Preliminary Study of Bio-Metal Organic Frameworks (Bio-MOFs) Based Chromium-Citric Acid for CO₂ Adsorption Application

S. A. Pratiwi¹, Nasruddin¹, A Zulys², Fayza Yulia¹, and Naufal Muhadzib¹

¹Department of Mechanical Engineering, Faculty of Engineering, Universitas Indonesia, Depok, 16424, Indonesia
²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok, 16424, Indonesia

*Corresponding Author’s email: nasruddin@eng.ui.ac.id

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Abstract: According to the Intergovernmental Panel on Climate Change (IPCC), carbon dioxide (CO₂) gas is one of the significant factors that caused climate change. In the IPCC’s special report regarding Carbon Dioxide Capture and Storage, there was discussion about several technologies for CO₂ gas capture. One of the technologies is using solid sorbent such as activated carbon, silica, metal oxides, and zeolite. Recently, there has been a significant increase in the research of Metal Organic Frameworks (MOFs) which are believed to be the most promising adsorbent in CO₂ adsorption application. It is a crystalline type of porous material consisting of the metal ions and the organic ligands. With all the advantages possessed by MOFs, these adsorbents are still difficult to be applied on industrial scale due to high fabrication cost. Composed of non-renewable feedstock raw materials, some MOFs are not environmentally friendly. To quickly response this challenge, we conducted investigation on the use of biologically derived MOF (Bio-MOF) in CO₂ capture application. A novel of Bio-MOF Chromium-Citric Acid (Cr-CA) has been explored. The synthesis process is carried out through the hydrothermal reaction method using eco-friendly solvent potassium hydroxide and Aquabidest. The characterization of MOF was carried out by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) testing, scanning electron microscope (SEM), thermal gravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) analysis. We would like to recommend that research about MOF with Chromium-Citric Acid content is conducted and investigated further on the performance of gas adsorption with this porous material.

Keywords: Bio-MOFs; Citric Acid; Adsorbent characteristic; CO₂ Adsorption

1. Introduction

Carbon dioxide (CO₂) capture and storage (CCS) is a process consisting of the separation of CO₂ from the sources, transportation to the storage location and long-term isolation from the atmosphere maker¹, ². Adsorption process is one of the CCS technologies that could be used to mitigate the climate change for reducing CO₂ in the atmosphere¹, ³. Pilot test results of coal-fired flue gas CO₂ recovery by adsorption processes show that CO₂ recovery is reaching about 99.0 by volume using two stages of pressure swing adsorption and temperature swing adsorption system. Compared to traditional adsorbents like zeolite, activated carbon, and silica which has drawbacks in high regeneration energy and low material resistance, Metal Organic Frameworks (MOFs) could be a substitute adsorbent in CCS system⁵, ⁶.

MOF is a crystallized porous material consists of the combination of the metals and the ligands. MOF was first popularized in the 1990s and it has attracted the attention of scientists in the last two decades⁷. Aside from common porous materials such as zeolites, silica, or activated carbon, MOF has special physical properties such as high thermal stability and porosity, easily controlled structure, and fast kinetic which make this type of adsorbent to be the most promising material that has been developed in various engineering branch applications such as natural gas, syngas, biogas in CO₂ removal⁸-¹⁰.

Most of the research and the usage of MOFs as sorbent in CO₂ adsorption uses raw materials derived from non-renewable petrochemical feedstocks which are not environmentally friendly¹¹. The need for environmentally friendly adsorbents, new research of bio-ligands as constituents of MOFs has begun to be explored. Biologically metal-organic frameworks (Bio-MOFs) with bio-ligand constituents have advantages such as being environmentally friendly, easy to produce, abundant availability, and having multiple reactive sites¹².

The challenge to develop MOF with the principle of renewability and recyclability with fabrication costs can be fulfilled by using Bio-MOF¹³. Therefore, in this study,
we tried to take advantage of the flexibility of ligands, citric acid, to build porous material with metal chromium nitrate. Bio-molecule citric acid derived from citrus fruits with high availability of raw materials has tricarboxylic acid structure which are expected to absorb more CO₂ molecules. By using this bio-ligand, the MOF fabrication cost will be much lower than other reported MOFs. The synthesized material will be characterized by various methods including XRD, SEM, BET, FTIR, and TGA to obtain the physical properties such as the crystallinity, the morphology, the porosity, the chemical functionalities, and the thermal stability. The results of this study are expected to be further investigated in CO₂ gas adsorption application14, 15).

2. Methodology

This research is conducted by using chromium (III) nitrate nonahydrate \([\text{Cr(NO)}_3\cdot9\text{H}_2\text{O}]\) as the metal and citric acid monohydrate \((\text{C}_6\text{H}_8\text{O}_7)\) as the ligand. The solvents are only using Aquabidest and Potassium Hydroxide (KOH) which is known to be more environmentally friendly than NaOH in adjusting the pH of the MOF solution16).

The synthesis process was carried out by referring to Xiang et al who produced MOF UTSA-16 with citric acid ligand with several modifications17). This synthesis process was conducted with hydrothermal reaction process with the composition of material mixture as following: Chromium Nitrate (2.5 gr), Citric Acid (2.1 gr), Potassium Hydroxide (1.7 gr), Ethanol (2.5 mL), and deionized water/Aquabidest (2.5 mL). Those materials were mixed and poured in the reactor inside the stainless-steel autoclave. The autoclave was heated gradually in the oven from the ambient temperature until reaching 120 °C in 30 minutes. After reaching 120°C, the temperature was maintained constant for 48 hours17).

When that process was completed, the reactor autoclave was cooled down gradually. After cooling down process, the crystal MOF would be obtained after centrifugation process was conducted. Dimethylformamide/DMF was added in the MOF to separate the excess ligand or any other substances which were not reacted with the MOF18).

After doing the synthesis process, the adsorbent characterization was undertaken. We want to observe the chemical functionalities contained in our Bio-MOF based citric acid. Fourier Transform InfraRed (FTIR) measurements is carried out to determine the bonding ion that formed in the MOF using detectors, which are DTGS KBr, and KBr beam splitter.

Pore volume, pore radius and specific surface area of MOF were measured using a Quantachrome NOVA 2200e type instrument from N₂ isothermal adsorption at 77 K. The samples were degassed at 90°C17) for 3 hours before measuring adsorption. Before and after the degassing process, material weighing process was performed to find out the reduced mass. The isotherm data is used to calculate the surface area with the BET equation.

XRD measurements were carried out using a Shimadzu XRD-6000 diffractometer with a step size of 0.02 using monochromatic CuKα radiation (wavelength ¼ 0.154 nm) operated at 40 kV and 40 mA. Microstructure, morphology, and MOF particle size were determined by Scanning Electron Microscopy (SEM) using JEOL JSM-6510LA which was equipped with EDS (Energy Dispersive X-ray Spectroscopy) device to analyze chemicals composition in MOF: MOF thermal stability was tested using Thermal Gravimetric Analysis (TGA). MOF samples were heated to 900°C with the range of 10 °C / min under nitrogen flow. Then, MOF weight loss was measured as the function of temperature.

3. Results and Discussion

FTIR results showed the clusters formed on the MOFs material that has been synthesized where it compares the spectrum of pure citric acid (a) and the Bio-MOF Cr-CA
Visible reflection point of carbonyl group (C=O) 1767.90 cm$^{-1}$ indicates the interaction of chromium molecules and carboxylic acid on the citric acid bio-ligand. Furthermore, the bond stretching with medium intensity at the wavelength of 3673.95 cm$^{-1}$ indicates the presence of vibration of the hydroxyl group (-OH) citric acid on the Bio-MOF adsorbent representing the binding of bio-ligand in this Bio-MOF\textsuperscript{19). Other medium-intensity peaks are also observed at 2981 cm$^{-1}$ and 2878 cm$^{-1}$ reproduced from stretching vibrations of C-H molecules. The high intensity peak at 2396 cm$^{-1}$ is attributed to O=C=O bond stretching. Other position wavenumbers have been described in Table 1.

| Position wave number (cm$^{-1}$) | Intensity Transmittance (%) | Reference adsorption band | note |
|---------------------------------|----------------------------|---------------------------|------|
| 3801.99                        | 106.744                    | 3700-3584                 | O – H (Alcohol – Free) |
| 3673.95                        | 104.273                    | 3700-3584                 | C – H (Alkane) |
| 2981.01                        | 101.906                    | 3000-2840                 | C – H (Aldehyde – Doublet) |
| 2878.63                        | 104.639                    | 3000-2840                 | |
| 2821.64                        | 103.074                    | 2830-2695                 | 2349 |
| 2396.71                        | 101.025                    | 2200-2000                 | O = C = O (Carbon Dioxide) |
| 2161.03                        | 95.554                     | 2175-2140                 | S – C Ξ N (Thiocyanate) |
| 2026.86                        | 96.230                     | 2140-1990                 | N = C = S (Isothiocyanate) |
| 1976.35                        | 96.820                     | 2000-1650                 | C – H (Aromatic Compound – overtone) |
| 1767.90                        | 101.803                    | 1800-1770                 | C = O (Conjugated Acid Halide) |
| 1648.40                        | 100.697                    | 1650-1600                 | C = C (Conjugated Alkene) |
| 1511.41                        | 100.362                    | 1550-1500                 | N – O (Nitro Compound) |
| 1362.76                        | 77.188                     | 1390-1310                 | O – H (Sulfonate) |
| 1131.59                        | 98.248                     | 1150-1085                 | C – O (Aliphatic Ether) |
| 1055.23                        | 90.107                     | 1085-1050                 | C – O (Primary Alcohol) |
| 823.07                         | 91.605                     | 880 ± 20 - 810 ± 20       | C – H (1,2,4 – trisubstituted) |

The thermal stability of the MOFs was measured by the thermal gravimetric analysis. The whole graph could be seen on Fig. 4. The measurement was carried out in the temperature range of 50°C - 900°C with an increase of 10°C / minute. The first reduction in mass occurred during the process of increasing temperatures in the range of 130°C - 430°C by 0.125 mg. After that in the temperature range of 700°C the adsorbent started to decompose and leaved up to chromium oxide. Further, at the temperature of 800°C the remaining material were destroyed and at the temperature of 900°C, Bio-MOF Cr-CA had been burned (97.3% by weight mass was lost). In this test, we could probably assume the right temperature for degassing to keep the material from being decompose or burnt.

In the SEM (Scanning Electron Microscopy) observation, the morphology of the MOFs material that has been formed can be seen. The results showed that the MOF material has the homogeneous shape. 1000x, 2500x, and 5000x magnifications were observed in the range of 5-10µm. SEM test results can be seen in Fig. 5, where MOF has a uniform shape and a large structure. The
particle structure of MOF could already be seen at 1000x magnification variation. The particle has uniformity size at 10μm. The morphology of the particles is observed having homogeneous grain with different sizes.

BET analysis was carried out at 11 points of N\textsubscript{2} adsorption at 77 K. Fig. 6 shows N\textsubscript{2} adsorption with the surface area of 35,550 m\textsuperscript{2}/g. The surface area of Bio-MOF Cr-CA has the same range as other Bio-MOF groups such as Bio-MOF 14 and MPM-I-Cl with the pore volume of 0.05 cm\textsuperscript{3}/g and it is still far from the surface area of non-renewable petrochemical MOFs\textsuperscript{17}. The surface area is not the only things that affects gas adsorption capacity. From the results of our previous study, the surface area of the Bio-MOF did not have a significant effect on the CO\textsubscript{2} adsorption capacity\textsuperscript{8}. On the contradictory to the pore volume, lowering the pore volume can enhance the interaction potential of the pore walls and CO\textsubscript{2} molecules\textsuperscript{20,21}.

The XRD investigation was performed to obtain the phase identification of crystalline material and showed the information on unit cell dimensions\textsuperscript{22}. The peak list could determine the size and the micro stain of the sample\textsuperscript{23}. The XRD pattern of MOFs of Citric Acid is shown in Fig. 7. The high intensity peaks at the angle of 20 represents good crystalline quality on Bio-MOF Cr-CA since the amorphous material will not produce sharp consistent peaks. Several sharp peaks were observed at the angles of 19\textdegree,29\textdegree, and 34\textdegree having the same spectrum with other chromium nitrate as the metal constituent of the MOFs\textsuperscript{24}. The peaks at 24\textdegree and 39\textdegree represent the citric acid ligand in Bio-MOF with the same intensity in several reported
MOFs using citric acid bio-ligand[25, 26].

4. Conclusions

The Synthesis of Bio-MOF based Chromium nitrate and citric acid was successfully carried out at 120°C within 48 hours based on the results of the FTIR, SEM, TGA, and XRD. Based on the thermal gravimetric result, it was found that this Bio-MOF can maintain its structure up to 700°C. So, it can be concluded that the material has good resistance to high temperatures. Second step purification was performed to remove unreacted substances in the framework of the Bio-MOF. This synthesis should be optimized to meet the expectations of the porosity and the crystallinity.

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Nomenclature

MOF  Metal Organic Framework
CO2  Carbon Dioxide
CCS  Carbon Dioxide Capture System
FTIR  Fourier Transform Infra-Red
BET  Brunauer-Emmett Teller
SEM  Scanning Electron Microscope
TGA  Thermal Gravimetric Analysis

References

1) D.M. Abouelella, S.-E.K. Fateen, and M.M. Fouad, "Multiscale Modeling Study of the Adsorption of CO2 Using Different Capture Materials," Evergreen Journal of Novel Carbon Resource Sciences & Green Asia Strategy, 5 (01) 43-51 (2018).
2) H. Huaizif, A. Budiyanto, and J. Sirait, "Study on the carbon emission evaluation in a container port based on energy consumption data," (2020).
3) M.-W. Wan, C.-C. Kan, B.D. Rogel, and M.L.P. Dalida, "Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand," Carbohydrate Polymers, 80 (3) 891-899 (2010). doi:10.1016/j.carbpol.2009.12.048.
4) A.H. Berger, and A.S. Bhown, "Comparing physisorption and chemisorption solid sorbents for use separating CO2 from flue gas using temperature swing adsorption," Energy Procedia, 4 562-567 (2011). doi: 10.1016/j.egypro.2011.01.089.
5) S. Keskin, T.M. van Heest, and D.S. Sholl, "Can metal–organic framework materials play a useful role in large-scale carbon dioxide separations?" ChemSusChem, 3 (8) 879-891 (2010). doi: 10.1002/cssc.201000114.
6) P. Amo-Ochoa, G. Givaja, P.J.S. Miguel, O. Castillo, and F. Zamora, "Microwave assisted hydrothermal synthesis of a novel CuI-sulfate-pyrazine MOF," Inorganic Chemistry Communications, 10 (8) 921-924 (2007). doi: 10.1016/j.inoche.2007.04.024.
7) B. Valizadeh, T.N. Nguyen, and K.C. Stylianou, "Shape engineering of metal–organic frameworks," Polyhedron, 145 1-15 (2018). https://doi.org/10.1016/j.poly.2018.01.004.
8) A. Zulys, F. Yulia, N. Muhadzib, and Nasruddin, "Biological–Metal–Organic Frameworks (Bio-MOFs) for CO2 Capture," Industrial & Engineering Chemistry Research, 60 (1) 37-51 (2020). https://doi.org/10.1021/acs.iecr.0c04522.
9) T. Ghanbari, F. Abnisa, and W.M.A. Wan Daud, "A review on production of metal organic frameworks (MOF) for CO2 adsorption," Science of The Total Environment, 707 135090 (2020). doi:10.1016/j.scitotenv.2019.135090.
10) Q. Yang, S. Vaesen, F. Ragon, A.D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, and P.L. Llewellyn, "A water stable metal–organic framework with optimal features for CO2 capture," Angewandte Chemie, 125 (39) 10506-10510 (2013).
11) S.L. Anderson, and K.C. Stylianou, "Biologically derived metal organic frameworks," Coordination Chemistry Reviews, 349 102-128 (2017). doi:10.1016/j.ccr.2017.07.012.
12) S.S. Nadar, L. Vaidya, S. Maurya, and V.K. Rathod, "Polysaccharide based metal organic frameworks (polysaccharide–MOF): A review," Coordination Chemistry Reviews, 396 1-21 (2019). doi:10.1016/j.ccr.2019.05.011.
13) J. Tang, J. Sisler, N. Grishkewich, and K.C. Tam, "Functionalization of cellulose nanocrystals for advanced applications," Journal of Colloid and Interface Science, 494 397-409 (2017). https://doi.org/10.1016/j.jcis.2017.01.077.
14) J.-R. Li, Y. Ma, M.C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P.B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," Coordination Chemistry Reviews, 255 (15) 1791-1823 (2011). doi:10.1016/j.ccr.2011.02.012.
15) S. Kayal, B. Sun, and A. Chakraborty, "Study of metal-organic framework MIL-101(Cr) for natural gas (methane) storage and compare with other MOFs (metal-organic frameworks)," Energy, 91 772-781 (2015). doi: 10.1016/j.energy.2015.08.096.
16) M.R. Abukhadra, and M.A. Sayed, "K+ trapped kaolinite (KaoI/K+) as low cost and eco-friendly basic heterogeneous catalyst in the transesterification of commercial waste cooking oil into biodiesel,"
17) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna, and B. Chen, "Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions" Nature Communication, 3 (1) 1-9 (2012). doi: 10.1038/ncomms1956.

18) I. Larasati, D. Winarni, F.R. Putri, Q.A. Hanif, and W.W. Lestari, "Synthesis of Metal-organic Frameworks Based on Zr4+ and Benzene 1,3,5-Tricarboxylate Linker as Heterogeneous Catalyst in the Esterification Reaction of Palmitic Acid," in: IOP Conference Series: Materials Science and Engineering, 2017. doi:10.1088/1757-899x/214/1/012006.

19) "The Advanced Light Source, in Characteristic IR Band Positions," B. Lab. https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Parameters/Infrared_Spectroscopy_Absorption_Table (accessed July 17, 2019).

20) J. An, and N.L. Rosi, "Tuning MOF CO2 Adsorption Properties via Cation Exchange," Journal of the American Chemical Society, 132 (16) 5578-5579 (2010). doi:10.1021/ja1012992.

21) C.L. Mangun, M.A. Daley, R.D. Braatz, and J.Economy, "Effect of pore size on adsorption of hydrocarbons in phenolic-based activated carbon fibers," Carbon, 36 (1) 123-129 (1998). https://doi.org/10.1016/S0008-6223(97)00169-3.

22) C.M.C. Barbara L Dutrow, Geochemical Instrumentation and Analysis, Science Education Resource Center at Carleton College. https://serc.carleton.edu/research_education/geochemsheets/index.html (accessed July 20, 2019)

23) S.A. Speakman, "Introduction to X-Ray Powder Diffraction Data Analysis," Center for Material Science and Engineering Massachusetts Institute of Technology.

24) R. Blix, "Röntgenanalyse des Chrom—Stickstoffsystems nebst einer orientierenden Konstitutionsuntersuchung des stickstoffhaltigen Ferrochroms," Z. Phys. Chem., 3 (1) 229-239 (1929). https://doi.org/10.1515/zpch-1929-0317.

25) R.O. Toro, Development and Characterization of Corn Starch Film by Blending with More Hydrophobic Compounds, 2015, Doctoral Thesis, Universitat Politecnica De Valencia.

26) F. Jiang, R. Li, J. Cai, W. Xu, A. Cao, D. Chen, X. Zhang, C. Wang, and C. Shu, "Ultrasound Pd/Au bimetallic nanocrystals embedded in hydrogen-bonded supramolecular structures: facile synthesis and catalytic activities in the reduction of 4-nitrophenol," J. Mater. Chem. A, 3 (38) 19433-19438 (2015). https://doi.org/10.1039/C5TA02260F