrane performance.

![Figure 3. Swelling degree of fabricated membranes](image-url)
Cummulative flux in clove oil filtration

Cummulative flux is total volume of permeate obtained during filtration process in a dead end filter for an hour. Permeate flux is one of the membrane performance parameter that shows the membrane productivity. The effect of ZnO loading in CA matrix on the membrane cummulative flux is shown in Figure 4. The variation concentration of nanoZnO impregnation in CA membrane gives a significant effect on cummulative permeate flux profile.

In the addition of nanoZnO filler as shown in the Figure 4, the commulative flux of permeate increased as the higher concentration of nano ZnO in CA polymer. This is due to the addition of nanoparticles during membrane fabrication prevents the formation of clogged pores, other than that the nano particles also keep the membrane from the compaction caused by pressure driven over the membrane [20]. In addition, the nano particles formed agglomerates that creating macro void. The macrovoid provides massive mass transfer through the membrane in dead-end filtration system. An increase in flux due to pore formation in membrane development is a contradiction with the performance of separation. The separation properties of the membrane decrease along with the larger pore formed during phase separation. In the development of membranes for the separation of eugenol and caryophyllene (this work), a non-pore membranes are preferred because they are effective in separating compounds with slight molecular size differences.

![Figure 4. Cumulative flux of clove oil filtration process](image)

Eugenol content of permeate

The performance of membrane separation in this study was evaluated by observing the concentration of eugenol in the permeate. The high concentration of eugenol in permeate shows good membrane separation performance. Separation of eugenol with caryophyllene is expected to occur based on differences in the affinity of each molecule. Eugenol is a compound that is more hydrophilic than caryophyllene [21,22]. Therefore, the membrane that is expected to be produced in this study is a non-pore membrane. The effect of adding nanoZnO in polymer CA to the performance of membrane separation is shown in Figure 5.
Based on Figure 5, a decrease in the concentration of eugenol in permeate occurs along with the increase in the concentration of nanoZnO in dope solution. In neat CA membranes, the concentration of eugenol in the permeate was 75% or increased by about 9% of the eugenol content in the feed. In the addition of nano ZnO as much as 0.5 wt-% the concentration of eugenol in the permeate became 72% or increased by about 4%. While the addition of nano ZnO more than 0.5 wt-%, the concentration of eugenol in the permeate was the same as the level in the feed. This shows that there is no separation in this condition. As shown in the SEM analysis, the addition of nano ZnO caused the formation of non-selective pores due to particle deattachment and agglomerate formation [23-25]. Pore formation on the membrane makes the membrane not selective against eugenol and caryophyllene. Separation will occur based on their molecular size (size exclusion), while the size of eugenol and caryophyllene slightly different. Therefore, it can be concluded that the addition of nanoZnO on the CA membrane is able to reduce the membrane swelling degree however it decreases the performance of membrane separation drastically. To overcome this problem, some modifications are needed to enhance the adhesive properties of nanoparticles and increase the degree of distribution of nanoparticles in dope solutions to prevent the agglomerate formation.

![Figure 5. Eugenol content in permeate](image)

**Conclusion**

Based on solubility test, CA membrane was the only polymer which was not soluble in eugenol, however swelling still occur. The addition of nano ZnO in CA membrane matrix significantly reduce the swelling degree of the membrane from 25% to 5%. The addition of nano ZnO in CA membrane created the macro void which is resulting in significant enhancement of flux but reduced the membrane selectivity (no separation process occur). Using neat CA membrane the eugenol content increased from 69% to 75%. The addition of high concentration of nano-ZnO (more than 0.5 wt-%) will produce large nano-particle cluster with macro-voids around the cluster which decreases the membrane selectivity.
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