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Synthesis of Aluminum Formate Metal-Organic Framework from Can Waste as a Carbon Capture Material Using the Solvothermal Method

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***Abstract**: This research uses a solvothermal method to synthesize and characterize aluminum formate-metal organic framework (ALF-MOF) from the beverage can waste. The solvothermal method was chosen because it produces materials with controlled structures and superior properties. This research also uses a Central Composite Design (CCD) experimental design to optimize the synthesis conditions. The ALF-MOF synthesis process was carried out by mixing $Al(OH)_3$ powder obtained from the extraction of aluminum in beverage can waste and HCOOH in DMF. The mixture was stirred and heated in an autoclave reactor at Al/HCOOH mole ratios (1:3, 1:5, and 1:7) and reaction times (1, 2, and 3 hours).*

Furthermore, the products were characterized using FTIR, XRD, SEM, and BET. Based on the results, it is known that the optimum synthesis conditions were achieved at the Al/HCOOH mole ratio and reaction time of 1:3.729 and 2.874 hours, respectively, with an ALF-MOF yield value of 87.71%. Characterization results showed the presence of COO groups and Al-O-Al groups. The ALF-MOF product also has an average particle diameter of 23.57 nm with a %crystallinity of 51.30% and a surface area of 128.507 m^2/gram.

***Keywords:** Aluminum, Carbon capture, CCD, MOF, Solvothermal*

INTRODUCTION

Increasing concentrations of greenhouse gases, especially carbon dioxide (CO_2), have led to global warming. In 2022 the CO_2 concentration reached 420.99 ppm (Allangawi et al., 2023). If the concentration of greenhouse gases is not reduced, it will potentially increase global warming between 1.5-4.5oC by 2030. Global warming and climate change can cause long-term environmental problems such as loss of biodiversity, weather changes, increase in global average temperature, melting of polar ice caps, and occurrence of droughts, floods, and hurricanes (Hassanpouryouzband et al., 2021).

The 2015 Paris Agreement gave birth to the concept of Net Zero Emission (NZE), where 191 countries agreed to reduce carbon emissions (decarbonization) both directly and indirectly to keep the global average temperature rise to 2°C. The Carbon Capture Utilization and Storage (CCUS) program is one of the key strategies to achieve NZE (Hasan et al., 2022). One way to capture carbon is by using separation techniques and adsorption methods. Adsorption methods effectively capture CO_2 by binding CO_2 gas to the adsorbent surface. Various organic/inorganic-based adsorbents, such as polymers, zeolites, silica, alumina, metal oxides, amine-based adsorbents, and other composite porous materials, have emerged as promising candidates. In addition, Metal-Organic Framework (MOF) is also known as an adsorbent in CO_2 capture via physisorption and chemisorption (Ha et al., 2022; Samanta et

al., 2021). MOFs are crystalline porous materials of metal ions bonded to organic ligands through coordinated covalent bonds. This material has advantages such as high porosity, large surface area supported by many active sites, uniform structure, easy functionalization, and good thermal stability (Safaei et al., 2019).

In this research, MOF synthesis was carried out by solvothermal method where aluminum was a metal ion, and formic acid (HCOOH) was an organic ligand, which produced the Aluminum Format-Metal Organic Framework (ALF-MOF) product. Aluminum is obtained from the recycling process (extraction) of beverage can waste containing aluminum. Factors influencing the synthesis of ALF-MOF include the selection of organic ligands, metal ion salts, molar ratio, pH, solvent, temperature, and reaction time (Yang et al., 2013). These factors must be optimized to obtain ALF-MOF with the best size, porosity/surface area, and structure characteristics. Optimization was conducted using the Design of Experiment (DoE) Response Surface Methodology (RSM) and central Composite Design (CCD) method. Meanwhile, ALF-MOF was characterized with tests such as FTIR, SEM, XRD, and BET to obtain ALF-MOF that is suitable for application as a CO2 adsorbent.

RESEARCH METHODS

Materials and Tools

The materials used in this research are beverage can waste, 10% NaOH, 32% HCl, Dimethylformamide (DMF) solvent, demine water, distilled water, and methanol. The tools used in this research are a Hydrothermal Autoclave reactor with a PTFE Hydrothermal Chamber, glassware (beaker glass, measuring cup, watch glass, and separating funnel), gloves, digital scales, hot plate, and stirring rod.

Methods

This research consisted of 2 stages, namely:

Stage 1. Aluminum extraction followed by $Al(OH)_3$ synthesis.

Aluminum from beverage can waste is obtained through an extraction process. Prepared can waste is mixed with 37% HCl while stirring at a constant speed for ± 35 minutes at 60 ºC. Then filter to remove insoluble substances, adding 10% NaOH drop by drop until $Al(OH)_3$ is formed. Dry the $Al(OH)_3$ obtained by oven.

Stage 2. Synthesis of ALF-MOF.

ALF-MOF synthesis was done in an autoclave hydrothermal reactor using a Dimethylformamide (DMF) solvent. Aluminum from waste cans as metal ion was mixed with formic acid (HCOOH) as an organic ligand. The molar ratio of aluminum to formic acid varied from 1:3, 1:5, and 1:7. The reaction time varied between 1, 2, and 3 hours. Figure 1 shows the flow chart of the ALF-MOF synthesis carried out.

Stage 1 products in $Al(OH)_3$ powder are mixed with organic ligands, namely formic acid, with a predetermined mole ratio and then stirred. As much as 30 mL of DMF solvent was added, then the mixture was homogenized. The mixture was poured into teflon and then into an autoclave hydrothermal reactor. The synthesis was carried out at 100ºC with the specified reaction time. The mixture was allowed to stand for 24 hours so that the temperature in the reactor dropped. Centrifugation was then carried out to obtain the ALF- MOF natant. Next, the natant was washed with methanol. The washing process aims to maximize the

filtered ALF-MOF and eliminate impurities. The final stage of this process is drying the ALF-MOF in an oven at 60ºC for 30 minutes.

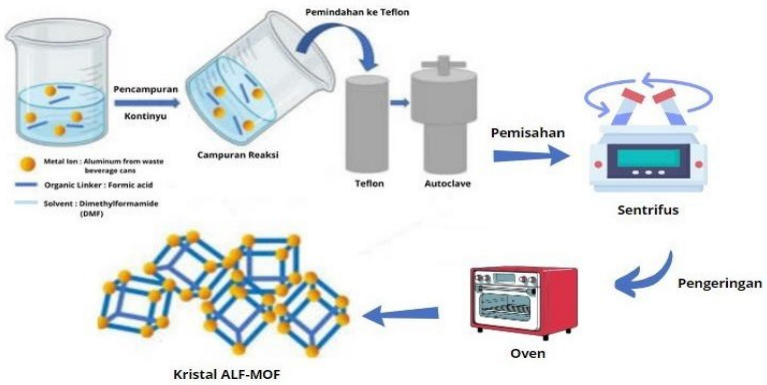

Figure 1. ALF-MOF Synthesis Flowchart

Optimization

The response surface methodology (RSM) experimental design with the central composite design (CCD) method was chosen for this research. Design Expert software (version 13) was used as a data processing tool to find the optimum process conditions. The coded and actual values of the variables used in the CCD design are given in Table 1.

Table 1. Level and Level Value

Level variables			Variables
1	0	-1	
1:7	1:5	1:3	Mole ratio Al/HCOOH (mole/mole)
3	2	1	Reaction time (hour)

Table 2. Two-variable CCD Matrix and Response

Run	A	B	Yield (%)
	Mole ratio Al/HCOOH (mole/mole)	Reaction time (hour)	
1	1:5	3	78.06
2	1:3	1	41.66
3	1:7	3	81.23
4	1:7	1	37.94
5	1:5	1	40.97
6	1:5	2	68.63
7	1:5	2	71.69
8	1:3	2	72.85
9	1:7	2	56.48
10	1:5	2	87.95
11	1:3	3	88.55
12	1:5	2	86.09
13	1:5	2	91.70

This variable was then combined with the CCD experimental design. Based on the CCD design research, 13 samples were obtained with a combination of optimization

treatments and response data, as seen in Table 2. To obtain data on response variables in the form of ALF-MOF yield values, the following Equation 1 was used:

$$Yield\ (\%) = \frac{mass\ of\ ALF{-}MOF\ (g)}{mass\ of\ cans\ (g)}\ x\ 100\% \qquad \text{(Eq. 1)}$$

Characterization of ALF-MOF Products

The characterization of ALF-MOF obtained includes morphology, porosity, particle size distribution, surface area, and functional groups. SEM (Scanning Electron Microscope) analysis using SU3500 (Hitachi, Japan) to determine the morphology and porosity of ALF-MOF, and then XRD (X-ray diffractometer) analysis was used to determine the percentage of crystallinity and particle size distribution. The surface area of ALF-MOF was searched by BET (Brunauer Emmett Teller) analysis using NOVATOUCH NTLX-4, and FTIR analysis was used to determine the functional groups of ALF-MOF.

RESULTS AND DISCUSSION

Response Model Analysis

Table 3. Response Model

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	78.54	1	4.29	68.39	88.69	
A-Mole ratio Al/HCOOH	-4.57	1	4.22	-14.55	5.41	1.00
B-Reaction time	21.21	1	4.22	11.23	31.19	1.00
AB	-0.9000	1	5.17	-13.12	11.32	1.00
A^2	-7.19	1	6.22	-21.90	7.51	1.17
B^2	-12.34	1	6.22	-27.05	2.36	1.17

Based on Table 3, the quadratic equation model for the yield response of ALF- MOF is obtained as shown in Equation 2 below:

$$Yield\ (\%) = 78{,}54 - 4{,}57A + 21{,}21B - 0{,}9AB - 7{,}17A^2 - 12{,}3B^2 \qquad \text{(Eq. 2)}$$

The equation shows that the yield response of ALF-MOF increases directly proportional to the reaction time. This is indicated by the constant value of the reaction time variable, which is a positive sign. The ALF-MOF yield response will decrease with the increase of the oil/methanol mole ratio and the interaction between oil/methanol mole ratios, which is characterized by a negative constant value. The condition to be achieved is the maximum yield of ALF-MOF, so the reaction time significantly influences the yield of ALF-MOF.

Optimization of ALF-MOF Synthesis

After various analyses, the Design Expert will provide an overview of the position of the changing/free variables that can potentially obtain the optimum yield of ALF- MOF in the form of a contour diagram (Figure 2).

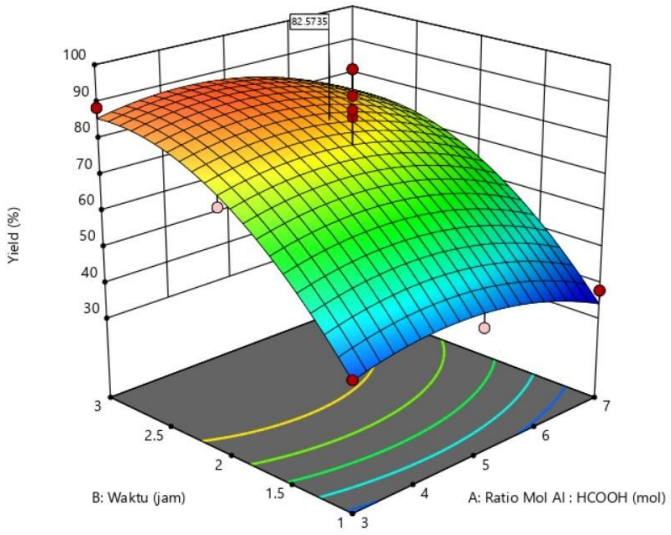

Figure 2. Optimum yield values

Based on Figure 2, the highest yield value of 91.7% was obtained at the Al/HCOOH mole ratio and reaction time of 1:5 and 2 hours, respectively.

Furthermore, Design Expert will provide suggestions for optimization conditions by changing the Goal (target) and Importance (level of importance) as in Table 4 as follows:

Table 4. Optimization using RSM

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Mole ratio Al/HCOOH	is in range	3	7	1	1	3
Reaction time	is in range	1	3	1	1	3
Yield	maximum	37,94	91,7	1	1	3

RSM's optimization process yielded 100 suggestions for operating conditions, resulting in a yield value of over 80%. The optimal conditions identified were an Al/HCOOH mole ratio of 1:3.729 and a reaction time of 2.874 hours, which achieved an ALF-MOF yield of 88.149%. Verification of these results was conducted three times, yielding an average ALF-MOF yield of 87.71%. Consequently, the percent error calculated was 0.5%.

Characterization of ALF-MOF

Crystallinity Percentage and Particle Size

X-ray diffraction (XRD) analysis was conducted to ascertain the crystallinity percentage and particle size distribution of the ALF-MOF. As depicted in Figure 3, the chemical composition of ALF-MOF is $C_{11}H_{13}N_3O_6$, which corresponds to 2,3,4,5-Tetramethyl-1-trinitromethylbenzene. The elemental percentages are as follows: Carbon (C) at 46.6%, Oxygen (O) at 33.9%, Nitrogen (N) at 14.8%, and Hydrogen (H) at 4.6%. Furthermore, as indicated in Table 5, the crystallinity percentage is measured at 51.30%, with

a total peak area of 9776.04262. This suggests that the ALF-MOF phase is predominantly amorphous.

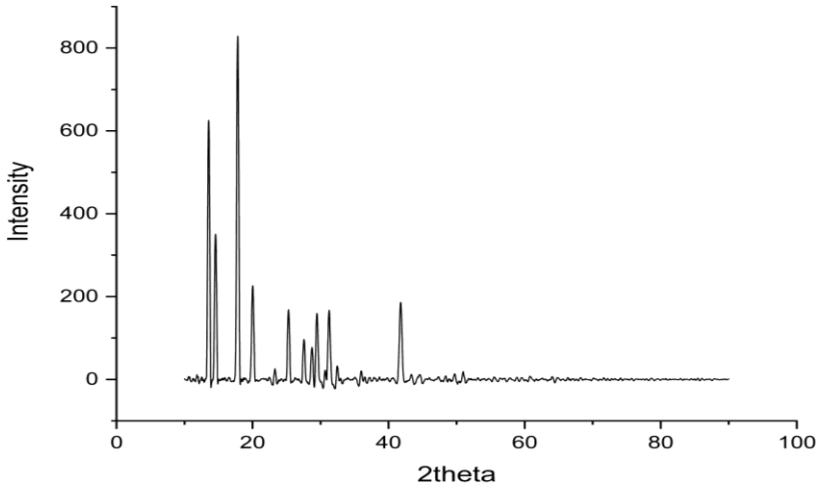

Figure 3. XRD analysis results

Table 5. Results of %Crystallinity

Peak area crystal fraction	2078,41
Total peak area	4051,87
% crystallinity	51,30 %

Table 6. Peak Area of ALF-MOF

I/I0 (peak height)	Counts (peak area)
1000	382,59
821,69	314,37
459,64	175,86
271,09	103,72
227,58	145,11
221,51	141,25
220,3	98,33
201,29	115,52
180,35	115
134,65	103,04
104,25	66,48
94,53	54,25
71,08	36,26
69,95	40,14
69,63	186,49
Peak Area	**2078,41**

Furthermore, from the XRD analysis, the average particle diameter of ALF-MOF is 23.57 nm with a particle size distribution between 0.25-0.35 nm.

Morphology and Porosity

The morphology and porosity of the ALF-MOF were analyzed using SEM (Scanning Electron Microscope). Figure 4 shows that the morphology of the ALF- MOF sample is cotton-like with aggregated microfilaments. Temperature is one of the factors that affect the structure and morphology of MOF

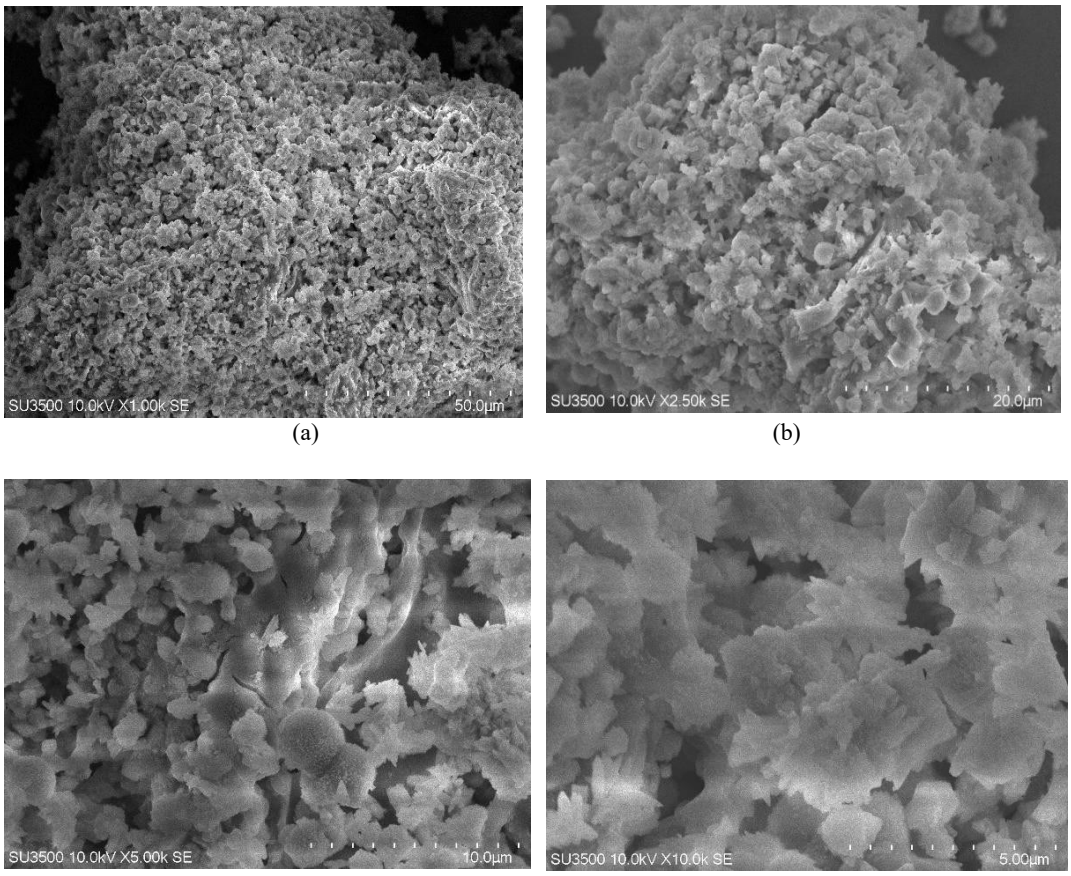

Figure 4. SEM analysis of ALF-MOF (a) 1000x magnification, (b) 2500x magnification, (c) 5000x magnification, (d) 10000x magnification

Then Table 7 presents the porosity results obtained from SEM analysis, with an x value of 1279 and a y value of 891.

Table 7. Porosity Data

H Max. (Grayscale Bar)	65535
H Min. (Grayscale Bar)	0
x (Dimensions)	1279
y (Dimensions)	891
z (H Max. - H Min.)	65535
Volume Total	7,47E+10
Volume Solid	3,08E+10
Volume Under H Min.	0
Volume Integrate	3,08E+10
Volume Pori	4,39E+10
Porosities	0,5882
Porosities (%)	**58,82 %**

Surface Area

The surface area of ALF-MOF was analyzed using BET (Brunauer Emmett Teller) utilizing degassing process at 150ºC for 3 hours. Based on the results of BET analysis, the carbon sorbent produced from ALF-MOF has a surface area/absorption capacity of 128.507 m2/gram.

Functional Groups on ALF-MOF

To determine the molecular structure and identify the functional groups present in ALF- MOF, Fourier Transform Infrared (FTIR) spectroscopy analysis was conducted.

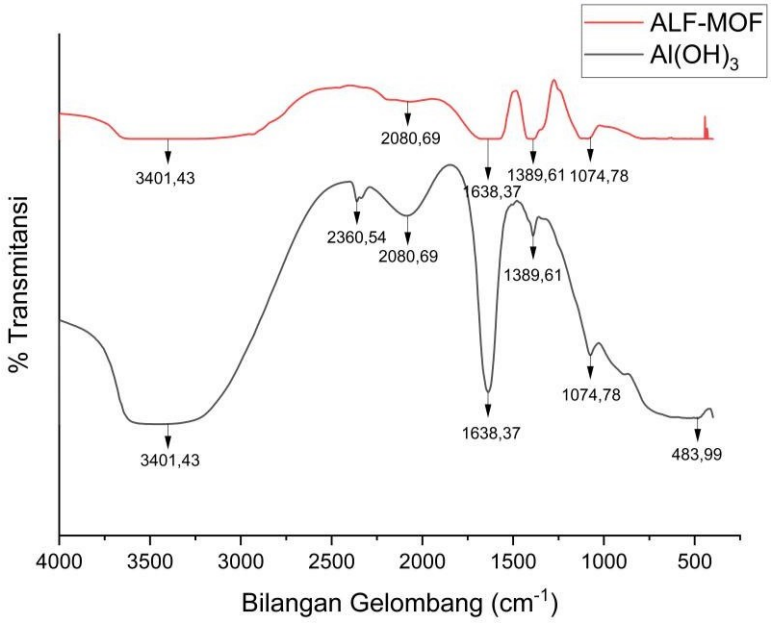

Figure 5. FTIR analysis

In Figure 5, the FTIR analysis results prove the hypothesis that the two spectra not only form COOH groups bound to aluminum but also form polymeric aluminum species. The broad peak in Figure 5 in the spectrum of $Al(OH)_3$ at 3401 cm^{-1} represents the OH group in $Al(OH)_3$ and also has similarities with the ALF-MOF product. After the synthesis, the OH group peak weakened, and peaks characteristic of carboxyl groups appeared in the FTIR spectra of $Al(OH)_3$ and ALF-MOF at 3401, 2361, 1638, and 1390 cm^{-1}. The firm peaks at 1638 and 1390 cm^{-1} may indicate COO-coupled groups due to the delocalization of electrons at two oxygen atoms. In addition, the peak at 1075 cm^{-1} indicates the presence of R-O-R groups. Considering the reaction product, it is possible that Al-O- Al is formed in this reaction system. The Al-O-Al bond provides more evidence of the presence of polymeric aluminum species in the reaction product.

CONCLUSIONS

Based on the research results, the following conclusions can be drawn:

1. ALF-MOF was successfully synthesized from beverage can waste by solvothermal method. The presence of COO functional groups at wave numbers 1638 cm^{-1} and 1390

cm^{-1} and Al-O-Al functional groups at 1075 cm^{-1} is evidence of the presence of polymeric aluminum species in the reaction product.
2. The optimum synthesis condition was reached at the Al/HCOOH mole ratio and reaction time of 1:3.729 and 2.874 hours, respectively, with a yield value of 87.71% ALF-MOF.
3. The ALF-MOF product also has an average particle diameter size of 23.57 nm with a crystallinity percentage of 51.30% and a surface area of 128.507 m^2/gram.

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REFERENCES

Allangawi, A., Alzaimoor, E.F.H., Shanaah, H.A., Mohammed, A.A., Saqer, H., El-Fattah, A.A., Kamel, A.H. 2023. Carbon Capture Materials in Post-Combustion: Adsorption and Absorption-Based Processes. *Journal of Carbon Research*. 9(17): 1-29.

Ha, N.T.T., Thao, H.T., Ha, N.N. 2022. Physisorption and chemisorption of CO2 on Fe- MIL-88B derivatives: Impact of the functional groups on the electronic properties and adsorption tendency—A theoretical investigation. *J. Mol. Graph. Model.* 112.

Hasan, M.M.F., Zantye, M., Kazi, MK. 2022. Challenges and opportunities in carbon capture, utilization and storage: A process systems engineering perspective. *Comput. Chem. Eng*. 166.

Hassanpouryouzband, A., Joonaki, E., Edlmann, K., Haszeldine, R.S. 2021. Offshore Geological Storage of Hydrogen: Is This Our Best Option toAchieve Net-Zero?. *ACS Energy Lett*. 6(6): 2181–2186.

Manurung, M. dan Ayuningtyas, I.F. 2010. Kandungan aluminium dalam kaleng bekas dan pemanfaatannya dalam pembuatan tawas. *Jurnal Kimia*. 4(2): 180-186.

Qian, Q., Asinger, P.A., Lee, M.J., Han, G., Mizrahi, R.K., Lin, S., Benedetti, F.M.,Wu, A.X., Chi, W.S., Smith, Z.P. 2020. MOF-Based Membranes for Gas Separations. *Chem. Rev*. 120(16): 8161–8266.

Raganati, F., Miccio, F., Ammendola, P. 2021. Adsorption of Carbon Dioxide for Post-Combustion Capture: A Review. *Energy Fuels*. 35: 12845−12868.

Rupam, T.H., Jahan, I., Palash, M.L., Harish, S. 2019. Green Synthesis and Adsorption Characterisation of an Aluminium Based Metal Organic Framework. *Proceeding of 21ST Cross Straits Symposium on Energy and Environmental Science and Technology (CSS-EEST)*. November 2019, Shanghai, China

Safaei, M., Foroughi, M.M., Ebrahimpor, N., Jahani, S., Omidi, A., Khatami, M. 2019. A Review on Metal-Organic Frameworks: Synthesis and applications. *TrAC Trends Anal. Chem*. 118.

Samanta, A., Zhao, A., Shimizu, G.K.H., Sarkar, P., Gupta, R. 2021. Post-Combustion CO_2 Capture Using Solid Sorbents: A Review. *Ind. Eng. Chem.Res*. 51(4): 1438-1463.

SIPSN. 2023. *Komposisi sampah*. URL: https://sipsn.menlhk.go.id/sipsn/. Accessed at 16 January 2024.

Witaryanto, T.S. dan Idzati, E.M. 2017. Inovasi Pembuatan Tawas Dari Limbah Kaleng Bekas. *Tugas Akhir*. Institut Teknologi Sepuluh Nopember.

Yang, G..P., Hou, L., Ma, L.F., Wang, Y Y. 2013. Investigation on the prime factors influencing the formation of entangled metal-organic frameworks. *CrystEngComm.* 15 (14), 2561– 2578.

Yusuf, V.Z., Malek, N.I., Kailasa, A.K. 2022. Review on Metal–Organic Framework Classification, Synthetic Approaches, and Influencing Factors: Applications in Energy, Drug Delivery, and Wastewater Treatment. *ACS Omega*. 7(49): 44507-44531.