Faculty of Engineering

DESIGN OF CYCLODEXTRIN METAL ORGANIC FRAMEWORK FOR CO_2 ADSORPTION

Shahrulneezam Bin Aediee Djunaidee

Bachelor of Chemical Engineering with Honours

2022

UNIVERSITI MALAYSIA SARAWAK

Grade: ________________
Please tick (/)
Final Year Project Report /
Masters
PhD

DECLARATION OF ORIGINAL WORK

This declaration is made on the 3 day of July 2022

Student's Declaration:

I, SHAHRULNEEZAM BIN AEDIEE DJUNAIDEE (56954), DEPARTMENT OF CHEMICAL ENGINEERING AND ENERGY SUSTAINABILITY, FACULTY OF ENGINEERING, hereby declare that the work entitled DESIGN OF CYCLODEXTRIN METAL ORGANIC FRAMEWORK FOR CO_2 ADSORPTION is my original work. I have not copied from any other student's work or from any other sources except where due reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

3RD JULY 2022	SHAHRULNEEZAM BIN AEDIEE DJUNAIDEE (65196)
Date submitted	Name of the student (Matric No.)

Lecturer Declaration

I IR. DR IVY TAN AI WEI hereby certifies that the work entitled DESIGN OF CYCLODEXTRIN METAL ORGANIC FRAMEWORK FOR CO_2 ADSORPTION was prepared by the above named student and was submitted to the "FACULTY" as a fulfillment for the conferment of BACHELOR OF ENGINEERING WITH HONOURS (CHEMICAL ENGINEERING) and the aforementioned work to the best of my knowledge, is the said students' work.

Received for examination by	Date:
IR. DR IVY TAN AI WEI (Name of supervisor)	24TH JULY 2022

I declare this Report is classified as (Please tick (√)):

☐	**CONFIDENTIAL**	(contains confidential information under the Official Secret Act 1972) *
☐	**RESTRICTED**	(Contains restricted information as specified by the organization where research is done)
√	**OPEN ACCESS**	

Validation of Report

We therefore duly affirmed with free consent and willingness declared that this said Report shall be placed officially in Department of Chemical Engineering and Energy Sustainability with the abide interest and right as follows:

- This Report is the sole legal property of Department of Chemical Engineering and Energy Sustainability, Universiti Malaysia Sarawak (UNIMAS).
- The Department of Chemical Engineering and Energy Sustainability has the lawful right to make copies for the purpose of academic and research only and not for other purposes.
- The Department of Chemical Engineering and Energy Sustainability has the lawful right to digitize the content to for the Local Content Database
- The Department of Chemical Engineering and Energy Sustainability has the lawful right to make copies of the Report for academic exchange between Higher Learning Institute.
- No dispute or any claim shall arise from the student itself neither third party on this Report once it becomes sole property of The Department of Chemical Engineering and Energy Sustainability, Universiti Malaysia Sarawak (UNIMAS).
- This Report or any material, data and information related to it shall not be distributed, published or disclosed to any party by the student except with The Department of Chemical Engineering and Energy Sustainability, Universiti Malaysia Sarawak (UNIMAS) permission.

Student's signature: ____________________
24TH JULY 2022

Supervisor's signature: ____________________
24TH JULY 2022

Current Address:
DEPT. OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, 94300 KOTA SAMARAHAN, SARAWAK.

Notes: * If the Report is **CONFIDENTIAL** or **RESTRICTED**, please attach together as annexure a letter from the organization with the period and reasons for confidentiality and restriction.

APPROVAL SHEET

This final year project, which entitled **“Design of Cyclodextrin Metal Organic Framework for CO_2 Adsorption”** was prepared by Shahrulneezam Bin Aediee Djunaidee (65196) as course fulfillment for the Bachelor of Engineering with Honours (Chemical Engineering) is hereby read and approved by:

24th JULY 2022

IR. DR IVY TAN AI WEI

(Final Year Project Supervisor)

Date

DESIGN OF CYCLODEXTRIN METAL ORGANIC FRAMEWORK FOR CO_2 ADSORPTION

SHAHRULNEEZAM BIN AEDIEE DJUNAIDEE

A dissertation is submitted in partial fulfillment
of requirements for the degree of
Bachelor of Engineering with Honours
(Chemical Engineering)

Faculty of Engineering
Universiti Malaysia Sarawak

2022

Dedicated to my beloved parents, family and friends, who always bestow me
sustainable motivations and encouragements

ACKNOWLEDGEMENT

The author wishes to thank all individuals, parties and organizations that have contributed and cooperated throughout this final year project especially to Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, UNIMAS. Special thanks are dedicated to the author’s supervisor, Ir. Dr Ivy Tan Ai Wei. The author would like to express his appreciation to his beloved family and friends for their contributions, supports and motivations in completing this thesis.

ABSTRACT

Carbon dioxide (CO_2) capture efficiency is a crucial issue for porous adsorbents. The insufficiency of typical adsorbents results in inadequate CO_2 removal adsorption capability. Since it demonstrates a greater rate of CO_2 adsorption at room temperature, Metal Organic Frameworks (MOFs) have been considered particularly effective for CO_2 adsorption. CO_2 adsorption by traditional liquid alkanolamine adsorbents does not match the criteria for environmentally acceptable development in industrial applications, and a somewhat hefty energy penalty is required to regenerate it. However, a novel class of MOF combined with an amino functionalised group has been proven to improve the adsorption potential and separation efficiency. The significant interaction between CO_2 and amino-functionalised group MOFs has become more fascinating to be studied, hence in this study, NH_2-γ-CD-MOF was constructed using VESTA Simulation through approximation crystalline structure using its bond angle and data from the study of Xu et al. (2019) as a reference, which was NH_2-β-CD-MOF. From the data simulated in VESTA, Mercury, and iRASPA, the work was proceeded using Grand Canonical Monte Carlo (GCMC) from Amsterdam Modeling Suite to simulate the application for CO_2 adsorption to determine its adsorption capacity. The volume of NH_2-γ-CD-MOF was found to have a unit cell volume of 29791.0 $\mathrm{Å}^3$ with a lattice parameter a, b, and c of 31 Å and $\alpha, \beta\ and\ \gamma$ of $90°$ with the space group of (CUBIC) $211\ \mathrm{I}432$. Other than that, the adsorption capacity exceeds traditional CD-MOFs by 6.5%. Lastly, the process of adsorption begins with chemisorption and physisorption at higher pressure.

Keywords Carbon Dioxide, Metal Organic Framework, Amino functionalised group, VESTA Simulation, Grand Canonical Monte Carlo

ABSTRAK

Kecekapan tangkapan karbon dioksida (CO_2) merupakan isu utama bagi penjerap berliang. Kekurangan penjerap biasa mengakibatkan keupayaan penjerapan penyingkiran CO_2 yang tidak mencukupi. Memandangkan ia menunjukkan kadar penjerapan CO_2 yang lebih tinggi pada suhu bilik, "Metal Organic Framework (MOF)" telah dianggap berkesan terutamanya untuk penjerapan CO_2. Penjerapan CO_2 oleh penjerap alkanolamin cecair tradisional tidak sepadan dengan kriteria untuk pembangunan yang boleh diterima oleh alam sekitar dalam aplikasi perindustrian, dan penalti tenaga yang agak besar diperlukan untuk menjana semulanya. Walau bagaimanapun, kelas baru MOF yang digabungkan dengan kumpulan amino telah terbukti dapat meningkatkan potensi penjerapan dan kecekapan pemisahan. Interaksi ketara antara CO_2 dan MOF kumpulan berfungsi amino telah menjadi lebih menarik untuk dikaji. Oleh itu dalam kajian ini, NH_2-γ-CD-MOF dibina menggunakan simulasi VESTA melalui struktur kristal penghampiran menggunakan sudut ikatannya dan data daripada kajian Xu et al. (2019) iaitu NH_2-β-CD-MOF. Data yang disimulasikan dalam VESTA, Mercury dan iRASPA menggunakan Grand Canonical Monte Carlo (GCMC) daripada Amsterdam Modeling Suite untuk mensimulasikan aplikasi penjerapan CO_2 untuk menentukan kapasiti penjerapannya telah dilakukan. Kajian isipadu NH_2-γ-CD-MOF mempunyai isipadu sel unit 29791.0 $Å^3$ dengan parameter kekisi a,b dan c ialah 31 Å dan $\alpha, \beta\ dan\ \gamma$ ialah 90° dengan kumpulan ruang (KUBIK) 211 I432. Selain itu, kapasiti penjerapan melebihi CD-MOF tradisional sebanyak 6.5%. Akhir sekali, proses penjerapan bermula dengan chemisorption dan physisorption pada tekanan yang lebih tinggi.

Kata Kunci Karbon Dioksida, Rangka kerja organik logam, Kumpulan berfungsi amina, VESTA simulation, Grand Canonical Monte Carlo

TABLE OF CONTENTS

2.0 LITERATURE REVIEW

3.0 METHODOLOGY

4.0 RESULT AND DISCUSSION

5.0 CONCLUSION AND RECOMMENDATION

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

LIST OF ABBREVIATIONS

BET	Brunauer–Emmett–Teller
CCS	Carbon Capture and Sequestration
CD-MOF	Cyclodextrin Metal-Organic Framework
CIF	Crystallographic Information Files
COFs	Covalent Organic Frameworks
CPs	Coordination Polymers
DFT	Derived Force Field
FCC	Face Centered Cubic
GCMC	Grand Canonical Monte Carlo
GSA	Gravimetric Surface Area
IUPAC	International Union of Pure and Applied Chemistry
MC	Monte Carlo
MD	Molecular Dynamic
MOFs	Metal-Organic Frameworks
POFs	Porous Organic Frameworks
PR-EOS	Peng-Robinson Equation of State
SSA	Specific Surface Area
VSA	Volumetric Surface Area

LIST OF NOMENCLATURE

Å	Angstrom
$cm^3\ g^{-1}$	Centimetre cubic per gram
cm^3	Centimetre cubic
$Ca(OH)_2$	Calcium Hydroxide
CO_2	Carbon Dioxide
°C	Degree Celsius
$g\ cm^{-3}$	Gram per centimetre cubic
$g\ mol^{-1}$	Gram per mol
$m^2\ g^{-1}$	Meter square per gram
nm	nanometer
NOx	Nitrogen Oxides
NaOH	Sodium Hydroxide
SOx	Sulphur Oxides
H_2O	Water
°	Degree
%, w/v	Percent Weight per Volume

CHAPTER 1

INTRODUCTION

1.1 Research Background

Overpopulation, climate change, waste disposal, natural resource depletion, and air, water, and soil pollution are just a few of the major global environmental concerns that the globe is facing. Years of urbanisation and industrialisation have had long-term, and in some cases irreversible, repercussions on our environment that must be addressed. A relatively young branch of green chemistry has exploded in popularity to address some of these crucial challenges. It embraces and implements the discovery and design of chemical products and processes that reduce or eliminate the usage and generation of hazardous compounds (Ajoyan et al., 2018). Carbon dioxide is the most significant source of greenhouse gas emissions globally, accounting for nearly 85% of all CO_2 emitted into the atmosphere from fossil fuel and industrial processes (The Intergovernmental Panel on Climate Change (IPCC), 2017). Daily emissions of high amounts of CO_2 and other greenhouse gases are causing an increase in surface air temperature, unsettling weather patterns, and ocean acidification. According to Chin (2018), in Malaysia alone, 236.1 metric tonnes of CO_2 were emitted in 2014 and continued to rise until today. As a result, Carbon Capture and Sequestration (CCS) is critical for lowering CO_2 emissions. CO_2 capture, transport, and storage are the three critical components of the system.

Due to the slight temperature difference between the flue gas and solid adsorbents running at low temperatures, solid adsorbents operating at low temperatures are advantageous for optimal energy utilisation in CCS facilities. Additionally, incorporating transition metal ions and organic backbones could alleviate the zeolite structure, restricting the number of accessible building units and difficulty in functionalisation, leading to the development of high-adsorbent materials, such as

MOFs. Additionally, activated carbon is limited to adsorb CO_2 under high pressure and low selectivity, whereas hydrophilic zeolite is unstable in water.

MOFs' chemical and structure diversity provides huge prospects for substantial technological improvements in various disciplines (Burtch et al., 2017). Due to MOF's versatility, it can be used to solve many problems and in various ways, depending on the mix of metal and organic linkers. Thus, the enormous potential for developing MOFs with novel properties represents an ideal chance to resolve issues that explicit inorganic and organic molecules are incapable of resolving. As a result, MOFs have garnered academic and industry interest in recent years. MOFs are regarded as an attractive candidate for adsorption because of their low regeneration temperature, high porosity, and surface area (Burtch et al., 2017). CO_2 capture from flue gas must be evaluated under strict process conditions, such as flue gas availability (post-combustion) at high temperatures and close atmospheric pressure, low CO_2 partial pressure in flue gas, and competitive adsorption by pollutants such as H_2O and SOx/NOx. The CO_2 capacity and CO_2/N_2 selectivity of known MOFs are not promising at low pressure. Significant limitations include the problematic long-term structural stability of MOF materials, the expensive cost of even the most basic organic linkers, and difficulties in developing robust MOF formulations.

The post-combustion pathway is the process of capturing and separating dilute CO_2 from a combustion system's flue gas in an oxidant environment (Zhang et al., 2020). According to Wu et al. (2020), to avoid solvent degradation, the exhaust flue gas emissions were denitrified and desulphurised, as well as dust removal and cooling prior to CO_2 capture. The flue gas, which was mainly composed of CO_2, H_2O, and N_2, was subsequently fed counter-currently to the absorber containing the solvent, as shown in **Figure 1.1**. According to Osman et al. (2020), post-combustion technology involved cooling the hot flue gas before sending it to a CO_2-absorber unit, which typically used monoethanolamine solvent as the sorbent. The CO_2-rich absorbent was then transferred to the CO_2-stripper unit, where the CO_2 gas was released, while the CO_2-lean absorbent was returned to the CO_2-absorber unit. This was followed by a final step in which pure CO_2 gas was compressed and dehydrated for pipeline and storage applications. While monoethanolamine absorption is the most often utilised and commercially available technique in the post-combustion approach, additional absorbents such as N-methyldiethanolamine and 2-amino-2-methyl-1-propanol are also used (Karnwiboon et al., 2019). Amine solutions are the most often used solvents due to their great capacity for CO_2 absorption and strong selectivity for acidic gases (Féron & Rochelle, 2016). However, they have limitations such as amine corrosivity, a large energy footprint during regeneration, and deterioration, which results in solvent loss and evaporation.

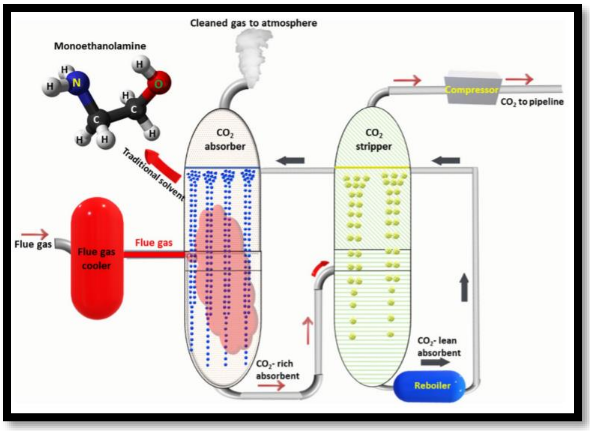

Figure 1.1: Post-combustion technology for CO_2 absorption (Osman et al., 2020)

Alfred Werner discovered the coordination polymer family, giving rise to metal-organic frameworks (Constable & Housecroft, 2013). Coordination polymers (CPs) are diverse materials formed by coordination bonding between metal centres and organic or inorganic ligands. Their structures can be one-dimensional, two-dimensional, or three-dimensional. Zn^{2+}, Cu^{2+}, Ag^{+}, and Cd^{2+} are the most common transition metals used as the metal centre.

Metal-organic frameworks (MOFs) have unique characteristics for CO_2 carbon capture, such as functionalised pore morphology and customised architectures. MOFs can have up to 75,000 different configurations, making finding specific pore-structure materials for carbon sequestration easier. Despite this, none of the MOF materials has been used commercially due to the high energy required for regeneration and rapid structural instability (Qazvini & Telfer, 2020). MOFs are one of the many materials that have been investigated in the subject of green chemistry. MOFs are a class of materials that combine organic and inorganic components, as shown in **Figure 1.2**. Changing the metal node and organic linker building blocks employed in synthesising these crystalline and porous materials allows for a wide range of structural variations in the final product. Along with altering the chemical identity and functioning of metal nodes and organic linkers, other features such as pore size, pore shape, and node connectivity can be fine-tuned. According to Li et al. (2018), the extraordinary designability of

MOFs has been studied in various applications, including gas adsorption and storage, catalysis, wastewater treatment, solar fuel generation, and chemical separations.

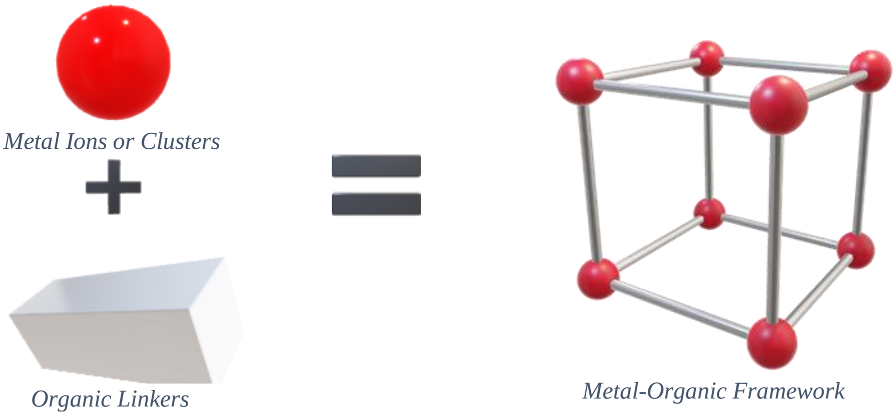

Figure 1.2: Generic illustration of metal nodes and organic linkers coming together to form MOFs (Pettinari & Tombesi, 2020).

The discipline of MOFs chemistry values both the development of green synthetic methods and procedures and the use of MOFs in green applications. Since MOFs have distinct and adaptable characteristics, they have the potential to be used in a wide range of environmentally conscious or “green” applications. The ultimate goal should be to link green MOFs synthesis with environmentally conscious applications in order to achieve the greatest possible positive environmental impact from these materials. Metal salts with benign anions or linker salts with harmless metal cations are preferable to avoid harmful by-products such as corrosive acids, mainly Hydrochloric acid and Nitric acid formed by the reaction of metal salts and protonated ligands in an aqueous solution. As a result, metal hydroxides and oxides are commonly used to ensure that water is the sole by-product and has high atomic efficiency (Kong & Li, 2021). Moreover, MOF design and use are greatly affected by organic-ligand choices since they significantly impact both the final topology and specific functions.

MOFs, a novel class of highly porous crystalline materials with adjustable pore topologies and adjustable pore structure features, have emerged as a solution for CO_2 adsorption; however, the organic precursors are expensive, non-renewable, and hazardous (Yan et al., 2016). Cyclodextrin Metal-Organic Frameworks (CD-MOF) have recently been developed using renewable γ-cyclodextrin (γ-CD). CD-MOF is an environmentally friendly polymer made from starch and has been selected as the most promising material for CO_2 adsorption. Six CD-MOF tori comprise a single cubic unit of CD-MOF (γ-CD). Each (γ-CD) unit has a big spherical pore with a diameter of 1.7 nm in the centre, and these units are joined to form the porous framework. The CD-MOF has a body-centred cubic packing of the (γ-CD) 6 units in its crystal structure (Nagai et al., 2018).

1.2 Problem Statement

The various strategies for capturing and separating CO_2 include adsorption, cryogenic distillation, biological approaches, membrane separation, and absorption. However, because of its excellent adsorption capacity, low cost, low energy consumption, and ease of operation, adsorption is the most prevalent method for CO_2 capture. Conventional adsorbents made of minerals like zeolites have been investigated for many years and have made tremendous progress during the last few decades. Their disadvantages, on the other hand, cannot be overlooked. For example, despite their desirable properties for carbon capture operations, zeolites have a high operating cost, as the creation of bicarbonates necessitates persons to rebuild the structure at high temperatures (Fakhraei Ghazvini et al., 2021). At high temperatures, the interactions between the adsorbent and the adsorbate deteriorated. Zeolitic structures, amine-functionalised porous media and aqueous alkanolamine absorbents are among the contemporary materials studied for CO_2 adsorption and absorption. However, existing technologies rely on a high level of energy to regenerate, and many materials are sourced from petrochemical sources which require a deal of time and resources to synthesise or are generated from harmful materials themselves.

As a result, there is an urgent demand for materials that are both energy-efficient and environmentally benign and have outstanding CO_2 adsorption capabilities. Recently, cyclodextrin (γ-CD), a sugar-related natural substance generated through microbiological processes and alkali metal salts, was used to make a range of MOFs. CD-MOF-2 has been found to have a highly selective CO_2 adsorption at low pressures. However, the structure of γ-CD-MOF is susceptible to moisture which limits the ideal CO_2 adsorption capacity. Cyclodextrin (CD), a naturally occurring and commonly available cyclic oligosaccharide, crystallises in the presence of alcohol vapour (Methanol or Ethanol) to form a porous MOF named CD-MOF, which is environmentally friendly and renewable. The primary disadvantage of these materials is their decomposition or dissolution when exposed to water. However, complexation or post-synthetic alteration of the framework can somewhat reduce this problem. It is critical that all CO_2 adsorptions must occur in the presence of moisture. As a result, hydrophobic frameworks are ideal for CO_2 adsorption in humid environments, which is why introduction of amino group could be a potential to solve the problem (Xu et al. 2019).

Computational simulations have been identified as critical tools for investigating and predicting the properties and uses of MOFs. MOF computational analyses are performed regularly to estimate the molecules' adsorption and diffusion in MOFs and provide comprehensive microscopic information that is typically unavailable or difficult to get experimentally. Hence, through modelling and simulation studies, this research will primarily focus on the molecular structure of NH_2-γ-CD-MOF of its unit cell coordination and the adsorption capacity of CO_2. Therefore, this study aims to develop and construct the molecule sequence or crystal by using VESTA Simulation Software, Mercury and iRASPA by using data on the atom’s angle and bond length between each atom. Then by adding amino group, which is $NH_{2,}$ into the molecule structure and later to be evaluated in Amsterdam Modelling Suite (GCMC) in terms of the adsorption capability of CO_2.

1.3 Research Questions

1. Does NH_2-γ-CD-MOF have a larger unit cell volume and accessible pore than other CD-MOF?
2. Does CD-MOF with added amino group better than other MOF in terms of adsorption capacity?
3. Does the adsorption of CO_2 occur of the surface NH_2-γ-CD-MOF?

1.4 Research Objectives

This research project aims to determine the feasibility of designing green and sustainable MOFs for CO_2 adsorption through modelling/simulation studies.

The objectives for this project are: