Preparation of Activated Carbon from Local Biowaste as Fillers for Mixed Matrix Membranes

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Abstract. Mixed matrix membrane combines the ability of polymer matrix to separate liquid subtances by using size exclusion approach and functionalized fillers which able to enhance the separation processes. Activated carbon might potentially used as fillers in mixed matrix membranes as this porous solid has ability on absorbing fluid phase subtances. Two indigenous locally produced biowaste were examined in this study for production of biomass derived activated carbon, *i.e.* candlenut and pangium shells. Chemically based activation process utilizing 10% of $ZnCl_2$, $CaCl_2$ and CH_3COOH, respectively. While carbonization temperature fixed at 400 °C and 600 °C, respectively. Based on the evaluation, activated carbon derived from candlenut shell can absorp iodine up to 629.905 mg/g and surface area of 694.661 m^2/g, by using CH_3COOH activator agent. The pangium shell derived activated carbon has the average iodine absorption value of 693.564 mg/g and surface area up to 764.864 m^2/g, using $CaCl_2$ activator agent. It is concluded that these biowaste have potential application of activated carbon as a separator for many industrial processes, including the utilization as absorber filling in mixed matrix membranes.

Keywords: activated carbon · candlenut shell · pangium shell · mixed matrix membrane · absorber · carbonization

1 Introduction

Membrane-based separation process gained attention as alternative method to replace conventional, complex and costly separation processes. Recently, there are plenty of developed membrane separation processes could be selected for specific purposes [1]. The wide range application of membrane separation processes has already studied, from wastewater treatment [2], water treatment [3], food processing [4], gas separation [5], and energy generation [6].

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Membranes are presently not only made from individual materials such as polymer, ceramic or metal, but also composite or mixed matrix membranes winning attention. Activated carbon, among others, could be utilized to enhance membranes permeability, rejection, mechanical strength and on the other hand provide a low fouling mixed matrix membranes [7]. Activated carbon particles embedded membranes have been used in ultrafiltration [8], membrane distillation [9], pervaporation [10], nanofiltration [11], and gas separation membrane [12].

Commercial activated carbon commonly derived from bituminous coal, coconut shell, and woods [13]. Recent studies reported the manufacture of activated carbon from other biomass source, such as oil palm empty fruit bunch [14, 15], palm shell [16], langsat (*Lansium domesticum*) empty fruit bunch waste [17], coconut leaves [18], pine cone shell [19] and microalgae [20]. Most of the studies reveals the potency of agricultural biowaste as activated carbon sources.

In this study, two Indonesian indigenous biowaste, *i.e.* candlenut and pangium shells, have been evaluated to be used as activated carbon biomass. Activated carbon can be made from a material containing both organic and inorganic carbon. The organic and inorganic materials that can be used as raw materials for the production of activated carbon are cellulose, hemicellulose and lignin are high, such materials include candlenut shell and pangium shell. Presentation of lignin content of 54.46%, hemicellulose and cellulose of 49.22% contained in raw material of candlenut shell. While pangium shell contains lignin 40.10% and 7.08% hemicellulose and cellulose of 12.24%. In addition to the three content, the hardness (density) of the feedstock also affects the adsorption produced by activated carbon, because the raw materials that have high hardness will require high temperatures in the carbonization process resulting in a high percentage of carbon as well.

Stages of the activated carbon manufacturing process include dehydration, carbonization and activation [21]. Dehydration is the process of removing water from raw materials. Carbonization is the process of decomposing organic cellulose to be carbon. On the carbonization of volatile elements will be removed so as to form pores. Carbonization is carried out at 400 °C and 500 °C. At 400 °C, depolymerization and rupture of bond C-O and C-C will occur. Cellulose will be degraded, lignin will begin to decompose to produce tar, pyrolysis solution, CO, CH_4 and gas H_2 will increase. At 600 °C temperature the gas formed will come out and to be formation of carbon pores. The content of tar, acids and aldehydes has come out all including hydrogen [22]. Activation is a process that the purpose is to enlarge the pores by breaking the carbon-hydrogen bonds or oxidizing surface molecules, thereby increasing the surface and affects the absorption power. Activation can be accomplished physically or chemically. Complete chemical activation by adding certain chemicals, and then perform immersion process [23]. The types of activators used in this study were $ZnCl_2$, $CaCl_2$ and CH_3COOH.

The use and utilization of local biowaste in the form of Candlenut sheet and pangium shell as activated carbon are by the green economy concept which is expected to be able to improve the community's economy while still paying attention to the environment with sustainable resources and development.

2 Material and Methods

2.1 Materials

Candlenut shell biowaste was collected from local farmers in Flores, East Nusa Tenggara, Indonesia and pangium shell biowaste was collected from local farmers in Trenggalek, East Java, Indonesia. Raw materials were collected and cleaned from dirt and residual flesh stick on the shell. The shells were then crushed until the size of 1–3 cm. The dehydration process used a temperature of 110 °C for 4 h to evaporate the water in the raw material. The carbonization process was carried out by placing the sample in a furnace (Thermo Scientific Type M110, U.S) at a temperature of 400 °C and 600 °C for 2 h. The sample then mashed by using a mortar and sifted through a 100-mesh sieve, and then stored the sample in a plastic clamp and glass bottle.

2.2 Activation Process

Three types of chemical activators ($ZnCl_2$, $CaCl_2$ and CH_3COOH) p.a. were supplied by (Merck, Darmstadt, Germany) were selected. The samples were first soaked in the solution of 10% for 24 h. Then, the suspension were washed to get neutral pH 7. The carbon particles were then separated from the solution by filtering with filter paper, to get paste form. Then carbon paste were then heated by using an oven (Thermo Scientific Type UT 6120, U.S) at 300 °C to dry the activated carbon paste for 1 h. Each series of experiments in the study was repeated three times.

2.3 Water Content

The activated carbon sample in each treatment weighed 1 g, and were then placed in a bowl that has been calibrate. The sample were heated in an oven at 105 °C for 4 h, then cooled in a desiccator and weighed. The heating process in the oven is repeated until a constant weight. The water content can be calculated by the following formula:

$$\%water\ content = \frac{a-b}{a} \tag{1}$$

where a is initial activated carbon weight (g), and b is activated carbon weight after being dried (g).

2.4 Iodine Number

In order to determine the absorbance capacity of the activated carbon, the iodine solution were selected. 0.25 g of activated carbon sample weighed and the mixed with 25 ml of 0.1N iodine solution. The solution were mixed for 15 min and filtered. The amount of 10 ml filtrate was titrated with 0.1 N sodium thiosulfate solution until light yellow. Then, 1% starch solution was added as indicator and the titration continued until the filtrate

becomes clear. The amount of sodium thiosulfate solution used must be recorded, to calculate the value of iodine absorption by using the following equation:

$$IAN = \left[\frac{10 - \left(\frac{BxC}{D} \right) \times 12.693 \times 2.5}{W} \right] \tag{2}$$

Where IAN is iodine number (mg/g); B is volume of total sodium thiosulfate used during titration (ml); C is normality of sodium thiosulfate (N); D is normality of iodine (N); W is mass of activated carbon (g); 12.693 is amount of iodine that corresponds to 1 ml of 0.1 N sodium thiosulfate solution.

2.5 Surface Area

The surface area of activated carbon was used to determine the pore surface area of the activated carbon produced. Based on the previous study, there was a high correlation between the iodine number and the specific surface area as measured by the BET method [24]. The calculated surface area (m^2/g) were calculated by the following equation:

$$Surface\ area \frac{m^2}{g} = \frac{iodine\ number\ (IAN)}{538,9} \times 594,3 \tag{3}$$

2.6 Imaging of SEM-EDX

The best result from the combination of carbonization temperature and activator derived from water content test results, absorption of iodine solution and surface area of activated carbon, were the observed under SEM-EDX (Inspect 24, FEI Ltd., U.S). imaging to investigate the pores formed.

3 Results and Discussion

3.1 Water Content

The average value of water content of the activated carbon derived from candlenut shell and pangium shells is shown in Fig. 1. The initial water content of candlenut shell was 8.55%, while the raw material content of the pangium shell was initially 10.40%.

After activation processes, carbonized pangium shell activated carbon has the lowest water content when treated at a carbonization temperature of 600 °C, and activated with 1.548% $CaCl_2$ activator solution. The activated carbon from the candlenut shell material has the lowest moisture content of 0.666%. under the carbonization temperature of 600 °C, and activated by acetic acid solution (CH_3COOH). Overall, water content of all samples were met SNI (Indonesian National Standard) 06-3730-1995, which the maximum water content is 15%.

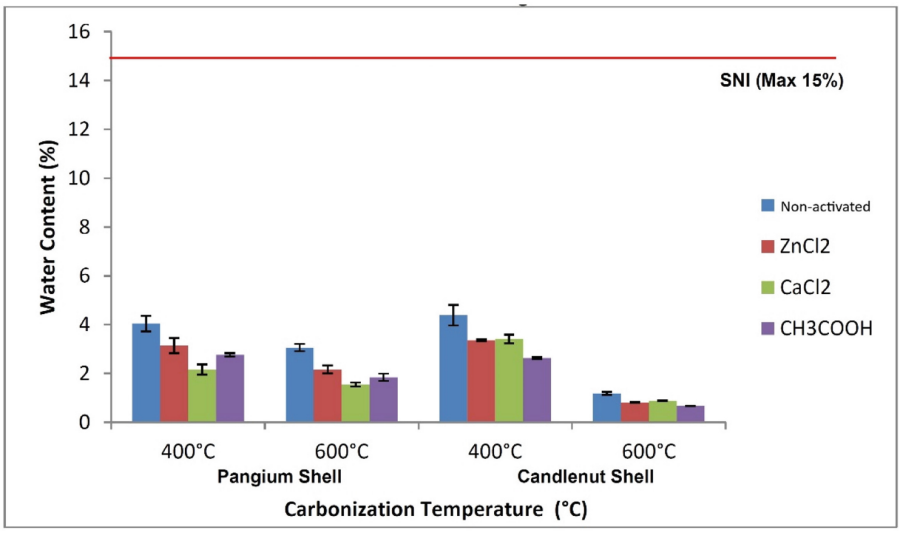

Fig. 1. Water content of activated carbon derived from pangium and candlenut shells, with different activator agents and carbonization temperature.

The best carbonization temperature was 600 °C. When H_2O reaches the boiling point at 100 °C, it will undergo a phase change and become a gas. At this time, free H_2O is bonded to carbon and forms a gas phase. Moisture might affects the pores of activated carbon. The higher the drying temperature, less water contained in the activated carbon, then could produce larger pores.

3.2 Absorption of Iodine Solution

The absorption capacity investigation of iodine solution on activated carbon aimed to understand the ability of activated carbon to adsorb low molecular weight components [25]. The absorption capacity of iodine can also be used to determine the absorption capacity of activated carbon for smelly components. The adsorption capacity of activated carbon for iodine is related to the surface area of activated carbon. The greater the amount of iodine, the stronger the ability to adsorb. The average result of iodine absorption test on activated carbon from pangium shell and candlenut shell is shown by Fig. 2.

As shown in Fig. 2, after carbonization at 600 °C and activated by $CaCl_2$ solution, the highest iodine value of pangium shell activated carbon was 693.564 mg/g. As for chandlenut shells, when the carbonization temperature was 600 °C and activated by CH_3COOH solution, the iodine number was the highest at 629.905 mg/g. High iodine number can be influenced by several factors. Factors that may affect include the difference in raw materials, time and carbonization temperature, the way of carbon activation, and the amount of activator concentration used in the activation process.

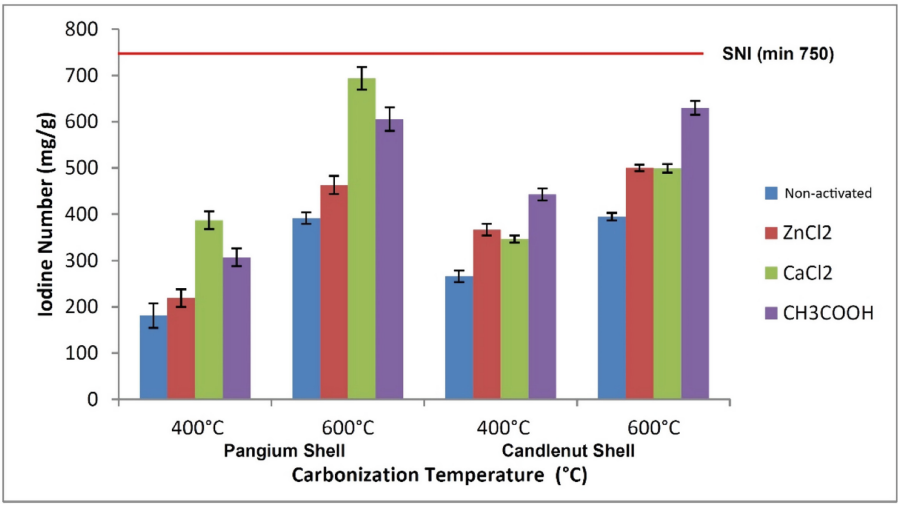

Fig. 2. Iodine number of activated carbon derived from pangium and candlenut shells, with different activator agents and carbonization temperature.

The candlenut shell and pangium shells contains lignin, cellulose, hemicellulose and high density value. The content of lignin, cellulose, hemicellulose and the density of a high material will produce carbon (C) with a high percentage as well. The content of lignin, cellulose hemicellulose and high density values will decompose into carbon when heated by using high carbonization temperature. The absorption capacity of iodine solution to activated carbon in this study did not meet the standard, due to the temperature of carbonization used was still too low to be able to decomposed the content of lignin, cellulose and hemicellulose.

Other factors that affect the absorption capacity of iodine solution are activator concentration and activation time. The longer the activation time of activated carbon, the greater the absorption capacity of the iodine solution. The longer the activation time will cause more impurities in the form of organic substances or inorganic substances dissolved from the surface of the pores of the carbon, thus causing an increase in absorption.

In this study the best use of activator agent on iodine absorption was produced on the pangium shell material while using $CaCl_2$ 10% solution and for the candlenut shell was reached maximum capacity when CH_3COOH 10% solution used. H^+ ions from the CH_3COOH solution diffuse into the carbon layer resulting in fractures and pore formation [23]. Pores formed will affect the absorption of iodine.

3.3 Calculation of Surface Area

The surface area of the activated carbon from candlenut shell and pangium shells is presented in Fig. 3.

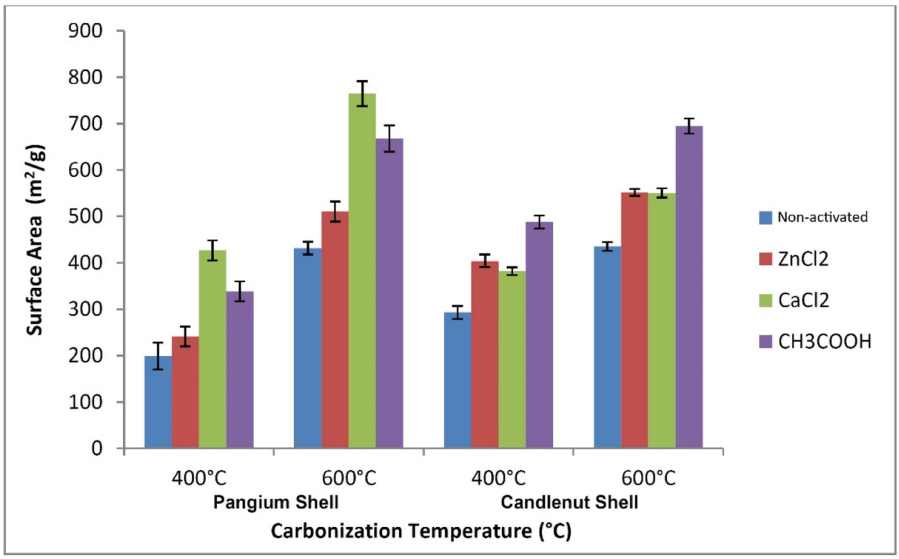

Fig. 3. Surface area of activated carbon derived from pangium and candlenut shells, with different activator agents and carbonization temperature.

As shown in Fig. 3, the highest surface area of pangium shell activated carbon of 764.864 m^2/g was achieved under the condition of carbonization temperature of 600 °C, and activated by using $CaCl_2$ solution. For the candlenut shell, after the carbonization temperature of 600 °C and activated by CH_3COOH solution, the largest surface area of 694.661 m^2/g was obtained.

Commercial activated carbon has a surface area of 300 m^2/g–3500 m^2/g, and could capture very fine particles ranging from 0.01 mm–0.0000001 mm. In this study, the surface area of the activated carbon from the pangium shell ranged from 199.289 m^2/g–764.864 m^2/g, and the surface area of the activated carbon from the candlenut shell ranged from 292.982 m^2/g–694.661 m^2/g. The activated carbon produced in this study met the standard of commercial activated carbon. The surface area of activated carbon is one of the factors that affect the adsorption capacity of activated carbon. The greater the surface area of activated carbon, the greater the adsorption capacity.

3.4 Analysis Imaging of SEM-EDX

From the previous results presented, the best result for activated carbon from candlenut shell was achieved when used 600°C carbonization temperature and 10% CH_3COOH activator solution. Meanwhile, the best result of activated carbon from the pangium shell was achieved when the carbonization temperature of 600 °C with the activator of 10% CaC_{l2} solution. The best results from both were then observed under the SEM EDX and shown in Fig. 4 and Fig. 5.

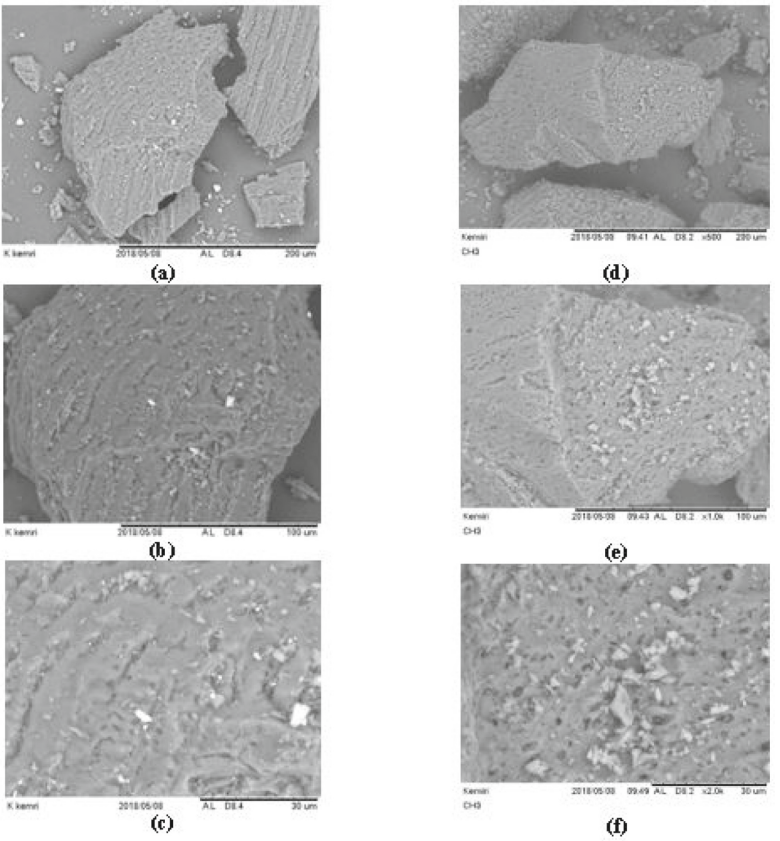

Fig. 4. SEM imaging of activated carbon from candlenut shell with carbonization temperature 600 °C without activation (a) magnification 500X (b) magnification 1000X (c) magnification 2000X, and activated carbon from candlenut shell combination carbonization temperature 600 °C with activator agent CH_3COOH (d) magnification 500X (e) magnification 1000X (f) magnification 2000X.

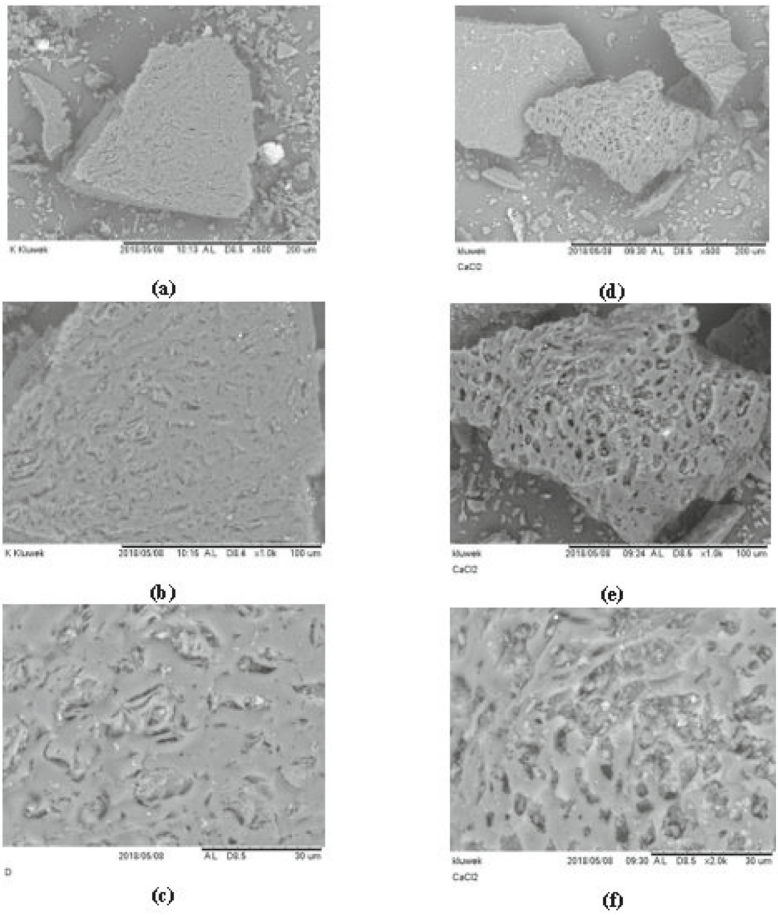

Fig. 5. SEM imaging of activated carbon from pangium shell with carbonization temperature 600 °C without activation, (a) magnification 500X (b) magnification 1000X (c) magnification 2000X, and activated carbon from pangium shell combination carbonization temperature 600 °C with activator agent $CaCl_2$ (d) magnification 500X (e) magnification 1000X (f) magnification 2000X. Finally, the component of the prepared activator carbons, measured by SEM-EDX, shown in Table 1.

Table 1. Percentage of Atomic Components

Atomic Components	**Candlenut Shell** (% weight)	**Pangium Shell** (% weight)
C	87.769	83.608
O	11.078	16.269
Ca	1.153	-
Al	-	0.122

4 Conclusion

Activated carbon were prepared from Indonesian local biowaste, i.e. candlenut shell and pangium shell. The best results from the candlenut shells were achieved when the carbonization temperature was 600 °C and 10% CH3COOH solution, with water content of 0.666%, iodine number 629.905 mg/g, calculation surface area of 694.661 m^2/g, and carbon component weight 87.769%. As for pangium shells, the best activated carbon was achieved by carbonization temperature of 600 °C, used activator agent of 10% $CaCl_2$, with water content of 1.548%, iodine number of 693.564 mg/g, calculated surface area of 764.864 m^2/g, and carbon component weight 80.845%. This local biowaste can be used for industrial applications, especially as a filler in mixed matrix membranes for various processes. In addition, the added value of biowaste can improve people's welfare while still paying attention to environmental sustainability in sustainable development through the green economy concept.

References

1. Wibisono Y 2014 Two-phase flow for fouling control in membranes. PhD thesis. University of Twente, The Netherlands.
2. Bilad, M.R. (2017) Membrane bioreactor for domestic wastewater treatment: Principles, challenges and future research directions. Indonesian Journal of Science Technology, 2 (1), 97-123.
3. Wibisono, Y., Ahmad, F., Cornelissen, E., Kemperman, A. and Nijmeijer, K. (2016) Dominant factors controlling the efficiency of two-phase flow cleaning in spiral-wound membrane elements. Desalination and Water Treatment, 57(38), 17625-17636.
4. Utoro P A R, Sukoyo A, Sandra S, Izza N, Dewi S R, Wibisono Y 2019 High-throughput microfiltration membranes with natural biofouling reducer agent for food processing. Processes 7: 1.
5. Nordin, N.A.H. (2018) Limitation in fabricating PSf/ZIF-8 hollow fiber membrane for CO_2/CH_4 separation. Indonesian Journal of Science Technology, 3 (2), 138-149.
6. Wibisono, Y., Nugroho, W.A., Chung, T.W. (2014b) Dry degumming of corn oil for biodiesel using a tubular ceramic membrane, Procedia Chemistry, 9, 210-219.
7. Eltom, A.E., Lessa, M.P.F., da Silva, M.J., da Rocha, J.C. (2012) Production and characterization of activated carbon membranes. Journal of Material Research and Technology, 1(2), 80-83.

8. Liu, Q., Huang, S., Zhang, Y., Zhao, S. (2018) Comparing the antifouling effects of activated carbon and TiO_2 in ultrafiltration membrane development. Journal of Colloid and Interface Science, 515, 109-118.
9. Zhao, L.H., Wu, C.R., Lu, X.L., Ng, D., Truong, Y.B., Xie, Z.L. (2018) Activated carbon enhance hydrophobic/hydrophilic dual layer nanofiber composite membranes for high-performance direct contact membrane distillation. Desalination, 446, 59-69.
10. Amaral, R.A., Habert, A.C., Borges, C.P. (2014) Activated carbon polyurethane membrane for a model fuel desulfurization by pervaporation. Materials Letters, 137, 468-470
11. Hosseini, S.M., Amini, S.H., Khodabakhshi, A.R., Bagheripour, E., van der Bruggen, B. (2018) Activated carbon nanoparticle entrapped mixed matrix polyethersulfone based nanofiltration membrane for sulfate and copper removal from water. Journal of Tai-wan Institute of Chemical Engineers, 82, 169-178.
12. Heidari, M., Hosseini, S.S., Nasrin, M.O., Ghadimi, A. (2019) Synthesis and fabrication of adsorptive nanoparticles (ACNs)/PDMS mixed matrix membranes for efficient CO_2/CH_4 and C_3H_8/CH_4 separation. Separation and Purification Technology, 209, 503-515.
13. Wibisono, Y., Sucipto, S., Perdani, C.G., Astuti, R., Dahlan, M. (2018) Halal compliance on drinking water industries: a future perspective, Proceeding of the 3rd International Halal Conference (INHAC2016); Muhammad, H.N.; Md Shariff, N.; Mahamood, S.; Fathullah, H.H.; Shahruddin, M.; Bhari, A., Eds.; Springer: Singapore.
14. Hameed, B.H., Tan, I.A.W., Ahmad, A.L. (2009) Preparation of oil palm empty fruit bunch-based activated carbon for removal of 2,4,6-trichlorophenol: Optimization using response surface methodology, Journal of Hazardous Materials, 164, 1316-1324.
15. Farma, R., Deraman, M., Awitdrus, A., Talib, I.A., Taer, E., Basri, N.H., Manjunatha, J.G., Ishak, M.M., Dollah, B.N.M., Hashmi, S.A. (2013) Preparation of highly porous binderless activated carbon electrodes from fibres of oil palm empty fruit bunches for application in supercapacitors, Bioresources Technology, 132, 254-261.
16. Yuliusman, Nasruddin, Afdhol, M.K., Amiliana, R.A., Hanafi, A. (2017) Preparation of activated carbon from palm shells using KOH and $ZnCl_2$ as the activating agent, IOP Conf. Series: Earth and Environmental Science, 75, 012009.
17. Foo, K.Y., Hameed, B.H. (2012) Preparation of activated carbon by microwave heating of langsat (Lansium domesticum) empty fruit bunch waste, Bioresources Technology, 116, 522-525.
18. Jawad, A.H., Rashid, R.A., Ishak, M.A.M, Wilson, L.D. (2016) Absorption of methylene blue onto activated carbon developed from biomass waste by H_2SO_4 activation: kinetic, equilibrium and thermodynamic studies, Desalination and Water Treatment, 57 (52), 25194-25206.
19. Li, K., Tian, S., Jiang, J., Wang, J., Chen, X., Yang, F. (2016) Pine cone shell-based activated carbon used for CO_2 absorption, Journal of Materials Chemistry A, 14, 5223-5234.
20. Sukoyo, Agung, Gunomo Djoyowasito, and Yusuf Wibisono. (2019) Unravelling the Potency of Activated Carbon Powder Derived from Cultivated Marine Microalgae as a Promising Filler in Mixed Matrix Membranes, AgriEngineering 1, no. 2: 188-204.
21. Wibisono, Y., Amanah, A., Sukoyo, A., Anugroho, F., & Kurniati, E. (2021). Activated Carbon Loaded Mixed Matrix Membranes Extracted from Oil Palm Empty Fruit Bunches for Vehicle Exhaust Gas Adsorbers. Evergreen, 8(3), 593-600.
22. Hendrawan, Y., Sajidah, N., Umam, C., Fauzy, M. R., Wibisono, Y., & Hawa, L. C. (2019, February). Effect of carbonization temperature variations and activator agent types on activated carbon characteristics of sengon wood waste (Paraserianthes falcataria (L.) Nielsen). In IOP Conference Series: Earth and Environmental Science (Vol. 239, No. 1, p. 012006). IOP Publishing.

23. Hendrawan, Y., Nurseta, D. Y., Utami, R., Trilaksana, M. I. A., Sumarlan, S. H., & Wibisono, Y. (2021, April). Effect of carbonisation temperature and activating agents on the characteristics of activated carbon produced from oil palm empty fruit bunch. In IOP Conference Series: Earth and Environmental Science (Vol. 733, No. 1, p. 012004). IOP Publishing.
24. Song-Yung Wang, Ming-Hsiu Tsai, Sheng-Fong Lo, Ming-Jer Tsai (2008) Effects of manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal, Bioresource Technology,Volume 99, Issue 15, Pages 7027-7033.
25. Cafer Saka (2012) BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with $ZnCl_2$, Journal of Analytical and Applied Pyrolysis, Volume 95, Pages 21-24.