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<https://doi.org/10.5109/4491651>

出版情報 : Evergreen. 8 (3), pp.593-600, 2021-09. 九州大学グリーンテクノロジー研究教育センター
バージョン :
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Activated Carbon Loaded Mixed Matrix Membranes Extracted from Oil Palm Empty Fruit Bunches for Vehicle Exhaust Gas Adsorbers

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(Received October 22, 2020; Revised May 30, 2021; accepted August 27, 2021).

Abstract: Mixed matrix membranes (MMM's) comprising cellulose acetate (CA) polymers with nano-activated carbon (nAC) were prepared and derived from Oil Palm Empty Fruit Bunches (OP-EFB) biowaste. At first, nAC's were prepared using carbonization-activation process, with pyrolysis temperatures applied at 300, 400, and 500°C, respectively. Furthermore, 100 kg/m³ ZnCl₂ solution were added for the activation process before sonicated at 28 kHz for 45 minutes. The adsorption performances were tested by using iodine value. The nAC prepared under carbonization temperature of 500°C, showed the best properties, *i.e.* 3.67% water content, 7.68% ash content, 22.87% volatile substances, 69.45% pure activated carbon levels and iodine value of 1000.35 mg/g, therefore selected and embedded into polymeric membrane matrices. In order to produce membranes matrix, cellulose was extracted from OP-EFB by 5-steps processes, *i.e.* preparation, hydrolysis, delignification, pulping and bleaching to obtain α -cellulose. The extracted α -cellulose then activated, acetelized, hydrolyzed, sedimented and dried to produce cellulose acetate (CA) polymers. Then, the CA matrixes filled with different ratios of CA:nAC, *i.e.* (4:1), (4:3), (4:5), to prepare mixed matrix membranes. The MMM's were then tested to adsorb CO, CO₂ and hydrocarbons produced by motorcycle combustion process. The highest pollutant removal was 16.12% and 11.77%, for CO and CO₂, respectively, while the highest HC removal was 15.23%. The biowaste-based MMM's were proven to decrease motorcycle exhaust gases from the testing chamber, comply with SNI (Indonesian National Standard) and contributed to environmental recovery.

Keywords: activated carbon; mixed matrix membrane; cellulose acetate; oil palm empty fruit bunches; vehicle exhaust gases; novel carbon resource sciences

1. Introduction

According to Indonesian Central Bureau of Statistics, the number of motorcycle ownership in Indonesia at 2018 tremendously increased and reached up to 120 million unit. The number made Indonesia ranked the third in Asian on motorcycle ownership, behind China and India. Motorcycle seems become preferable transportation mode in the future, concerning many barriers toward public transportation including long travel time, security and safety issues, limited route and poor schedule¹. Yet, the condition also gives negative impacts. The motorcycle exhaust gases, CO, CO₂ and hydrocarbons, contribute to high pollutants level in the air and affect on human health, including lung damages².

Parallel to promoting the policy to decrease the number of private vehicles, including motorcycles and enhancing the quality of public transportation, the effort to reduce emission are also particularly important. The accumulation of exhaust gases in the earth atmosphere contributes to greenhouse effect, global warming, and climate change. Many researchers proposed the use of material that can adsorb the exhaust gases, including ionic liquids³, silica gels, zeolite, alumina active, graphene, metal organic framework (MOF) and composite membranes⁴. Membrane technology performed a good capability for separation, purification and adsorption of substances⁵⁻⁷. Mixed matrix membrane is polymeric membranes matrix filled with organic or inorganic substances, used for adsorption of liquids such as enzymes and proteins⁸⁻⁹, and adsorption of CO₂, CH₄, and H₂ gases¹⁰.

Activated carbon is porous carbon material which has capability to adsorb molecules¹¹⁻¹²). Activated carbon derived from carbon-rich biomass, including agricultural waste and biowaste such as coconut shells, woods, and oil palm empty fruit bunches (OP-EFB)¹³⁻¹⁵). Due to its adsorption capability and low cost, powdered activated carbon can be used as filler in the mixed matrix membranes, to enhance separation of fluids¹⁶). However, to the best of our knowledge, there was no report on the utilization of activated carbon in polymeric membranes to reduce exhaust gases from vehicles.

In this work therefore, the use of mixed matrix membranes comprises of cellulose acetate (CA) polymers derived from OP-EFB as membrane matrixes and nano-activated carbon (nAC) from pyrolyzed OP-EFB as membrane fillers were prepared and utilized for adsorption of motorcycles exhaust gases in order to reduce emissions to the atmosphere. The aims of this study are two-fold, for utilizing and reducing OP-EFB biowaste¹⁷) and capturing the motorcycle gas emissions before released to the earth atmosphere.

2. Experimentals

2.1. Materials

Oil palm empty fruit bunches (OP-EFB) were taken from PT. Sawit Arum Madani, Blitar, Indonesia, as biowaste from crude palm oil production. The OP-EFB were cleaned from dirt and remained flowers and fruits. Clean OP-EFB then sun dried, removed the thorny parts and chopped into 1-3 cm length biomass.

The biomass were then divided into two portions. A portion was dehydrated, carbonated and activated to obtain nano-activated carbon (nAC) and the other was hydrolyzed, delignified, pulped, bleached and finally synthesized to produce CA. Some chemicals added during the processes, such as demineralized water, nitric acid (HNO₃), sodium hydroxide (NaOH), sodium sulfite (Na₂SO₃), hydrogen peroxide (H₂O₂), sulfuric acid (H₂SO₄), acetic acid (CH₃COOH) (anhydrous and glacial), dimethylformamide (DMF), zinc chloride (ZnCl₂), potassium iodide (KI), iodine, and sodium thiosulfate (Na₂S₂O₃). Motorcycle gas pollutants (CO, CO₂ and HC) were directly obtained from injection-type Yamaha Mio-GT motorcycle.

2.2. Extraction of α -cellulose

Cellulose were extracted from OP-EFB biomass via 5-steps processes, *i.e.* preparation, hydrolysis, delignification, pulping, and bleaching. Preparation step includes cleaning, sun drying, and chopping. The chopped biomass then milled using diskmill and dried using oven until reach 4-5% of moisture content. The dried OP-EFB powder then hydrolyzed by mixing of 150 gram OP-EFB powder and 1 L of 3.5% (v/v) HNO₃ and heated on 90°C for 2 hours. The sample then washed until reach neutral pH. The hydrolysis step was aimed at removing the amorphous structure of cellulose and obtaining the crystal portion. The next step was

delignification, conducted by adding 2% NaOH and 2% Na₂SO₃ (w/v) into the powder obtained from hydrolysis step, and heated on 50°C for 1 hour. The sample then washed until reach neutral pH. The delignification process aims to break the OP-EFB lignocellulose chain.

Further step was pulping process by immersing the sample into 17.5% NaOH (w/v) and heated by oven on 80°C for 30 minutes. The sample then washed until reach neutral pH. The immersion with NaOH promote swelling of cellulose structure, and becoming open structure. After immersion, hydroxyl functional group (-OH) more accessible and clear penetration into inner structure of the cellulose. The final step was bleaching by adding 10% H₂O₂ (v/v) into the pulp and heated on 60°C for 15 minutes, and continued by dried in the oven on 110°C for 6 hours. The white-yellowish and odorless α -cellulose powder was finally obtained with the degree of 80.4% followed the previous method¹⁸).

2.3. Synthesis of cellulose acetate

The α -cellulose powder then synthesized by adding 10% glacial CH₃COOH and stirred by 275 rpm, on 38°C for 60 minutes. Furthermore 2% H₂SO₄ were added and stirred by 275 rpm, on 38°C for 45 minutes. Mixed hydrous and glacial CH₃COOH with ratio 3:2 then added and again stirred by 275 rpm, on 38°C for 30 minutes. By those sequence processes, acetylation process occurred. Maintaining the temperature in mild condition was very important to prevent depolymerization of cellulose molecular chains.

For hydrolysis process, glacial CH₃COOH and demineralized water with ratio 2:1 the added and stirred by 275 rpm on 50°C for 30 minutes. The solution centrifuged by 1500 rpm for 15 minutes, sedimented and filtered until neutral pH, and dried by using oven on 70°C for 6 hours. The powdered cellulose acetate (CA) have been resulted, in the form of odorless and white powders. The level of substitution obtained around 2.2-2.7 was suitable for membrane applications. A Fourier transform infrared spectroscopy (FTIR, Shimadzu 8400S, Japan) was used to check the resulted CA compounds.

2.4. Synthesis of nano-activated carbon

Nano-activated carbon (nAC) was produced from OP-EFB through the process of cleaning and sun drying. The raw material was reduced in size to 1-3 cm and then followed by dehydration treatment with a temperature of approximately 110°C for four hours until the mass of the OP-EFB sample becomes constant. The process was continued with carbonization at temperatures of 300, 400 and 500°C with a time of 10 minutes, respectively. The results of the carbonization process were charcoal, and the size will be uniformed to 100 mesh using a sieve.

The activation process was carried out using 10% (w/v) ZnCl₂ solution. The best combination of temperature and activator treatment includes parameters of water content, ash, vapor, and pure activated carbon,

and its absorption of iodine was used for the synthesis of nano-activated carbon¹⁹). This synthesis was carried out by chemical activation assisted by ultrasonic waves with a frequency of 28 KHz for 45 minutes, then allowed to stand for 24 hours at room temperature and filtered. The filtrate was rinsed with distilled water to remove impurities and neutralize pH. The process was followed by drying using a temperature of 105°C for 3 hours to obtain nano-activated carbon (nAC). The activated carbon size was analyzed by using a particle size analyzer (PSA, Cilas 1090, France).

2.5. Preparation of mixed matrix membrane

MMM synthesis has been carried out by mixing the matrix, filler, and dimethylformamide as the solvent. Treatment variations were given based on differences in the mass ratio of CA and nAC, as measured by using analytical balance Mettler Toledo AL204, which are 4:1, 4:3, 4:5 and 4:0 as a control.

Therefore, obtained 4 (four) variations of MMM, pristine CA, CA: nAC (4:1), CA: nAC (4:3); CA: nAC (4:5), respectively. The ratio of CA:DMF was 10:90 (%w/w). Each suspension variation was stirred for 20 hours and followed by a sonication process for 1 hour. Then the solution was poured on a flat glass plate, casted with the thickness of 0.5 mm and allowed to dry in the oven for 24 hours at a temperature of 100°C. MMM was peeled from flat glass after dry conditions.

2.6. SEM analysis

Morphological observations of MMM were carried out using a scanning electron microscope (SEM, Hitachi TM3000, Tokyo Japan) and its constituent elements were known through an energy dispersive X-ray (EDX, Swift ED3000, Oxford UK) to confirm the presence of CA and nAC as MMM matrices and fillers.

Samples were prepared by freeze-fracturing the membrane in liquid nitrogen, coated with a gold layer 1.5-2 nm thick using a sputter coater under the argon flow to reduce sample run off due to electron beams²⁰).

2.7. Adsorption of exhaust gases

The level of MMM adsorption on motorcycle pollutant emissions (CO, CO₂, and HC) was carried out by using a fuel injection motorcycle (Yamaha Mio-GT, Japan) and motorcycle emission test using a gas analyzer (Technotest 488, Italy) in conditions before and after MMM inserted in a stainless-steel tube with a length of 13 cm and diameter 2 cm (as shown in Fig. 1).

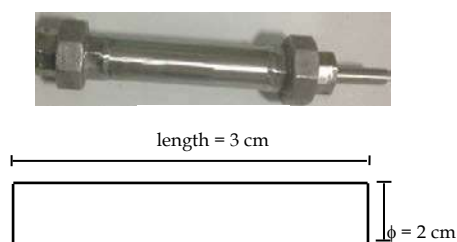


Fig. 1. Chamber apparatus for testing of exhaust gases.

Quantitative data that appears on the gas analyzer screen for control (without MMM in the adsorbent media) and all MMM variations were calculated through Equation 1 to get data of each % removal of CO, CO₂, and HC gas pollutant emissions from motorcycle exhausts.

$$R = \frac{E_0 - E_1}{E_0} \times 100\% \quad (1)$$

where:

R = Percent removal of each pollutant (%)

E₀ = concentration of pollutants without MMM (ppm vol (HC) and % vol. for CO and CO₂)

E₁ = concentration of pollutants with MMM (ppm vol (HC) and % vol. for CO and CO₂)

3. Results and Discussion

3.1 Overview of overall processes

The overview of processes, from preparation of OP-EFB, extraction of α-cellulose, synthesis of cellulose acetate, synthesis of nano-activated carbon, fabrication of mixed matrix membranes and exhaust gas adsorption test were summarized in Fig.2.

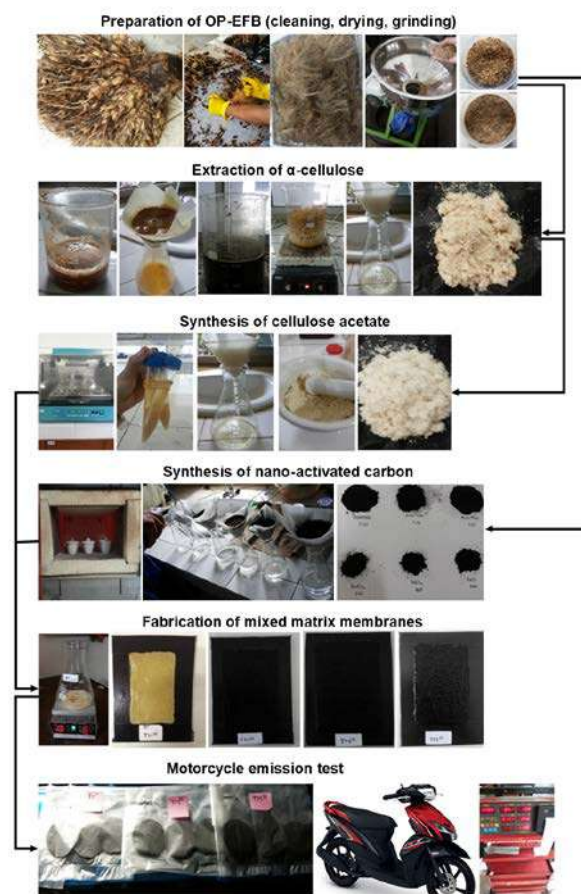


Fig. 2. Overview of overall processes.

3.2 Molecular characterization of the CA

Functional group analysis was carried out to determine the compounds after the acetylation reaction by identifying the typical absorbance values and functional groups contained in the CA by using FTIR²¹⁾. Fig. 3 shows the IR spectra of the compound.

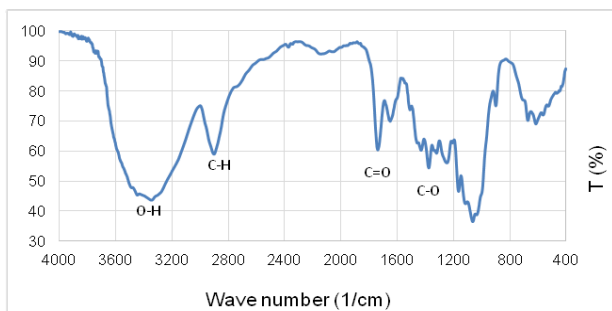


Fig. 3. FTIR spectra of the obtained CA powder.

From the IR spectra shown in Fig. 3, the chemical structure of cellulose acetate was composed of three functional groups, namely the C-O, O-H, C-H, and C = O groups. In the IR spectra also found that the O-H functional groups that have not been completely acetylated as seen in the wave number 3345 cm⁻¹ with a low peak depth level. This is in accordance with the criteria based on the degree of substitution and acetyl content in cellulose acetate. It is concluded that there was still an O-H group in cellulose that is not substituted.

The C-O group appears in the region of wave number 1374 cm⁻¹ and the C-H group in the region of wave number 2900 cm⁻¹. Based on the IR spectra, there is also an indicator of CA formation in the presence of C = O functional groups at wave number 1737 cm⁻¹ which is a carbonyl functional group from the acetylation process using acetic anhydride. Based on the IR spectra, it can be seen that process of cellulose acetylation of oil palm empty fruit bunches into CA have been successfully carried out.

The morphology of OP-EFB synthesized CA was observed by using SEM and are shown in Fig. 4. As shown, the morphology of the CA was consist of micron-sized cylindrical fibers which are interconnected and have perforated layers. The morphology of CA fiber was obtained due to the process of acetylation of cellulose compounds with acetic anhydride.

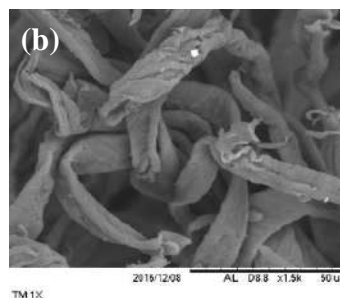
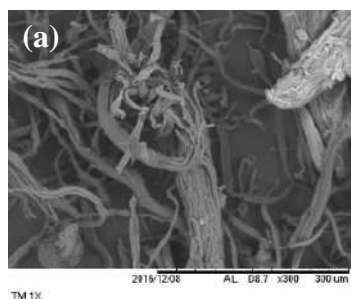


Fig. 4. SEM images of CA derived from OP-EFB, at the magnification of: (a) 300 and (b) 1500 times.

The EDX measurement aims to show the artificial CA content that has been produced and presented in Table 1.

Table 1. EDX spectrum in the synthesized CA

Element	Weight %	Weight % σ	Atomic %
Carbon	50.586	0.626	57.692
Oxygen	49.414	0.626	42.308

Based on the EDX spectrum, it is concluded that the main constituent elements of CA are carbon and oxygen atoms, no other elements are found indicating the absence of impurities or other compounds in CA, as it is already known that CA is a compound composed of carbon, oxygen, and hydrogen atoms.

3.3 Synthesis and characterization of nano-activated carbon

The 10% (w/v) ZnCl₂ was used as activator agent in the preparation of nAC. The agent could expanded the surface of carbon particle, thereby increasing the ability of adsorption. The ZnCl₂ was selected because as an acid salt, the ZnCl₂ could easily interacts with oxides or oxygen, and suitable for OP-EFB which has a high lignocellulose and oxygen contents.

The obtained nAC has been characterized and compared according to Indonesian National Standard (SNI 1995) of activated carbon and the results are presented in Fig. 5.

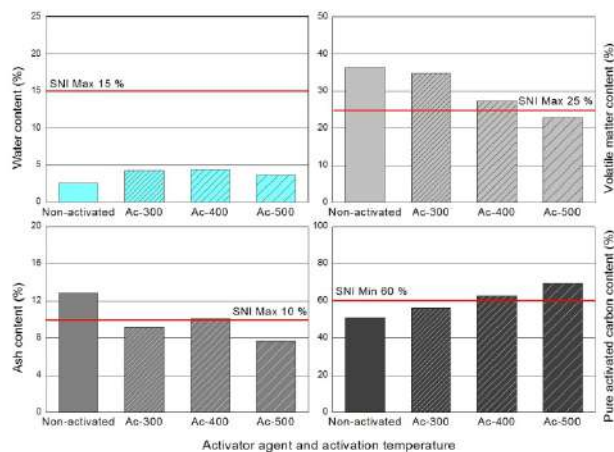


Fig. 5. Properties of powdered activated carbon derived from OP-EFB.

Based on the results shown in Fig. 5, the best activated carbon testing is activated carbon with a carbonization temperature of 500°C, because the test parameters of water content, ash content, levels of volatile substances, and pure activated carbon levels have met the SNI 1995 standard, i.e., 3.67% water content, 7.68% ash content, 22.87% volatile substances and 69.45% pure activated carbon levels. The iodine adsorption was presented in Fig. 6, the iodine number of activated carbons resulted from the 500°C carbonization temperature, shows the highest value of 1000.35 mg/g. The iodine number expresses the ability of activated carbon to absorb colored solutions less than 10 Å or 1 nm in size. The amount of absorption of activated carbon to iodine also illustrates the number of formed micropores structures. Based on the results in Fig. 6, it is known that the higher the carbonization temperature, the higher the absorption of iodine.

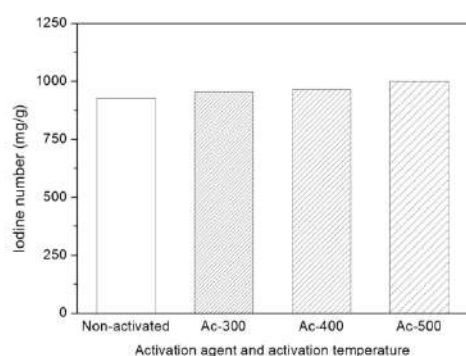


Fig. 6. Iodine number of powdered activated carbon.

Nano activated carbons (nAC) were then characterized its size and size distribution. The particle size distribution analysis showed that the percentage of nano-sized particles ($0.04 \leq \text{nAC} \leq 1 \mu\text{m}$) is 4.02 percent with obscuration of 13 %, while 50% of all particles were activated carbon with a size of $\leq 7760 \text{ nm}$.

3.4 Synthesis and characterization of mixed matrix membranes

Mixed matrix membranes synthesized from CA polymer derived from OP-EFB with variations in the filler's composition in the form of nAC, from carbonization temperature of 500°C. Four different variation ratio of CA:nAC (4:1), (4:3), (4:5), and pristine CA without adding the nAC filler, were mixed with dimethylformamide (DMF) with ratio of CA: DMF is 10:90 (%w/w). The DMF was selected because the similarity in the solubility parameter (δ) between CA and DMF, i.e. 10.7 for CA polymers and 9.4 for DMF²². Low difference in solubility parameters between the solvent and polymer supports a good dissolution process during membrane preparation. The mixture was stirred for 20 hours, and then sonicated with a frequency of 28 kHz.

The membrane surface morphology was observed using a scanning electron microscope and the images

presented in Fig. 7. Significant differences were seen between the four membranes, distribution of white spots on the surface of the cellulose acetate (CA) fiber matrix. White spots were not found on Pristine CA (membranes without nAC) but found on all other three membranes with the addition of nAC. White spots on SEM images represents the spread of nAC particles on the CA matrix.

The nAC particles embedded in the surface of CA polymer matrices and acts as adsorbent for the gases. Meanwhile, the pores developed between the CA matrices provide extensive surface area to enhance adsorption performance.

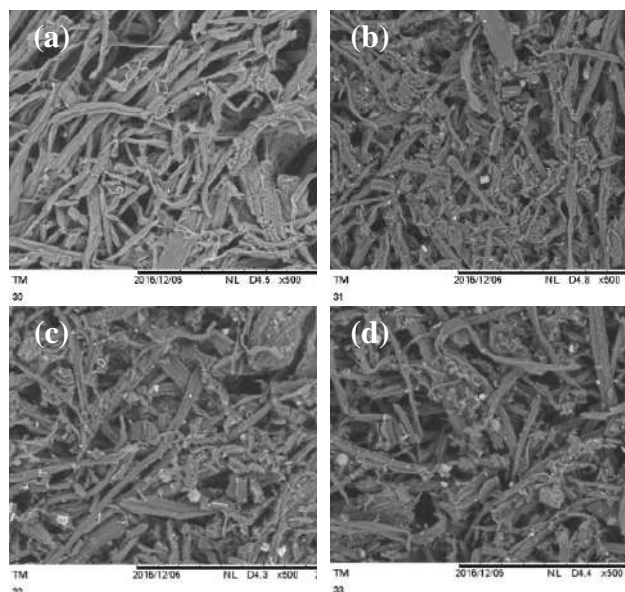


Fig. 7. SEM images of MMM surface: (a) Pristine CA, (b) CA:nAC (4:1), (c) CA:nAC (4:3), and (d) CA:nAC (4:5).

As for elemental composition of the MMMs were characterized by using the EDX and the summary was presented in Table 2.

Table 2. Summary of MMM elemental analysis using EDX

Element (%)	Pristine CA	CA:nAC (4:1)	CA:nAC (4:3)	CA:nAC (4:5)
Carbon	54.723	59.179	65.391	65.665
Oxygen	45.038	40.168	33.528	32.955
Silicon	0.143	0.181	0.367	0.434
Calcium	0.096	0.125	0.154	0.282
Zinc	n.a.	0.347	0.559	0.664

As presented in Table 1, the main constituent of the CA powder were carbon and oxygen atoms, and small portions was in the form of silica and calcium atoms. In the Table 2, the mixed matrix membranes were also composed of carbon, oxygen, silica and calcium atoms. The difference lies in the presence of zinc atoms, the membranes which filled with nAC.

The elements of carbon and oxygen are derived from the cellulose acetate matrix, in addition to the carbon atom comes from the filler (nAC). The nAC filler causes the composition value of carbon atoms in the mixed

matrix membranes were higher than the pristine CA membrane. The presence of silica was mainly due to the carbonization stage of the nAC which causes the silica body covering the surface of the OP-EFB fiber cell to split and form silica oxide compounds. The presence of calcium atom was presumably due to impurity from the synthesis process or originating from the OP-EFB itself as raw material for cellulose acetate (CA) and nAC²³, where the nutrient content in the form of calcium with a maximum limit of 0.83%.

The zinc element present in mixed matrix membranes comes from nAC due to imperfect washing during the manufacturing process, thus the ZnCl₂ activator reacts with oxides on the membrane to form zinc oxide compounds. Zinc chloride compounds can be formed due to the rest of the zinc chloride compound on carbon which were resulted from chemical activation reacted with oxygen²⁴. Among the mixed matrix membranes, the percentage of zinc content is directly proportional to the amount of nAC added in the membrane matrix as a filler.

3.5 Membrane adsorber for emission pollutants

The synthesized MMMs were tested for their performance in adsorbing motorcycle emission pollutants. Fig. 8 shows the MMM performance in adsorbing motorcycle emission pollutants.

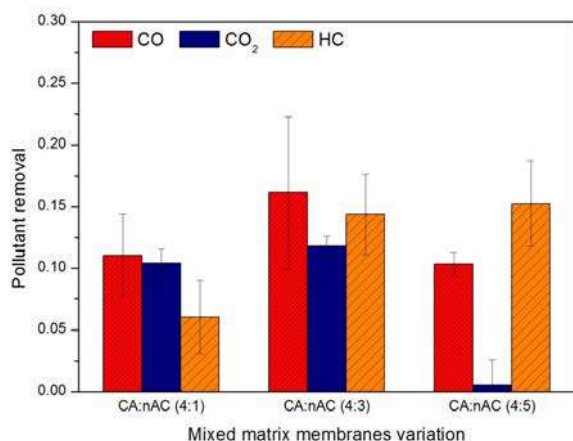


Fig. 8. Percent of motorcycle emission pollutant removal by the mixed matrix membranes.

As shown in Fig. 8, the highest pollutant removal was provided by mixed matrix membrane CA:nAC (4:3), especially for CO and CO₂ adsorption levels by 16.12% and 11.77%, respectively. While the highest HC adsorption was performed by CA:nAC (4:5) by 15.23% removal. The differences might be resulted in the adsorption of other pollutants, such as NO_x, N₂, C, H₂, and H₂O^{25,26}. Adsorption of pollutants into activated carbon depends on the activated carbon pore size and surface properties^{27,28}. The weight of membrane sheets were measured prior and after adsorption test, and there were increasing of membrane sheet mass of 0.27 gr, 0.16 gr and 0.30 gr for CA:nAC (4:1), CA:nAC (4:3) and CA:nAC (4:5), respectively. The presence of water molecules after adsorption test, might contributed to the increase. The H₂O could adsorb in the membrane pores

before the gas pollutant, and affect the final pollutant removal. The lowest mass increase of CA:nAC (4:3) compared to other two, provided the highest cumulative percent (of CO, CO₂, and HC) removal.

4. Conclusions

Mixed matrix membranes (MMM) have been successfully synthesized from OP-EFB biowaste. The raw materials were converted becomes cellulose acetate (CA) polymer and nanosize activated carbon (nAC). The MMM were used as membrane adsorber for gas pollutants from motorcycle emissions. The highest percentage of removal of CO and CO₂ pollutants was 16.12% and 11.77%, provided by CA:nAC (4:3) mixed matrix membrane, while 14.37% of HC pollutants were reduced by CA:nAC (4:5) mixed matrix membranes. The interaction between the mixed matrix membrane materials and individual exhaust gases should be further investigated to obtain better understanding on underlying mechanisms. Nonetheless, the biowaste has been proven to become functional material to reduce carbon released in the atmosphere.

Acknowledgement

The authors would like to thanks The Indonesian Palm Oil Estate Funds (BPDPKS) for providing funding for this research and awarded the best research student for A.A. Ilham Trilaksana was acknowledged for activated carbon preparation.

Nomenclature

MMM	Mixed matrix membrane (–)
nAC	Nano activated carbon
OP-EFB	Oil palm empty fruit bunches
CA	Cellulose acetate
SNI	Indonesian National Standard
DMF	Dimethylformamide
R	Percent removal (%)
E	Concentration of pollutant (ppm HC) (% vol)

Greek symbols

α	Alpha cellulose (–)
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