Metal-Organic Frameworks: Screening M-MOF-74 (M = Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, and Zn) Based for Carbon Dioxide Adsorption

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Abstract. The release of carbon dioxide in the environment is increasing yearly due to human activities and it will affect greenhouse gas. To overcome this issue, adsorption technology found to be the best candidate due to its performance to capture high CO_2 with lower capital cost. Much attention has focused on metal-organic framework (MOF) due to high potential of CO_2 capture compared with conventional adsorbents. More research has been done on MOF-74 due to presence of the open-metal site that favors CO_2 binding. The presence of metal in MOF-74 able to give higher surface area and porosity of the molecules thus result in higher adsorption of CO_2. However, there is limited research related to metal in MOF-74 where most focused on the Mg-MOF-74 due to its ability to adsorb twice of CO_2 compared with zeolites. Yet, Mg-MOF-74 found to lose stability in presence of water where it's only able to recover 15% from initial adsorption. Synthesizing MOF-74 requires high cost and providing not a promising result for each synthesizes. Thus, this paper introduces to screen MOF-74 for different metal centers using modeling approach by Material Studio. As result, Ni-MOF-74 shows the highest adsorption of CO_2 with 12.35mmol/g compared to other metals.

1 Introduction

Carbon Dioxide (CO_2) is one of the most pressing challenges that we face nowadays. Fossil fuels are the main energy used for energy supply due to the massive development of industries. Thus, fossil fuel plant have released significant quantity of carbon dioxide into atmosphere that aggravates climate change and global warming [1, 2]. In 2014, it is reported over 24% of CO_2 emission comes from fossil-fuel plant[1]. Although renewable energy increasing eventually, electricity generation from natural gas is expected to remain an important power source until 2030 due to the lower capital cost[1, 3]. Therefore, the release of CO_2 will be higher due to extensive operation of a power plant.

There are several techniques to capture CO_2, which is cryogenic distillation, membrane, absorption and adsorption. However, membrane seems to be able to perform in low pressure and temperature only otherwise its structure will rupture. Cryogenic distillation requires high energy used that leads to the high capital cost. Moreover, absorption technology will cause an environmental impact due to release of absorbent solvent to the environment. Adsorption method seems to have a potential in reducing energy requirement and operational costs with its ability to capture high CO_2[4, 5]. Adsorption is an adhesive between atoms, ions and molecules from fluid of gas or liquid into the surface. There are certain criteria that need to meet for adsorbents of carbon dioxide capture, which are first, selectively adsorbs CO_2 over nitrogen and water at low CO_2 partial pressure, robust in the presence of water and lastly can be synthesized in large quantity with reasonable price[2]. Most commonly used adsorbents are alumina, activated carbon, zeolite and silica gel that satisfied with these criteria. However, these adsorbents result in low capacity in carbon dioxide capture with difficulty of the regeneration process[6].

Recent studies have found a new adsorbent that satisfies with the capacity and kinetic for adsorption mechanism, which is Metal-Organic Framework (MOFs)[6]. MOFs have been considered as novel adsorbents due to a high surface area, large pore volumes and tuneable pore size[3]. Metal-Organic Framework (MOFs) is a class of crystalline materials that consists of a coordination of bonds between transition-metal cations and multi-dentate organic linkers[2, 7, 8]. MOFs can impact in high porosity to its structure due to its coordination of polymer synthesized by assembling of metal ions, and linkers coordinates. Various applications can be used for MOFs including gas adsorption and storage, separation, can act as catalyst, adsorption of organic molecules, drug delivery, luminescence polymerizations and magnetism[7]. Metal Organic Frameworks result in large pore volume thus capture high capacity of CO_2 at high pressures up to 40 bars compared to conventional adsorbents such as zeolites and activated carbon[9]. These MOFs can be designed with specific metal atoms, different covalent functional, hydrophobicity and preferred porosity for the different purpose of study[2, 10]. Their structure can be designed

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according to targeted properties based on geometries of organic linkers and coordination modes of inorganic metal ions. Over 5000 MOFs have been captured in literature for carbon dioxide adsorption properties, such as MOF-177 that capture 4.5 times more of carbon dioxide at 35 bars meanwhile MOF-74 adsorb almost twice carbon dioxide compared to zeolites at 0.1 to 1.0 bar[11].

One of the most anticipate study series of MOFs is known as M-MOF-74 (2, 5-DOT = 2,5-dioxididoterepthalate where M= Mg(II), Zn(II), Mn(II), Fe(II) and Ni(II) of transition metal in periodic series)[2]. The presence of the open metal site in MOF-74 favor to CO_2 binding mode with a pore diameter between 1.1 to 1.2 Å [2, 12]. Mg-MOF-74 reported to have higher surface area (BET: 1495 m^2/g) which gives higher adsorption capacity of CO_2 compared to other metals[3]. This is due to lighter molecular weight of magnesium (Mg) which is 24.395 g/mol compared with zinc (Zn) 65.38 g/mol and nickel (Ni) 58.69 g/mol state as a fact that magnesium (Mg) will be the best metal centers. However, capacity of CO_2 adsorption for Mg-MOF-74 found decrease and loss in stability with presence of water compared with Co-MOF-74 and Ni-MOF-74 that retained of 60% and 85% from initial capacities respectively[3]. However, there is limited literature related to M-MOF-74 (where M= Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, and Zn) for comparison on which metal centers give higher carbon dioxide capture and robust in the presence of water. Thus, further studies need to be done onto differ from metal centers in accordance of performance for robustness in water, higher selectivity and able to operate in higher pressure and temperature[6].

Molecular simulation has been done to investigate and predict metal-organic framework properties. Due to various MOFs have been explored, the role of computation is needed to overcome the limitation of the experiment by providing microscopic info that is not accessible through experiment[13]. MOFs cannot be synthesized in short period of time[11]. Furthermore, synthesizing all types of MOFs without screening will increase the cost and require a longer period. Therefore, to ensure its effectiveness and address systematically for this challenge, a screening of M-MOF-74 using computational method needed in this study.

The aim of this research is to evaluate the capacity of MOF-74 in capturing carbon dioxide (CO_2) by using simulation tools. M-MOF-74 selected as the adsorbent in this research due to its ability to capture high CO_2 due to presence of open metal sites that increase CO_2 binding, and certain metal that gives high robustness in water compared with other MOFs. Molecular simulation is a potential solution to predict which metal-organic framework will result in the best performance due to the experimental method required high cost of linker with different metal centers. Thus, economical approach in selection of suitable M-MOF-74 (where M= Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, and Zn) based for adsorption of CO_2 are essential.

2 Methodology/ Simulation Theory

Grand Canonical Monte Carlo (GCMC) simulation was used to calculate the adsorption isotherm of gases on the different type of solid surfaces for homogenous, surface of the slit pores and also metal organic framework[14]. In GCMC, the local density and orientation profiles provided to study the packing structure of the molecules (gases) in the pores for changing of pressure and temperature[15]. In Monte Carlo simulation, constant is considered for temperature, volume and chemical potential[14]. There are four different movement types for GCMC simulation method including translation, insertion, rotation and deletion of molecules adsorbed[8].

In accordance of Metropolis sampling, the random displacement for accepted probability of ρ_{move} = min [exp (-ΔU/kT);]: where the probability for insertion (P_{ins}) acceptance is shown in Equation 1[8];

$$p_{ins} = \min\left[\frac{V}{N+1} exp\left(\frac{\mu-\Delta U}{kT}\right)\right]; 1] \quad (1)$$

Meanwhile, particle deletion (P_{del}) shows in Equation 2[8];

$$p_{del} = \min\left[\frac{N}{V} \exp\left(\frac{\Delta U-\mu}{kT}\right)\right]; 1] \quad (2)$$

Where $\Delta U = U_{new} - U_{old}$ is the change in new (trial) and old (current) configuration of potential energy. In the system of Metropolis, it requires volume = V, temperature = T and chemical potential = μ. GCMC allows fluctuations of density and energy in micro state thus its expressed the output density, or the average of adsorbate molecules attached varies with chemical potential, ($N=f(\mu)$) at a fixed temperature[15]. Grand Canonical ensemble is a complicated integral that impossible to be solved using conventional numerical integration. Thus, the role of molecular simulation is needed for implementation of Monte Carlo integration.

The software used in this simulation study is Material Studio to compute behaviour of atomic and molecule materials for prediction. There are various modules can be obtained through material studio such as amorphous cell, reflex tools, forcite and sorption. Sorption module will be used as its able to perform GCMC method for adsorption of CO_2. Figure 1 indicate the overview of the simulation of MOF-74 using Material Studio software.

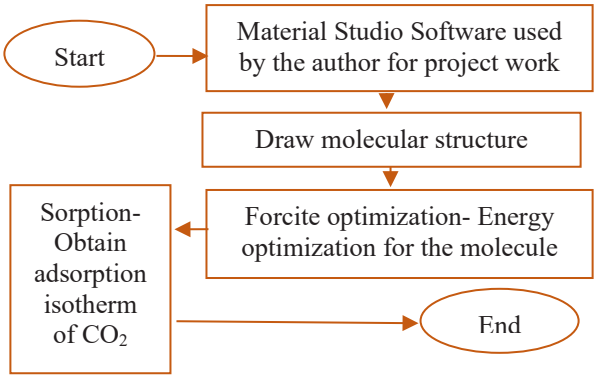

Fig. 1. Flowchart for obtain CO_2 adsorption analysis for MOF-74 simulation

In Figure 1, it is shows that Material Studio was used for MOF-74 screening and molecular structure was obtained to run the simulation. The molecular structure is set to 2x2x2 unit cells with hexagonal shaped structure. Then, the energy of the molecular structure was optimized by using forcite optimization. After energy optimization, the adsorption isotherm of CO_2 obtained by sorption module where GCMC calculation were applied. The temperature was set to 298 K and pressure 0 to 1 bar. After simulation, the results obtained were compared with literature for validation.

In this project, MOF selected is MOF-74 with nine different metals in periodic table, which are magnesium (Mg), nickel (Ni), cobalt (Co), titanium (Ti), copper (Cu), chromium (Cr), iron (Fe), zinc (Zn) and manganese (Mn). The molecules are compared to identify which open metal sites of MOF-74 give the best result of carbon dioxide adsorption. The structure framework of MOF-74 is obtained from Cambridge Structural Database (CSD) and optimized to form hexagonal structure for allowing comparisons with experimental and theoretical data available in the literature[7].

2.1. Forcite Geometry Method

Forcite Geometry used for energy calculation to determine the attraction of van der Waals between adsorbent and adsorbate. Forcite offers molecular mechanics tools where the calculation depending on forcefield. The forcefield related is Compass, Universal Forcefield (UFF), and Dreiding calculation forcefield to handle chemical system. Geometry optimization required in order to minimize the repulsive effect of like charge molecules and to maximize attractive effect of the different charge molecules[16]. Therefore, it is important to obtain a forcefield that suitable for open metal site in this adsorption. Forcefield that set with universal is known as coarse and harsh approached. Various of a parameter available for universal forcefield (UFF) together with hard coded make this forcefield as error resistant. COMPASS forcefield selected as it is specified for each MOF-74 metal selection thus reduce the error obtained.

2.2 Sorption Method

Sorption isotherm is needed to identify the separation process. This sorption method can predict the adsorption isotherm based on GCMC calculation. It's also will model the effects of structural changes, ion exchange and differing charge distributions. Sorption method varies with the task such as Henry Constant, Adsorption Isotherm, and Locate[16]. The author is using Adsorption Isotherm task to calculate the adsorption of carbon dioxide.

3 Results and Discussions

The purpose of an adsorption isotherms is to identify the capacity of MOF-74 to adsorb carbon dioxide. Figure 2 shows the adsorption capacity for screening of M-MOF-74 (where M= Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, and Zn) at constant temperature 273K and pressure 0.1 bar.

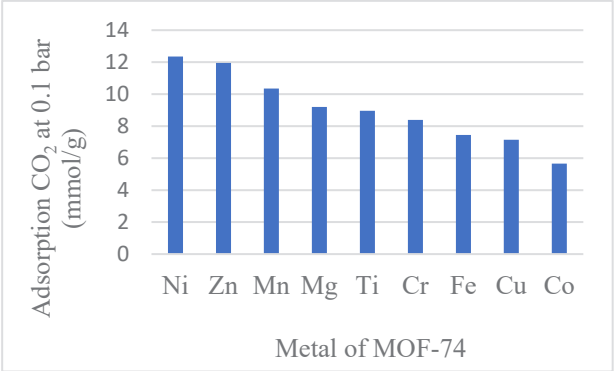

Fig. 2. Adsorption of CO_2 for screening MOF-74

During simulation, it must be sure that the structure stability and feasibility to minimize error occur that cause failure in CO_2 adsorption. The structure must be in periodic structure with optimizes the molecular structure. From Figure 2, it is shown that the highest adsorption capacity achieves by nickel-metal centers followed with zinc, manganese, magnesium, titanium, chromium, iron, copper and cobalt respectively. From previous literature, Mg/DOBDC gives the best performance compared with other metals due to higher ionic character of the Mg/DOBDC bond[13, 17]. However, must be noted that the water stability of Mg-MOF-74 is lower and decrease in CO_2 adsorption when presence of water compared to Ni/DOBDC and Co/DOBDC[6]. However, it is found that changing metal from Mg in M/DOBDC to Zn, Ni, and Mn provides a big chance in CO_2 uptake. M/DOBDC (where M= Ni, Zn, Mn, Mg, Ti, Cr, Fe, Cu, Co and DOBDC = dioxybenzenedicarboxylate) MOFs have open metal sites that can interact with adsorbate molecules, and Ni/DOBDC performs quite particularly well. At pressure 0.1 bar, Ni-MOF-74 obtains result of 12.35 mmol/g followed with Zn-MOF-74 at 11.95 mmol/g. The lowest adsorption capacity shows by Co-MOF-74 that achieve 5.66 mmol/g. However, the simulation capacity will be higher compared with theoretical literature due to ideal

condition assumptions and theoretical data obtained by experiments and synthesizing. The identity of the metal, its accessibility and the local environment also play a role in simulation and should be studied in the future.

Table 1 indicate the comparison for simulation with theoretical value of MOF-74. However, data available from literature only for Mg, Zn, Ni, Co and Mn metal of MOF-74[3, 17].

Table 1. Simulation and literature comparison

Metal MOF-74	Literature 1[17] (mmol/g)	Literature 2 [3] (mmol/g)	Simulation (mmol/g)
Magnesium	6.52	4.93	9.20
Cobalt	6.30	1.25	5.66
Nickel	5.08	3.90	12.35
Zinc	5.00	2.83	11.95
Manganese	N/A	2.67	10.35

It is shown that from both literature that the highest adsorption capacity is magnesium metal. However, from the simulation it is found that nickel gives the highest value, but the other metal also gives satisfied value compared with literature. There is the difference in simulation and literature value due to different surrounding condition. Upon simulation, there is ideal condition without the environment factor that needs to be considered compared with experimental. Figure 3 shows simulated and literature CO_2 uptake at pressure 0.1 bar.

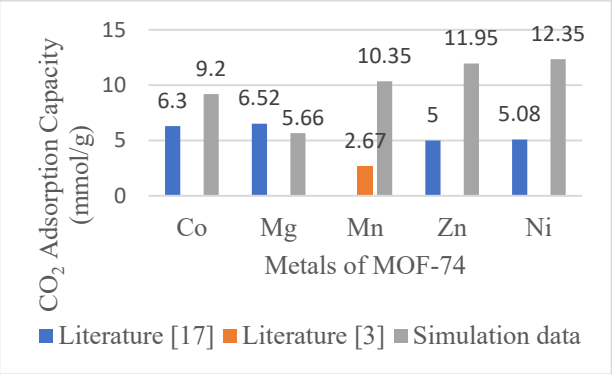

Fig. 3. Comparison CO_2 uptake between simulated and literature data

A comparison of CO_2 uptake for simulated and literature 1 and 2 shows in Figure 3. The data are compared between simulation with the highest reported value in the literature. There is generally not a good agreement between other metals except cobalt and magnesium at 0.1 bar. Our forcefield is not expected to perform well for strong interactions between open metal sites and CO_2. A detail study must be done in the future upon the molecular structure and its affinity. Identifying the best candidates is an important task in screening, where we found that Ni-MOF-74 gives the best selection of 12.35 mmol/g compared with other metals. In order to support this selection, some literature reported that Ni-MOF-74 also gives the best performance in presence of water (85% recovery of CO_2 adsorption) whereas Mg-MOF-74 only recovered 18% of CO_2 adsorption from initial value when presence of water[3, 18]. It is testified according to literature that the stability of series MOFs were observed under water adsorptions with 80% relative humidity (RH) at room temperature and loss in surface area were estimated from nitrogen adsorption at 77 K for solid stability after exposure[19].

From this research, it can be concluded that the model can be improved severely. For example, the model of simulation should be included polarization or orbital interactions. These interactions are expected to play a role in adsorption of CO_2 for MOF-74. Using X-Ray Diffraction and IR spectroscopy for the molecule of MOF-74 can help to improve the trend model.

4 Conclusion

As the conclusion, the simulation to screen M-MOF-74 (where M= Co, Cr, Cu, Fe, Mg, Mn, Ni, Ti, and Zn) for adsorption of carbon dioxide have been completed. The presence of open metal sites in MOF-74 favor to CO_2 binding mode that gives higher adsorption capacity. Although Mg-MOF-74 gives an outstanding result compared with other metals for adsorption capacity in dry condition (6.52 mmol/g) as shown in literature, a drastic degradation of CO_2 adsorption occurs under humid condition. Meanwhile, the adsorption capacity in this study shows Mg-MOF-74 obtain 9.20 mmol/g, which is higher compared to literature due to its ideal condition in computational screening but lower than nickel, manganese, and zinc metal in this study. Therefore, Ni-MOF-74 can be considered as suitable candidate in this screening study where the adsorption capacity is 12.35 mmol/g compared with other metals. Plus, it also provides a promising structure stability with presence of water as reported in previous literature. Thus, further study should be done onto the effect of attraction energy of molecule, intermolecular energy and van der Waals forces to support this selection.

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