Adsorption of Carbon Dioxide by Metal Organic Framework for Indoor Air Quality Enhancement

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Abstract. Air pollution has become a severe environmental issue among millions of people around the globe. However, the risk of exposure to indoor air pollution is much higher than outdoor air pollution. The most effective way to improve indoor air quality (IAQ) by reducing the indoor CO₂ content is by capturing and storing. There are several types of adsorbents used to capture CO₂, namely physical adsorbents and chemical adsorbents. Metal-Organic Framework (MOF) is one of the recent interests arising physical adsorbents which possesses high adsorption capability. In this study, MOFs fabricated with different metals and organic ligands were used to evaluate their performance in CO₂ adsorption under an enclosed office space. Magnesium, chromium, and copper metals were used as the main element in the MOF fabrication coupled with trimesic acid as an organic ligand. The MOFs' morphologies generally illustrated that magnesium MOF exhibited a dispersed nanorod flask crystal, chromium MOF showed agglomeration crystal, whereas fine crystal rod was observed in copper MOF. The elemental analysis from EDX and XRD confirmed that the metals were successfully embedded with the organic ligand, which is similar to the literature studies. The CO₂ gas adsorption study suggested that magnesium MOF fabricated with trimesic acid possess superior CO₂ adsorption capability as the recorded CO₂ concentration reduced from 960 ± 73 ppm to 895 ± 57 under 2 hours continuous sampling time. The CO₂ adsorption study reveals that the magnesium MOF with trimesic acid ligand yields a promising result on indoor CO₂ concentration reduction. This result suggested that the MOF possesses a great potential to be applied in the indoor air quality enhancement with the integration to the existing air purification and/or filtration system.

1. Introduction
Air pollution has become a serious environmental issue among millions of people around the globe. Modern people spend about 80% of their time indoors on average such as work in the office, school, residential, or even sport inside a building. However, the risk of exposure to danger for indoor air pollution is much higher than outdoor air pollution [1]. Sick building syndrome occurs when there is a poor level of indoor air quality (IAQ) [2]. The symptoms of sick building syndrome are watery eyes, headaches, dizziness, coughing, sneezing, fatigue and upper respiratory congestion. This might bring adverse effects to the respiratory or human health effects such as lung disease, worsening asthma, pharyngitis, epistaxis, nasal congestion, fever, vomiting, myalgia, hearing loss, conjunctival irritation and even affect the working performance and increase of absenteeism [3]. Therefore, IAQ play a vital role in both productivity and human health.

One of the indoor air pollutants that will lead to poor IAQ and human health is CO₂. The increment of CO₂ concentration in the indoor air will lead to dizziness and difficulty to breathe. Additionally, a high
concentration of CO₂ also will lead to a sharp and acidic odour in the room. Because of this, the National Institute of Occupational Safety and Health Malaysia (NIOSH) recommends the threshold CO₂ concentration in a room is below 1,000 ppm and the effect of CO₂ indoor levels for better IAQ [4]. The effect of the CO₂ mentioned had lead to servious health effect such as sick building syndrome and respiratory related disease which will led to absentism to work and school.

CO₂ could be reduced by the solid adsorbents, namely zeolite, activated carbon, and MOF. Zeolites are crystalline materials that are built up of silicon, aluminum, and oxygen in an ordered manner. The atoms formed a rigid framework and pore between them, such as a honeycomb-like structure. The ratio of silicon to aluminum can be adjusted to produce different zeolites for specific applications [5]. Next, activated carbons are amorphous solids made from carbonaceous materials. They have a high surface area and the capacity to serve as an adsorbent. Due to their non-polarity surface, the non-polar organic compounds tend to attach to their surface or pores [6]. MOFs are newly developed adsorbent which is a crystalline solids that have high porosity and tunable, which received significant attention from the industry [7]. The comparison of three solid adsorbents shows that the surface area of MOFs (500 to 10,000 m²/g) is significantly higher than the surface area of zeolite (720 m²/g) and activated carbon (214 m²/g) [8 – 10]. The surface area of the adsorbent is proportional to the amount of adsorbate that will be adsorbed. This enables MOF to adsorb many more CO₂. Besides, MOFs also have greater capacity and pore size (1.5 to 33.5 mmol/g, 2.5 to 11.1 Å) respectively relative to zeolite (0.5 to 8.0 mmol/g, 3.0 to 10.0 Å) and activated carbon (0.3 to 6.3 mmol/g, 3.0 to 100.0 Å) for CO₂ adsorption [8 – 10]. In this study, three different types of MOF made from magnesium nitrate hexahydrate, chromium (VI) oxide and copper (II) nitrate trihydrate with trimesic acid were fabricated in a laboratory scale and test for its carbon dioxide gas adsorption.

2. Methodology

2.1. Materials

The magnesium, chromium and copper metal organic framework was made by magnesium nitrate hexahydrate, chromium (VI) oxide and copper (II) nitrate trihydrate, respectively. The organic ligand utilized in this study was trimsestic acid (TMA) and co-solvent used was ethanol. All the chemicals used in this study were purchase from Sigma Aldrich.

2.2. Fabrication of the metal organic framework

The metal organic framework in this study was carried out by the solvothermal method. The metal oxide (either magnesium, chromium or copper) was first dissolved in the distilled water, subsequently, the organic ligand (trimesic acid) and ethanol as co-solvent. The molar ratio of the mixture for the metal oxide and organic ligand is at the ratio of one to one in this work. The solution was stirred by an overhead mechanical stirrer to obtain a homogenous solution. The mixture is then placed in the Teflon line autoclave and heated in the vacuum oven at 80 °C for three days. Further, the mixture was taken out from the vacuum oven and cooled at room temperature to obtain a crystal metal organic framework. The dried crystal shall keep in a vacuum cabinet to maintain its dryness before the gas adsorption test. The magnesium, chromium and copper metal organic framework used in this study are labeled as Mg-TMA, Cr-TMA and Cu-TMA for ease of reference.

2.3. Characterization

In this study, various characterization was applied to study the physical and chemical properties of the fabricated MOF. The surface morphology and chemical composition of the fabricated MOF were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). SEM is a material characterization technique that will produce a clear and high-resolution image of sample size and surface morphology. The SEM is carried out under an accelerated voltage of 12kV. A small amount
of powdered MOF samples on the sample holder and the samples are fixed on the holder by using carbon tape. The surface of samples is required to coat with a thin layer of gold by a sputter-coated machine to increase the conductivity of the samples and the small grain size of gold enables a clearer image. Energy dispersive x-ray (EDX) is an x-ray technique used to identify the MOFs elemental composition. The signals produced from SEM are the characteristics of x-rays. X-rays generate in SEM begin from the energy produced when the electron beam hits the surface of samples and so the atom electrons use the energy to jump to an energy shell. Therefore, the electron leaves and leads to a positive charge hole which will then attract the negative charge of electrons from a higher energy shell. Hence, the energy difference between two shells (the hole with low energy shell fills by high energy shell) is produced in the form of an x-ray which can be measure by EDX.

2.4. Carbon dioxide gas adsorption study

An experiment is set up as shown in Figure 1 to measure the CO$_2$ adsorption performance of the fabricated MOFs. Before the gas adsorption experiment, the mass of the empty teabag and the initial mass of MOF sample was weighed and recorded. Furthers, weighed and recorded the mass of the teabag with MOF again after the weighted MOF sample was placed into an empty tea bag. Then, the teabag with MOF sample was placed in a hollow stainless-steel cylinder tube which both ends of the tube were sealed tightly. This is to prevent the leaking of CO$_2$ gas when the CO$_2$ gas flows into the cylinder tube via a pipe for approximately two hours. Later, the sample MOF has sufficient time to adsorb the supplied CO$_2$ in a closed system. The inlet and outlet concentration of CO$_2$ were recorded every 5 minutes to get the difference which then can be used to calculate the CO$_2$ adsorption capacity of the MOF. The best performance MOF from the CO$_2$ adsorption study will be then used to evaluate the CO$_2$ reduction in an indoor enclosed volume of approximately 28.3m$^3$. The initial CO$_2$ concentration was measure by a CO$_2$ meter and the indoor air will be drawn into the stainless-steel vessel containing MOF sample. The CO$_2$ concentration outlet of the stainless steel vessel will be measured and the difference in initial and outlet CO$_2$ concentration will be the rate of CO$_2$ adsorbed (Figure 2).

![Figure 1. Carbon dioxide gas adsorption setup](image-url)
3. Results and Discussions

3.1. Morphologies of Metal Organic Framework

Mg-TMA possesses dispersed nanorod flask crystal as exhibited in Figure 3(a). These structures formed due to simultaneous nucleation and crystal growth under solvothermal method [11]. Tahmasian, Morsali and Joo (2013) reported the size of these structures is dependent on the concentration that produces by initial reagents. In the case of a higher concentration of initial reagents, uniform morphology and smaller size of inhomogeneous nanorods can be obtained [12]. Cr-MOFs exhibited a large amount of agglomerate crystal structure and the size of crystal structures of Cr-MOFs was relatively small which were estimated in the range of 100 micrometers to 5 micrometers (Figure 3(b)). Lower crystallinity of Cr-TPA can be seen when the molar ratio of the organic ligands increases. The surface area of the MOFs to volume ratio becomes lower when there is large agglomeration of the crystal structure which may hinder the good gas adsorption capabilities [13, 14]. Cu-TMA exhibit coarse crystal rod of Cu-TMA have been observed (Figure 3(c)). The formation of this coarse crystal structure was attributed to the interaction and the overall stoichiometry of Cu-MOFs might be affected by few factors such as the component concentration and the purity, counter ions size and the reaction conditions such as temperatures, solvent and mixing rates [15, 16].
Figure 3. SEM image of (a) Mg-TMA, (b) Cr-TMA and (c) Cu-TMA

3.2. EDX Analysis

The elemental content of the fabricated MOF was analyzed by the EDX techniques (Table 1). Given the irregularity of the samples, the measurement of the weight percentage was calculated by the average of 5 sampling spots from samples to ensure reproducibility. The fabricated MOF were suggested to be successful based on the result from the EDX analysis. The element of magnesium, chromium and copper were detected in the Mg-TMA, Cr-TMA and Cu-TMA, respectively, suggesting the presence of the metal in the fabricated MOF. Additionally, the occurrence of the carbon and oxygen in all the MOF suggested that the organic ligands were successfully linked to the metal oxide to form MOF.

| MOFs   | Carbon  | Oxygen   | Magnesium  | Chromium | Copper   |
|--------|---------|----------|------------|----------|----------|
| Mg-TMA | 34.59 ± 1.73 | 53.67 ± 3.48 | 11.74 ± 0.93 | Not detected | Not detected |
| Cr-TMA | 49.54 ± 2.91 | 48.97 ± 2.87 | Not detected | 11.49 ± 0.83 | Not detected |
| Cu-TMA | 39.95 ± 2.43 | 43.39 ± 3.02 | Not detected | Not detected | 16.66 ± 0.71 |

3.3. Carbon Dioxide Gas Adsorption Study

Mg-TMA sample shows the highest CO$_2$ adsorption capacity recorded at 4.6 mmol/g followed by Cu-TMA and Cr-TMA in this study (Table 2). The good performance recorded by Mg-TMA might be attributed to the number of open metal sites in MOF framework greatly affect CO$_2$ adsorption capacity which means that bonding between Mg metal sites in the MOF with CO2 molecule that acts as adsorbate molecule is stronger than the other metal such as Cu and Cr. This is because the bonding of the ionic character of the Mg-O bond can trap the CO$_2$ into MOF easily. Different types of metal and organic ligands use might form different crystal structures of MOF. On the other hand, the lowest performance of CO$_2$ adsorption by Cu-TMA suggested the coarse crystal size led to a lower surface area to volume ratio, therefore, reducing the gas adsorption ability of this MOF. Subsequently, Mg-TMA was used to study the CO$_2$ adsorption in the indoor air condition. The initial enclosed space CO$_2$ concentration was recorded at 960 ± 73 ppm. The CO$_2$ concentration was then recorded at 895 ± 57 ppm after two hours of sampling time, indicating a reduction of 6.77% of CO$_2$ concentration.
4. Conclusions

In a nutshell, the main cause of the IAQ problem is indoor air pollution that releases gases or particles especially CO$_2$ molecules. Inadequate ventilation indoor may lead to an increase in the CO$_2$ level which can then cause sick building syndrome. According to NIOSH, the CO$_2$ concentration in a room must be below 1,000 ppm else consider an inadequate ventilation room. Hence, the right ventilation can help to prevent the IAQ problem, and the researchers must develop some effective methods or technology to capture CO$_2$. Strong action and study are needed in the IAQ topic. In this paper, MOF samples have been chosen to capture CO$_2$ due to several outstanding features such as the topologies surface of MOFs which is more adaptable than the other existing porous materials. There are three types of MOF namely, Mg-TMA, Cr-TMA and Cu-TMA were successfully fabricated, and its gas adsorption performance was studied. The SEM images suggested that Mg-MOF exhibited the highest surface area attributed to its fine nanorod flask crystal. The EDX analysis suggested that the metal oxides were well attached to the organic linker. The gas adsorption study shows that Mg-TMA possess the highest gas adsorption capacity. Subsequent study shows that the Mg-TMA able to reduce the 960 ± 73 ppm to 895 ± 57 ppm under 2 hours continuous sampling time suggested this MOF possess the potential to be applied for CO$_2$ reduction for indoor air quality improvement.

References

[1] Chen S., Guo C., Huang X. 2018. *J. Environ. Econ. Manag.* **92**, 465.
[2] Khamal R., Isa Z., Sutan R., Razif N., Ghazi N. H., 2019. *Ann. Glob. Health.* **85** 1.
[3] Liu H., Salvo A., 2018. *J. Environ. Econ. Manag.* **92** 300.
[4] Department of Occupational Safety and Health, Malaysia. 2010. *Industry Code of Practice on Indoor Air Quality. Kuala Lumpur.* Department of Occupational Safety and Health, Malaysia.
[5] Abd A.A., Naji S.Z., Hashim A.S., Othman M.R., 2020, *J. Environ. Chem. Eng.* **8** 104142.
[6] Li H., Wang K., Sun Y., Lollar C., Li J., Zhou H.C., 2018. *Mater. Today.* **21** 108.
[7] Wen Y., Zhang J., Xu Q., Wu X.T., Zhu Q.L., 2018. *Coord. Chem. Rev.* **376** 248.
[8] Younas, M., Sohail, M., Kong, L., Bashir, K., Sethupathi, S., 2015. *Int. J. Environ. Sci. Technol.* **13** 1839.
[9] Li, P., Chen, J., Zhang, J. and Wang, X., 2015. *Sep. Purif. Rev.* **44** 19.
[10] Hauchhum, L. and Mahanta, P., 2014. *Int. J. Energy Environ. Eng.* **5** 349.
[11] Jhung S. H., Jin T., Hwang Y.K., Chang J., 2007. *Chem. Eur. J.* **13** 4410.
[12] Tahmasian A., Morsali A., Joo S.W., 2013. *J. Nanomater.* **10** 1.
[13] Gargiulo N., Peluso A., Aprea P., Hua Y., Filipović D., Caputo D., Eiić M. 2014. *RSC Adv.* 4 90.
[14] Liang J., Huang Y., Cao R., 2019. *Coord. Chem. Rev.* **378** 32.
[15] Sahiner, N., Sel, K., Ozturk O.F., Demirci S., Terzi G., 2014. *Appl. Surf. Sci.* **314** 664.
[16] Liu Y., Ghimire P., Jaroniec M., 2019. *J. Colloid Interface Sci.* **353** 122.