PAPER • OPEN ACCESS

Garlic-based phenolic nanopowder as antibiofouling agent in mixed-matrix membrane

View the article online for updates and enhancements.

Garlic-based phenolic nanopowder as antibiofouling agent in mixed-matrix membrane

Yusuf Wibisono[1, 2,4], Ade Y. Putri[1], Shinta R. Dewi[3], Angky W. Putranto[1], Nimatul Izza[1]

[1]Bioprocess Engineering, Univ. of Brawijaya, Jl. Veteran No.1 Malang 65145,
 Indonesia
[2]MILI Water Research Institute, PO Box 301 ML, Malang 65101, Indonesia
[3]Food Water Waste, The University of Nottingham, Nottingham, UK
[4]Corresponding author, Email: Y_Wibisono@ub.ac.id

Abstract. The mixed matrix membrane has been developed in this work by using cellulose acetate as a membrane matrix and garlic-based phenolic nanopowder as an anti-biofouling filler. The membrane prepared using the phase inversion method, utilizing dimethylformamide (DMF) as a solvent. Three variation of garlic extract (GE) nanopowder concentration of 0.5%, 0.75%, and 1% were used, respectively. The mixed matrix membranes were tested their final thickness, morphology by using SEM, tensile strength, elasticity, clean water flux, and bacterial adhesion. Anti-biofouling activities of the garlic extract nanopowders were confirmed from the *Escherichia coli* bacterial adhesion, which 32 cells adhered in the pristine membrane surface, whereas nanopowder concentration of 0.5%, 0.75%, and 1% mixed matrix membranes show 9, 12 and 10 cells adhered in the membrane surface, respectively. The phenolic compounds in the mixed matrix membranes were able to inhibit bacterial growth and potentially used for a safe and non-toxic tool for food processing, including juice clarification.

1. Introduction

Membrane is a selective and semipermeable thin layer between two phases and can be employed for food processing, for instance to clarify fruit juices [1]. However, a major obstacle in membrane processes is the presence of biofouling [2, 3]. Prevention of biofouling can be done, among others, by impregnated an anti-biofouling agent in the membrane matrix [4, 5].

Garlic contains phenolic substances which have the ability as an antimicrobial material. Antibacterial activity of garlic extract can control pathogenic bacteria, both Gram-negative and positive [6]. In this work, garlic extract was filled in the cellulose acetate polymers matrix to form a mixed matrix membrane with enhanced anti-biofouling properties. The effects of adding garlic extract with different concentration were investigated in terms of mechanical and physical properties as well as the biological properties of the membranes.

2. Material and Methods

2.1. Garlic extraction

Garlic as the main substances of this research was obtained from the local market, peeled and washed prior extracted. The garlic extract has been made by using a microwave-assisted extraction (MAE) method with extraction time of 3 minutes and garlic to ethanol ratio 1:8 (w/v). The extraction process following the methods from previous work [7].

2.2. Membrane fabrication

Mixed matrix membranes were fabricated from cellulose acetate powder and dimethylformamide solvent (Merck, Germany), added with garlic extract with a concentration of 0.5, 0.75, and 1%. Table 1 below shows details on membrane composition.

Table 1. Membrane composition

Process parameters	Composition			
	DMF Solvent (mL)	Garlic extract/GE (%)	Cellulose Acetate/CA (gram)	Casting thickness (mm)
Pristine	20	0	4.00	0.3
0.5% GE	20	0.50	3.98	0.3
0.75% GE	20	0.75	3.97	0.3
1% GE	20	1.00	3.96	0.3

The three components were stirred using a magnetic stirrer in a covered beaker glass until it reached a homogeneous solution. The solution then left unstirred for 24 hours to remove possible bubbles in the solution. After 24 hours, the solution was poured and cast using a membrane casting knife (Elcometer, UK) with a casting thickness of 0.3 mm. The cast membrane sheet immediately immersed in the coagulant bath filled with distilled water for approximately 10 minutes until the membrane sheet completely solidified. The solid membrane sheet was then dried using nitrogen gas.

2.3. Membrane properties measurement

Membrane thickness was measured using a micrometer with 0.01 mm accuracy. Measurements were made at five points, including the bottom, top, right, left, and middle edges. The results were then averaged.

Tensile strength and elasticity testing were used to find out how much the ability of the membrane to withstand the applied force. Elongation at break is the change in the maximum length of the membrane sheet before it breaks. A used device for the mechanical properties was Imada ZP-200n, Japan.   Clean water flux was calculated by using the following equation (1):

$$J = \frac{V}{A.t}$$

(1)

Where :
J = flux (L/m^2.hour)
V = volume of permeate (Liter)
A = membrane surface area (m^2)
t = filtration time (hour)

The clean water flux was tested under the cross-flow condition using a customized membrane module test. The membrane diameter was set at a diameter of 6 cm, and transmembrane pressure was set at 0.5 bar provided by a pump. The clean water flux measurement has been done every 3 minutes for 27 minutes.

Antibacterial properties of the membrane were investigated by the measured adhesion rate of *Escherichia coli* onto to membrane surface. At the first stage, the bacterial culture was prepared by using a sterilized Nutrient Broth (NB). Bacteria were taken using inoculation loop, then immersed *E. coli* bacteria on NB media and became the initial culture. The initial culture was then incubated for 24 hours at 37 ^{o}C. Dilution was carried out by using peptone and the solution was homogenized. The diluted solution was placed in a beaker glass, and the membrane sample sheets were immersed in the solution. The solution was then incubated at 37 ^{o}C for 8 hours. After 8 hours of immersion, the membrane sheets were collected and immersed in the formamide solution to fix the cells adhered to the membrane surface. The membrane samples were observed under a SEM (FESEM-FEI Quanta FEG650, USA) to calculated the averaged number of bacteria attached to the membrane surface. An image processing software (ImageJ, USA) was used to determine bacterial attachment.

3. Results and Discussion

3.1. Membrane thickness

Measurement of membrane thickness has been done to calculate the shrinkage rate of the membrane after casting and drying. The initial casting thickness was 0.3 mm. The final membrane thickness based on different composition is shown in figure 1.
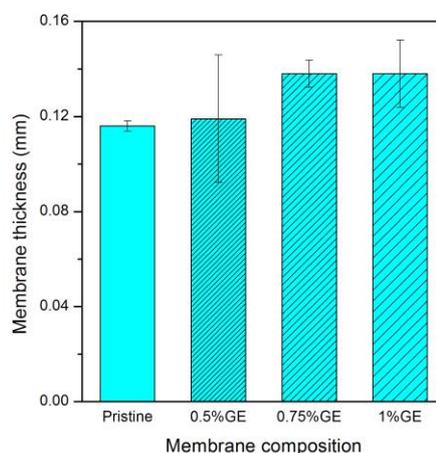

Figure 1. Final membrane thickness of different membrane compositions.

As shown in figure 1, the pristine membrane had a mean thickness of 0.115 mm. By adding garlic extract, the mean thickness was increased to 0.119 mm, 0.138 mm, and 0.138 mm, for the addition of garlic extract of 0.5%, 0.75%, and 1%, respectively. The addition of garlic extract, however, did not increase the membrane thickness significantly.

3.2. Mechanical properties of the membranes

The membrane tensile strength and elongation at break of the membranes are shown in figure 2.
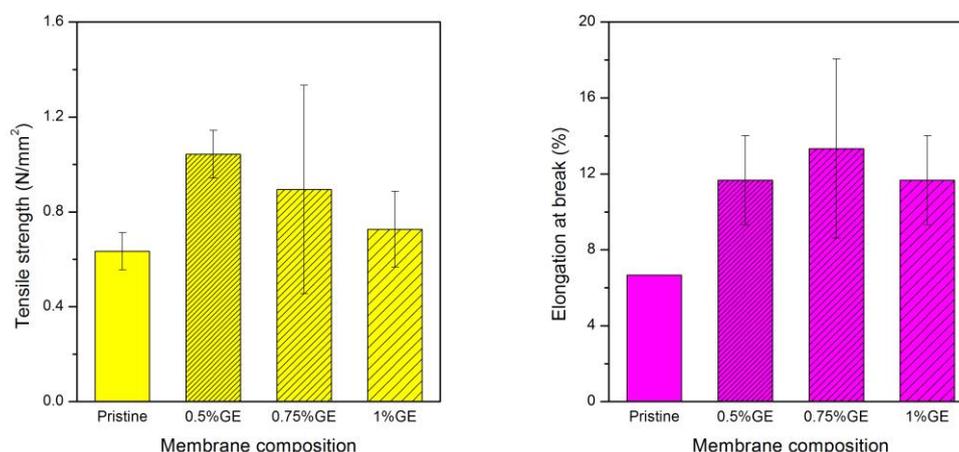
**Figure 2.** Membrane tensile strength (left) and elasticity (right) of different membrane compositions.

As shown in figure 2, the pristine membrane could handle mechanical force up to 0.634 N/mm^2. While adding garlic extract into the cellulose acetate matrix could affect the tensile strength with the value of 1.043 N/mm^2 0.894 N/mm^2, and 0.727 N/mm^2, for the addition of garlic extract of 0.5%, 0.75% and 1%, respectively. There was no significant change of the membrane tensile strength due to the addition of garlic extract, in which the condition was also found from the previous report [1].

Increasing filler concentration might increase tensile strength at a certain peak point, but the decreasing due to aggregation of the fillers and imbalanced distribution of the fillers in the polymer matrix [8].

As for membrane elongation at break, the pristine membrane observed at 6.67%. By adding garlic extract from 0.5%, 0.75% and 1%, the membranes elongation at break were increased to 11.665%, 13.335% and 11.665%, respectively. The addition of fillers with different concentrations might affect the mechanical value while the filler aggregated or was not distributed evenly on the membrane matrix [9].

3.3. Membrane mass transfer of water flux

Measurement of clean water flux passed the membrane pores is very important to measure mass transfer through the membrane. Measurements of clean water flux from different membrane compositions are shown in figure 3.
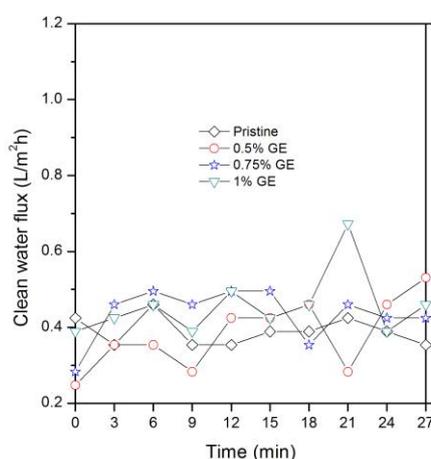
Figure 3. Continued clean water flux across the membranes.

As shown in figure 3, the stable flux observed over time. In the beginning, the pristine and modified membranes were showed similar flux values. Although the membrane with the addition of garlic extract showed a little bit flux increase, the flux change was not significant. The condition was observed until 27 minutes of running. The pristine membrane has an average flux value of 0.39 L/m^{2}h. Averaged clean water flux changed into 0.38 L/m^{2}h, 0.43 L/m^{2}h and 0.45 L/m^{2}h, for the adding of 0.5%, 0.75% and 1% of garlic extract, respectively.

3.4. Membrane morphology

The surface, cross-section and macro void structure of the membrane can be seen from observation by using an SEM. Image crosssection of the membrane under SEM is shown in figure 4 below.

As shown in figure 4, an asymmetrical membrane formed with the surface structure is denser than the bottom structure. The pristine membrane has a large macro void size and tends to be the same and evenly distributed. Membrane with the addition of 0.5% garlic extract, shows the formation of large pores, namely macro void which is irregular in structure and tends to be dense when compared with the pristine membrane. The interaction between cellulose acetate and garlic extract caused cavities between the mixing materials. The existence of large pores and scattered in several places may be caused by the air trapped in mixing the casted solution so that during the phase inversion process is filled with water as non-solvent and leaves the macro void pore [10].
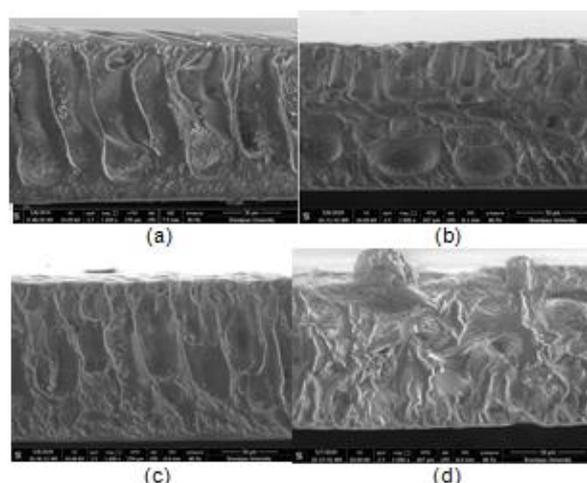
Figure 4. Cross-section SEM images of the membranes: (a) Pristine;
(b) 0.5% GE; (c) 0.75% GE; and (d) 1% GE.

Membrane with the addition of 0.75% garlic extract showed the formation of macro void which tends to be more regular and smaller when compared with the results of 0.5% garlic extract. It has an active layer and a supporting layer that was denser when compared to the pristine membrane. Membrane with the addition of 1% garlic extract has no clear macro void, instead of small microvoid and irregular shape pores observed. The higher concentration of fillers might affect the polymer solidification and pore development.

3.5. Membrane antimicrobial properties
Antibacterial activity measurement of cellulose acetate membrane with garlic extract fillers was found out how effective the garlic extract in inhibiting the attachment of bacteria onto the membrane surface. The result of *E. coli* bacterial adhesion is shown in figure 5.
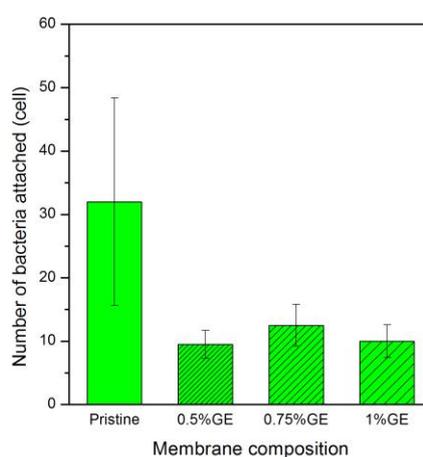
Figure 5. Bacterial attachment onto the membrane surface for different membrane compositions.

As shown in figure 5, the pristine membrane had the highest averaged number of bacterial adhesions of 32 cells. Adding garlic extract were able to decrease bacterial attachment up to 40-60% lower. There was no significant difference between garlic extract concentrations.

Phenol content in garlic extract seems effectively inhibiting bacterial growth on the membrane surface [11]. Flavanoid, which is a derivative of phenol compounds, works to denature bacterial proteins and destroying bacterial cells.

4. Conclusion

Mixed matrix membrane-based cellulose acetate impregnated garlic extract was manufactured by using DMF as the solvent. The used of garlic extract was aiming at improving the antibacterial properties of the membranes. The membranes were tested their mechanical properties, *e.g.,* tensile strength and elasticity, and mass transfer properties, *i.e.,* clean water flux through the membrane. There is no significant change for the addition of garlic extract into the membrane matrix compared with the pristine ones. However, the garlic extract addition was able to enhance the antibacterial properties of mixed matrix membranes by 40-60% decreased compared with the pristine membrane. Phenol content in garlic was assumed responsible for inhibiting bacterial attachment onto the membrane surface. Using natural antibacterial compounds would help the utilization of the mixed matrix membrane for food processing, *e.g.,* fruit juice clarification.

References

[1] Utoro P A R, Sukoyo A, Sandra S, Izza N, Dewi S R, Wibisono Y 2019 High-thorughput microfiltration membranes with natural biofouling reducer agent for food processing. Processes 7: 1.

[2] Wibisono Y 2014 Two-phase flow for fouling control in membranes. PhD thesis. University of Twente, The Netherlands.

[3] Shalahuddin I, Wibisono Y 2019 Mekanisme fouling pada membran mikrofiltrasi mode aliran searah dan silang. Jurnal Rekayasa Proses 13 (1), 6-15.

[4] Barambu N U, Bilad M R, Wibisono Y, Jaafar J, Mahlia T M I, Khan A L 2019 Membrane surface patterning as a fouling mitigation strategy in liquid filtration. Polymers 11 (10):1687.

[5] Pratiwi M K, Masyrifah L, Hawa L C, Dewi S R, Izza N, Argo B D, Sucipto S 2018 Enhanced antibiofouling properties of chitosan-based membranes by coating and blending of Moringa oleifera L extract. IOP Conference Series: Materials Science and Engineering 434 (1): 012191.

[6] Sadeghian A, Ghazvini K 2002 Antimicrobial activity of garlic extract againts Shigella. Iranian Journal of Medical Sciences 27 (3): 142-144.

[7] Izza N, Dewi S R, Setyanda A, Sukoyo A, Utoro P, Al Riza D F, Wibisono Y 2018 Microwave-assisted extraction of phenolic compounds from *Moringa oleifera* seed as anti-biofouling agents in membrane processes. MATEC Web of Conferences 204, 03003.

[8] Ahmad A, Waheed S, Khan S M, Gul S, Shafiq M, Farooq M, Sanaullah K, Jamil T 2015 Effect of silica on the properties of cellulose acetate/polyethylene glycol membrane for reverse osmosis, Desalination 355 (1): 1-10.

[9] Chou W L, Yu D G, Yang M C, Jou C H 2007 Effect of molecular weight and concentration of PEG additives on morphology and permeation performance of cellulose acetate hollow fibers, Separation and Purification Technology 57(2): 209-219.

[10] Wibisono Y, Faradilla A, Utoro P A, Sukoyo A,Izza N, Dewi S R 2018 Natural anti-biofoulant *Moringa oleifera* impregnated cellulose acetate mixed matrix membrane for juice clarification. J. Chem. Eng. Env.13, 100–109.

[11] Cahayani W A, Tanuwijaya C, Chi L X, Mulyastuti Y 2019 Antibacterial activity of garlic (*Allium sativum*) extract and molecular docking studies of allicin. AIP Conference Proceeding 2108 (1): 5110020